

International Conference on the Chemistry of Glasses and Glass-Forming Melts

In celebration of the 300th Anniversary
of the birth of Mikhail Vasilievich Lomonosov

Lady Margaret Hall
University of Oxford



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Mikhail V. Lomonosov (1711-1765): “To Glass, all his Labour was Applied.”

Tatiana Moiseva

St.-Petersburg Scientific Center of RAS, scientific secretary of Lomonosov Commission, (St.-Petersburg), Publishing House ‘Lomonosov’, sub-editor (Moscow),

Mikhail Lomonosov (1711-1765), the scientist, technologist, poet, artist, the first native Russian academician played very important role in Russian culture. Thank to his activity Russia came in the common European cultural world of 18 c. The famous Russian poet Alexander Pushkin called Lomonosov ‘the first Russian University’.

Lomonosov was the organizer of the first scientific and educational Chemical laboratory, Moscow University, the first factory of color glasses in Russia. By the end of his life Mikhail Lomonosov had been the chief of all Scientific Departments, Gymnasium and the University of the Academy of Sciences. His prestige was considerable in Russia, and his scientific works were known abroad, they published in several European scientific journals. Lomonosov corresponded with many famous European scientists. Leonard Euler supported him. The first native Russian academician became the honor member of Academy of Arts, Academy of Sciences of Bologna, the Royal Swedish Academy.

His biography, his indefatigable nature and versatile activity exceeded the limits of ordinary life. Many volumes wrote about Mikhail Lomonosov, his life. There are a lot of legends, far-fetched stories about him and his actions. Mikhail Lomonosov was unusual figure in Russian society of 18c. His ambition was to educate himself to join the learned men on whom the tsar Peter I the Great was calling to transform Russia into a modern nation. Lomonosov was born in a small coastal village near Arkhangelsk in North of Russia in family of prosperous fisherman and trader. In spite of common Russian traditions he could get the best education in Russia and Europe. He knew several languages (8-20, according different information). He was the reformer of Russia languages and introduced the living scientific terms in it. Lomonosov wrote main of his scientific works in Latin and at the same time he was the first who began to read and published scientific works in Russian. It was very important step for adaptation modern European scientific knowledge in Russia.

His main scientific interests of Lomonosov were connected with physical and chemical themes. the dominant ideas of his scientific work set in «276 Notes on Corpuscular Philosophy and Physics». Appointed a professor by the Academy in 1745, he translated Christian Wolff's *Institutiones philosophiae experimentalis* («Studies in Experimental Philosophy») into Russian and wrote, in Latin, important works on the *Meditationes de Caloris et Frigoris Causa* (1747; «Cause of Heat and Cold»), the *Tentamen Theoriae de vi Aëris Elastica* (1748; «Elastic Force of Air»), and the *Theoria Electrici-*

tatis (1756; «Theory of Electricity»). In 1745 he was elected first of native Russian full professor of chemistry at the St.-Petersburg Academy.

In 1748 Lomonosov opened the Chemical laboratory of Academy of Sciences; it then began a prodigious amount of his activity. He began to read the lectures on chemistry in Russian for the students connecting with the training. At the same time he passionately undertook many tasks and recorded in three years more than 4,000 experiments, the results of which enabled him to set up a coloured glass works and to make mosaics with these glasses. Anxious, he wrote “Discourse on the Usefulness of Chemistry”, 1751 and in 1752 an Introduction to the physical chemistry course that he was to set up in his laboratory. The theories on the unity of natural phenomena and the structure of matter he set forth in the discussion “Origin of Light and Colours”, 1756.

Lomonosov combined his poetic gifts with his scientific engagement to produce scientific poetry. the “Ode” to Empress Elizabeth and “Letter to I.I. Shuvalov Concerning the Usefulness of Glass”, 1752; celebrated his fruitful union of abstract and applied science. “A Letter on the Uses of Glass” is the first Russian literary work to hail Copernicus’s heliocentrism and get metaphors to portray the of scientific ideas of the kind advanced by Huygens, Newton. This poem finished the words: **“To Glass, all my Labour was Applied.”**

Advanced solid-state NMR methods for the characterisation of glass networks

G. Tricot*, L. Montagne, O. Lafon, J. Trebosc, F. Méar, L. Delevoye, J-P. Amoureux.

Univ. Lille Nord de France, CNRS UMR 8181, Unité de Catalyse et de Chimie du Solide, Université Lille 1, Ecole Nationale Supérieure de Chimie de Lille, 59652 Villeneuve d'Ascq Cedex, France

Solid state Nuclear Magnetic Resonance spectroscopy has proven to be a technique of choice for the structural characterisation of vitreous materials. During the last decades, this spectroscopy has benefited from both technical and methodological improvements, leading to highly resolved and informative spectra from which the local order of silica, phosphorous, alumina or boron moieties can be easily and efficiently investigated. However, in case of very complex structures, generally resulting from the association of two or more network former oxides, the NMR spectra are composed of very broad resonances coming from the superimposition of several signals with close chemical shifts. In such cases, the spectra analysis can be ambiguous and can lead to mis- or over-interpretation of the NMR data. We will show in this communication how the combination of advanced 1D/2D MAS-NMR correlation techniques can be used to provide additional information, helping in the 1D MAS-NMR spectra analysis. This work will be illustrated by the analysis of 1D ^{31}P MAS-NMR spectra of alumino-phosphate and boro-phosphate glasses that have benefited from qualitative information coming from $^{31}\text{P}(\text{X})$ CP-HETCOR and $\text{X}(^{31}\text{P})$ HMQC techniques and quantitative data derived from $^{31}\text{P}(\text{X})$ REAPDOR and $\text{X}(^{31}\text{P})$ REDOR experiments (when $\text{X} = ^{11}\text{B}$ or ^{27}Al). The first results obtained with up to date NMR techniques on borosilicate networks will be also presented.

Superstructural units in Pyrex – a DOR NMR study

A. P. Howes, A. Samoson[†], M. E. Smith, D. Holland*, R. Dupree

Department of Physics, University of Warwick, Coventry CV4 7AL, UK

[†]Tallinn University of Technology, Akadeemia Tee 1, Tallinn, Estonia

N.M. Vedishcheva

Institute of Silicate Chemistry, Sankt Petersburg 199034, Russia

1D and 2D ^{11}B Double-Rotation (DOR) NMR experiments, in combination with thermodynamic modelling, are able to provide unique structural information about Pyrex glass. By removing both dipolar and quadrupolar broadening of the NMR lines, high resolution spectra are obtained that allow unambiguous, accurate peak fitting to be carried out, of particular importance in the case of the 3-coordinated $[\text{BO}_3]$ (B3) trigonal planar environments. The data obtained are of sufficient quality that they can be used to test the distributions of borate and borosilicate superstructural units predicted by the thermodynamics-based Model of Associated Solutions. The model predicts the dominant boron-containing chemical groupings in Pyrex glass to be those associated with B_2O_3 and sodium tetraborate (with smaller amounts of sodium triborate, sodium diborate, sodium pentaborate, danburite and reedmergnerite). Excellent agreement is found between model and experiment with the ^{11}B peaks with isotropic chemical shifts of -1.4 ppm and 0.5 ppm assigned to B4 species from borosilicate units and borate superstructural units respectively. The peaks with isotropic shifts of 14 ppm and 18.1 ppm are then assigned to B3 in borate superstructural units (mainly triborate and pentaborate along with connecting B3) and boroxol rings respectively. The assignments of the DOR NMR peaks, are supported by the presence of cross-peaks in ^{11}B spin-diffusion DOR NMR spectra which can be explained in terms of transitional links from boroxol rings to B3; from B3 to borate superstructural units; from borate superstructural units to borosilicate superstructural units, and then finally to the majority silica network. Pyrex is thus shown to have a heterogeneous structure, with distinct molecular groupings that are far removed from a random distribution of network polyhedra with only short-range order.

Structure of oxynitride phosphate glasses

Francisco Muñoz

Instituto de Cerámica y Vidrio (CSIC), Kelsen 5, 28049 Madrid (Spain)

Nitridation of phosphate glasses attracted the attention of researchers since it was discovered that nitrogen for oxygen substitution greatly improves their chemical resistance. Numerous compositions have been studied so far, due to the potential applications that oxynitride glasses might present. However, even though this way to improve the very low chemical durability of phosphate glasses appears very effective, nowadays this research field seems to be limited to the study of amorphous thin film electrolytes. It is well known that nitrogen modifies glass properties: generally, the glass transition temperature, density, elastic modulus, refractive index and electrical conductivity increase with nitrogen content and, especially, the chemical resistance of the glasses is drastically enhanced. The most studied way to perform nitridation is through a second melting of the phosphate glass under an ammonia flow. Nitrogen incorporation in phosphate glasses depends not only on the thermal treatment conditions but also on composition and, therefore, the structure of the base glass. The nitrogen content increases linearly with the treatment temperature for a constant processing time, and it also increases with the time of reaction at a constant T up to a maximum, which is thought to be influenced by the increased viscosity of the melt.

This contribution intends to present a review of the chemical structure of oxynitride phosphate glasses, where NMR and XPS techniques have been the most usual ways to characterise the structure, though Infrared as well as Raman are also employed. Nitrogen substitutes both bridging and non-bridging oxygens of the PO_4 tetrahedra, giving rise to the formation of new structural units, the PO_3N and PO_2N_2 . These new species of phosphorous introduce a higher bonding density through the $\text{P}-\text{N} < (\text{P})_2$ (Nt) and $\text{P}=\text{N}-\text{P}$ (Nd) bonds between adjacent phosphate chains, being the source for the drastic modification of the glass properties. It has been seen that the variation of $\text{P}(\text{O},\text{N})_4$ groups, as well as that of Nt and Nd, depends on the phosphate glass composition through the influence of the modifier cations in the PO_4 tetrahedra, and that the environment of elements such as Li or Pb changes along with nitrogen content even though no nitrogen is thought to be present in the coordination sphere of the cations.

Effect of B_2O_3 and Al_2O_3 addition on the structure of phosphate glasses

Hiromichi Takebe*, Yoshikazu Suzuki & Tomoyo Uemura

Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, 3, Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan

Multi-component phosphate glasses are attractive for optoelectronic, biomedical and environmental applications due to their interesting properties such as high radiative transition probability of rare-earth ions, low photoelastic constants, low glass transition temperature and chemical reactivity. In order to improve/control both thermal stability and water durability, the structural modification with the additions of B_2O_3 and/or Al_2O_3 with relatively-small amounts (≤ 10 mol%) is studied for barium phosphate glasses by using Raman and infrared spectroscopy. The addition of B_2O_3 forms the ring-type metaborate (RTMB), diborate, and BO_4-PO_4 groups in addition to PO_4 Q^2 units. These mixed anion structures improve the thermal stability against surface crystallisation at high temperature. However, the existence of RTMB may degrade the water durability of barium phosphate glasses. The result of Raman spectra suggests that the codoping of B_2O_3 and Al_2O_3 reduces the fraction of RTMB and the formation of $\text{B}-\text{O}-\text{Al}$ bonds. These structural changes result in good water durability in $\text{BaO}-\text{P}_2\text{O}_5-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ glasses.

Structure of the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ high-alkali melts: a high-temperature Raman spectroscopy investigation

Armenak A. Osipov* & Leyla M. Osipova

Institute of Mineralogy UB RAS, Chelyabinsk region, 456317, Russian Federation

The Raman spectra of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ melts were measured and short-range (SRO) and intermediate range order (IRO) structures were investigated. The local structures of the $40\text{M}_2\text{O}.60\text{B}_2\text{O}_3$ and $50\text{M}_2\text{O}.50\text{B}_2\text{O}_3$ melts ($\text{M}=\text{Li}, \text{Na}$) are qualitatively similar and consist of $[\text{B}\text{O}_{4/2}]^-$, $\text{B}\text{O}_{3/2}$, $\text{B}\text{O}_{2/2}\text{O}^-$, and a small amount of $\text{B}\text{O}_{1/2}\text{O}_2^{2-}$ species. The $\text{B}\text{O}_{2/2}\text{O}^-$ asymmetric triangles are the dominant structural units in this composition range. The concentration of these structural units increases with increase in temperature of $40\text{M}_2\text{O}.60\text{B}_2\text{O}_3$ melts and weakly depended on temperature of $50\text{M}_2\text{O}.50\text{B}_2\text{O}_3$ melts. The $\text{B}\text{O}_{1/2}\text{O}_2^{2-}$ fraction significantly elevates with increasing in M_2O content and attains its maximum in the $67\text{M}_2\text{O}.33\text{B}_2\text{O}_3$ melts. The increase in $\text{B}\text{O}_{1/2}\text{O}_2^{2-}$ fraction occurs simultaneously with decrease in concentrations of $\text{B}\text{O}_{3/2}$ symmetric triangles, $\text{B}\text{O}_{2/2}\text{O}^-$ asymmetric triangles, and $[\text{B}\text{O}_{4/2}]^-$ tetrahedra. In addition, the closer to $67\text{M}_2\text{O}.33\text{B}_2\text{O}_3$ composition the BO_3^{3-} units start to be formed in both systems whereas CO_3^{2-} ions are present only in structure of the sodium borate melts. The concentration of $\text{B}\text{O}_{1/2}\text{O}_2^{2-}$ pyroborate units decreases and fractions of ortho- and metaborate units increase with increase in temperature. The six-membered borate rings with one or two $[\text{B}\text{O}_{4/2}]^-$ tetrahedra are the main superstructural groups of lithium borate melts at Li_2O concentrations less than 50 mol%. Moreover, the closer to metaborate composition $\text{B}_3\text{O}_6^{3-}$ metaborate rings are also present in sodium borate melts with Na_2O content ~50 mol%. These rings are absent in structure of lithium borate melts of the same compositions. The fractions of the triborate and metaborate rings decrease rapidly with increase in modifier oxide concentration more than 50 mol% whereas the ditriborate rings are present even in $67\text{M}_2\text{O}.33\text{B}_2\text{O}_3$ melts. Increase in temperature leads to increase in fractions of so-called 'loose' or 'independent' fundamental structural units and this is a general tendency of structural transformation of all investigated melts. The work supported by the SFP 'Scientific and scientific-pedagogical personnel of innovative Russia' and RFBR (grant 10-05-96029-r_ural_a).

Disorder of glass structure in terms of configurational entropy

Akira Takada

Asahi Glass Co. Ltd., 1150 Hazawa-cho, Kanagawa-ku, Yokohama, 221-8755, Japan

The residual configurational entropy of glasses is still the subject of controversy. There are two ways to define the residual entropy due to the nonergodicity on glass. One is based on the time evolution of configurations and the other is based on the sampling from the probability population. First, the change of entropy in the non-equilibrium states is investigated for several simple phenomena. Second, the residual entropies estimated from two different methods; one is based on calorimetric formula and the other is based on the probability population, are compared employing newly constructed model. The calculated results indicate that two estimated values of residual entropy are almost equivalent and non-zero. Finally, the configurational entropy in glass is interpreted in terms of atomistic structure.

Rings and configuration entropy in glass prepared by MD

Ondrej Gedeon & Jan Machacek

Institute of Chemical Technology, 166 28 Prague, Czech Republic

Marek Liska

Vitrum Laugaricio, Trencin, Slovak Republic

Molecular dynamics was used to prepare structure of $5\text{K}_2\text{O} \cdot 0.95\text{SiO}_2$ glass. Algorithms based on the remove of the non-essential bonds (transient as are being inscribed into structure by ultrafast computational cooling) are used to decrease the number of overbonded atoms. The algorithms were found to be very effective and led to the experimentally comparable amount of the overcoordinated silicon atoms what made topological network of glass more realistic. Therefore it seems the use of the appropriate method for bond analysis can overcome the extended overcoordination commonly attributed to the fast cooling rate in molecular dynamics. The decomposition of the established glass topological network into disjunctive set of rings and the residual network units (topologically open and linear) is suggested. The decomposition into disjunctive structural units enables to calculate configurational entropy on base of ideal mixing. The calculated 'ring-entropy' reflects topology of rings in glass and therefore is closely related to medium range order of glass. Temperature evolution of 'ring-entropy' enables to calculate the specific heat drop at glass transition temperature as well as residual entropy at 0 K measured in calorimetric experiments. Both calculated values are within uncertainty of the available experimental data.

A combined molecular dynamics, first-principles and NMR structural study of sodium silicate glasses

O. Villain,* Th. Charpentier

CEA, IRAMIS, UMR 3229-SIS2M, LSDRM, CEA Saclay F-91191 Gif-sur-Yvette France.

F. Angeli, S. Schuller, S. Ispas

We present a structural study of sodium silicate glasses (23, 40 and 45% Na_2O) combining experimental NMR results (^{23}Na , ^{29}Si and ^{17}O NMR) and simulation results.⁽¹⁾ Indeed, it has been shown recently how the introduction of first-principles calculations of NMR parameters combined with Molecular Dynamics (MD) simulations yields a very promising quantitative support of the NMR experiments.^(2,3,4) Hence MD simulations are carried out in order to generate few glassy structural models, used afterwards as input for NMR first-principles calculations. The calculated NMR parameters (isotropic chemical shift, quadrupolar coupling constant and quadrupolar asymmetry parameter) are then compared to experimental ones. Moreover, calculations allow to correlate relevant structural parameters (bond angles and bond lengths, coordination numbers) with NMR parameters, without crystalline reference compounds. These data offer better insights into the structural organisation of the glass network, including both chemical and topological disorder (distribution of alkali in glass). Finally, our approach was found to be sensitive enough to investigate the effect of addition of a small quantity of molybdenum oxide (about 1 mol%) on the ^{17}O MAS spectrum, opening new possibilities for investigating the Mo environment in silicate glasses.

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Nucleation and growth of crystalline Ag nanoparticles in glass

Manfred Dubiel,* Jörg Haug and Holger Kruth

Institute of Physics, Martin Luther University of Halle-Wittenberg, Von-Danckelmann-Platz 3, D-06120 Halle, Germany

Metal nanoparticles embedded in glass have been thoroughly studied because of their specific optical properties. The present work is directed to the fabrication of monometallic nanoparticles and their structural investigation. We investigated the formation of Ag nanoparticles (sizes of 1 to 7 nm) by Ag/Na ion exchange procedures in soda-lime glass. In the case of ion exchange processes well below the glass transformation temperature, x-ray absorption spectroscopy at the S, Ti and Fe K-edge demonstrated that polyvalent Fe ions served as thermosensitive reductive. XANES and EXAFS data revealed the oxidation of Fe^{2+} to Fe^{3+} as well as the oxygen coordination of iron ions. Experiments at the Ag K-edge showed that the initial stage of Ag nucleation includes intermediate phases like metastable Ag structures. The growth of particles takes place by a transformation of this species into crystalline silver nanoparticles that could be confirmed by transmission electron microscopy (TEM).

Crystallisation kinetics and luminescence properties of $\text{Er}^{3+}/\text{Yb}^{3+}$ doped NaYF_4 nano-glass-ceramics

A. de Pablos-Martín,* A. Durán, M. J. Pascual

Instituto de Cerámica y Vidrio (CSIC), Kelsen 5, 28049 Madrid, Spain

J. Méndez-Ramos, J. del-Castillo, V. D. Rodríguez

Dpto. Física Fundamental y Experimental, Electrónica y Sistemas, Universidad de La Laguna, 38206 La Laguna, Tenerife, Spain

Rare earth (RE) ions doped oxyfluoride glass-ceramics (GC's) containing fluoride nano-crystals have been extensively investigated within the new materials for photonic applications. Oxyfluoride GC's combine the transparency and mechanical and chemical resistance of the aluminosilicate glasses with the low phonon energy and good solubility for RE ions of the fluoride crystals. Transparent GC's and the inclusion of the optically active doping ions in the crystalline phase can be obtained through a strict control of the composition and thermal treatments in order to precipitate nano-crystals below 20 nm.

NaYF_4 is considered one of the most efficient hosts for up-conversion when doping with $\text{Er}^{3+}/\text{Yb}^{3+}$. NaYF_4 exists in two polymorphs: the hexagonal ($\text{Na}_{1.5}\text{Nd}_{1.5}\text{F}_6$ type) structure and the cubic (fluorite type) one. Although, hexagonal $\beta\text{-NaYF}_4$ is considered better host lattice for the luminescence of RE ions than the $\alpha\text{-NaYF}_4$, since RE^{3+} in hexagonal phase is located in three different cation sites, $\beta\text{-NaYF}_4$ crystallisation is mainly obtained by procedures different of melt-quenching and subsequent heat treatment from a glass composition.

This work is focused on the crystallisation of NaYF_4 nano-crystals in three glasses in the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-YF}_3\text{-ErF}_3\text{-YbF}_3$ produced by melt-quenching-heat treatment method and using dilatometry, DSC, TEM and XRD. The optical absorption and luminescence measurements confirm the incorporation of Er^{3+} and Yb^{3+} ions into the NaYF_4 nano-crystals, causing shortening the distance between them and favouring energy transfer processes. As a consequence, bright up-conversion luminescence from NIR into visible is obtained. Moreover, the efficiency of these materials for down-conversion processes is explored.

Nanoparticle-containing oxide glasses: transparent magnets

I. Edelman, O. Ivanova, R. Ivantsov, E. Petrakovskaja, V. Zabluda

L.V. Kirensky Institute of Physics, SB RAS, Krasnoyarsk, Russia

L. Hennet

CEMHTI, UPR3079 CNRS et Université d'Orléans, France

D.Thiaudiere

Synchrotron SOLEIL, Gif-sur-Yvette, France

M.-L. Saboungi

CRMD, UMR 6619, Université d'Orléans-CNRS, France

S. Stepanov

S.I. Vavilov State Optical Institute, St.-Petersburg, Russia

A. Artemenko

ICMCB, UPR 9048 CNRS, France

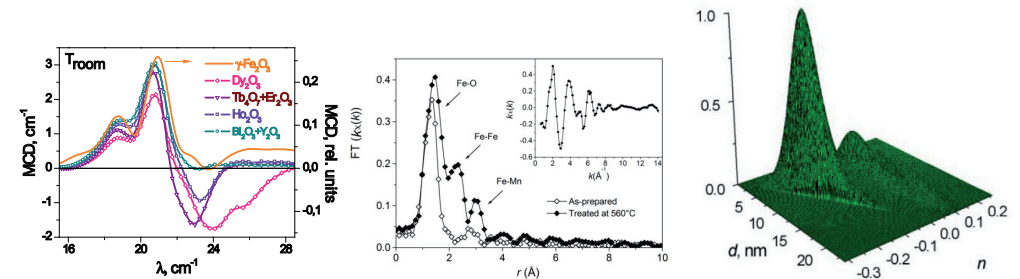
J. Kliava*

LOMA, UMR 5798, Université Bordeaux 1-CNRS, France

An extraordinary property of borate glasses is the ability of forming magnetic nanoparticles at very low doping with transition and rare-earth element oxides.^(1,2) We report a combined Faraday Rotation, MCD, electron magnetic resonance (EMR), transmission electron microscopy (TEM) and synchrotron radiation (x-ray diffraction, XANES, EXAFS) studies of glasses $K_2O-Al_2O_3-GeO_2-B_2O_3$ co-doped with low concentrations of Fe_2O_3 and MnO or RE_2O_3 with $RE=Tb, Dy, Ho, Yb, Gd$. After thermal treatment, nanoparticles of different sizes and shapes appear in the TEM images of the glasses. Such samples show non-linear field dependence of magnetization with hysteresis and temperature-independent MCD spectra (Figure 1 (left)). The nature of the nanoparticles has been identified as ferrites of different compositions. The XANES and EXAFS measurements confirm this attribution (Figure 1 (centre)). By computer simulating the EMR spectra of thermally treated glasses, a superparamagnetic nature of the nanoparticles is confirmed and their morphological characteristics are deduced: relatively broad size and shape distribution with the average diameter of ca. 3 to 4 nm (Figure 1 (right)).

The formation of magnetic nanoparticles confers to the potassium-alumina-borate glasses magnetic and magneto-optical properties typical of magnetically ordered

substances. At the same time, they remain transparent in a part of the visible and near infrared spectral range and display a high Faraday rotation value. Such materials are promising candidates for new magneto-optical devices.



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ASAXS study of the precipitation of ferrimagnetic nanocrystals in the $\text{Na}_2\text{O}/\text{MnO}/\text{SiO}_2/\text{Fe}_2\text{O}_3$ system

V. S. Raghuwanshi* A. Hoell

Helmholtz-Zentrum Berlin GmbH, Albert Einstein Str. 15, D-12489 Berlin, Germany.

D. Tatchev

Institute of Physical Chemistry, Bulgarian Academy of Sciences, ul. Acad. G. Bonchev, block 11, 1113 Sofia, Bulgaria.

R. Harizonova, I. Gugov

University of Chemical Technology and Metallurgy, Bul. Sv. K. Ohridski, 1756 Sofia, Bulgaria.

C. Rüssel

Otto-Schott-Institut, University Jena, Fraunhoferstrasse 6, 07743 Jena, Germany.

Most of the oxide glass ceramics having nano-scale ferrimagnetic crystals and show magnetic and electrical properties have many future applications are expected in ferrofluids, medicals, electronics etc. The conductivity and magnetic properties depend on structural parameters of the nanoparticles. The main aim of this work is to evaluate the effect of heat treatment on the shape, size, composition, volume fraction and distribution of the nanoparticles in a glass matrix which acts as a chemical container for the nanoparticles. We study the crystalline precipitated phase of type Mn and Fe oxide in the silicate glasses by Anomalous Small Angle X-ray Scattering (ASAXS).

Ferrimagnetic nanocrystal of Fe and Mn containing phases were obtained by annealing of a glass of composition $13.6\text{Na}_2\text{O}-62.9\text{SiO}_2-8.5\text{MnO}-15.0\text{Fe}_2\text{O}_3$ (mol%) at 550°C for different time intervals. The phase composition and microstructure of the formed glass-ceramics were studied by x-ray diffraction (XRD), scanning and transmission electron microscopy, small angle x-ray Scattering (SAXS) and ASAXS.

XRD reveals the formation of ferrimagnetic spinel phase of type $\text{Mn}_x\text{Fe}_{1-x}\text{Fe}_2\text{O}_4$ where $x=0.342-0.55$ during the heat treatment of the glasses. Electron microscopy results reveals the formation of spherical particle having sizes between 10–60 nm after annealing.

The ASAXS experiment was performed at 7T-MPW-SAXS beamline at Helmholtz Zentrum Berlin (BESSY II) near the K-absorption edges of Fe and Mn to evaluate the distribution of the Fe and Mn atoms in the glass ceramics.

The measured SAXS/ASAXS curves were fitted well by spherical core-shell model with lognormal distribution. Simulated curves reveal the average particle size for the sample annealed at 550°C for 40 min is 20 nm where core diameter is 16 nm and shell is 2 nm thick and for the sample annealed at 550°C for 180 min has size of 44 nm where core diameter is 41 nm and thickness of the shell is 1.5 nm. Results show that the size of the core is increasing with the annealing time. Also the ASAXS curves were fitted by varying only the contrast of the core and the shell at different energies for Fe and Mn edge, which reveals that Fe atoms are present in both core and shell but the core has greater concentration of Fe than the shell.

Ruby copper thin layers in float glass by using spray pyrolysis or ionic exchange in melted copper compounds

Rita Rodrigues¹, Luís Costa¹, Andreia Ruivo^{1,2*}, Rui Coelho da Silva³,
António Pires de Matos¹

¹VICARTE, Research Unit "Glass and Ceramics for the Arts", Universidade Nova de Lisboa,
2829-516 Caparica, Portugal

²REQUIMTE, Chemistry and Technology Network, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa, 2829-516 Monte da Caparica, Portugal

³Instituto Tecnológico e Nuclear, Estrada Nacional 10, 2686-953 Sacavém, Portugal

In this communication we report the formation of thin layers of ruby copper in float glass using either the spray pyrolysis technique or an ionic exchange process in melted copper compounds.

In the first method a solution of copper acetate in a mixture of water and methanol was sprayed onto a plate of float glass heated at about 400°C. After annealing at 650°C for 45 minutes a red colour was developed in the surface of the float glass. This colour was obtained only in the side of the glass plate with tin.

In the other process a mixture of copper sulphate and sodium sulphate was melted at 575°C and the float glass was dipped in it for 45 minutes. A red colour was observed in both sides of the float glass but with much higher intensity on the tin side.

The colour obtained was due to nanoparticles of copper as indicated by optical absorption spectroscopy. Rutherford backscattering was used to characterize the thin layer surface. The results obtained are discussed.

Colouring glasses using nanoparticles synthesised within polyelectrolytes multilayers assembled through the layer-by-layer method

M. G. Ventura,* T. Almeida, A. J. Parola & A. P. Matos

Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa, Department of Chemistry,
Monte de Caparica, Caparica 2829-516,

The metal nanoparticles of Au, Ag and Cu have unique optical properties which are associated with their strong surface plasmon resonance (SPR) in the visible part of the spectrum. Thin films containing metal nanoparticles have potential applications in several areas including glass industry, in which films are used to give colour and other physical properties like thermo and electrochromic properties. The layer-by-layer (LbL) deposition of polyelectrolytes is considered one of the most simple and adaptable techniques for the formation of thin films which can be applied in several substrates independently of its nature, size and topology. In this work polyelectrolyte multilayers (PEMs) produced through LbL assembly technique were used for the in situ synthesis of metal nanoparticles on glass surface having in mind its application in glass art pieces. By controlling the assembly and post-assembly conditions, gold, silver, copper or a mixture of two metals were loaded onto the PEMs composed by two polyelectrolytes charged oppositely. Different polyelectrolytes and other parameters such as the pH used during assembly and post assembly, and the reduction conditions were tested to optimise the intensity of the obtained colour. Temperatures near the glass transition temperature (T_g) were used during the thermal treatment in order to fix the nanoparticles and hence the colour on the glass surface. Samples were characterized by ultraviolet-visible absorption spectroscopy, transmission electron microscopy (TEM), energy dispersive x-ray (EDX), and x-ray diffraction (XRD). The red colour was obtained through Au nanoparticles while the yellow and orange colours were obtained through the mixture in different proportions of Au and Ag nanoparticles. Further studies will comprise the optimisation of Cu nanoparticles synthesis and the addition of lanthanides to the different systems in order to obtain luminescent coloured films.

Effect of P_2O_5 and MnO_2 on crystallisation of Zn-and Zn-Mn ferrites glass ceramics

S. A. M. Abdel-Hameed, M. A. Marzouk*

Glass Research Department, National Research Center, Dokki, Cairo, Egypt.

M. M. Farag

Biomaterial department, National Research Center, Dokki, Cairo, Egypt

This work pointed out the crystallisation and characterisation of magnetic glass ceramic contains Zn and Zn-Mn ferrites in the system $Fe_2O_3 \cdot ZnO \cdot CaO \cdot SiO_2$. The influence of adding different addition from P_2O_5 and/or MnO_2 on the sequence of crystallisation process and microstructure was studied. The DTA of the glasses revealed decrease in the thermal effects by increasing P_2O_5 and/or MnO_2 . The x-ray diffraction patterns show the presence of nanometric magnetite crystals in a glassy matrix after cooling from melting temperature. Heat treatment at 800°C for 2 h under reducing atmosphere revealed increase in of magnetite crystallized; minor hematite and Ca_2SiO_4 were appeared. The microstructure studied using TEM revealed crystallite size in the range of 10–30 nm. The crystallite size was increased by increasing amount of MnO_2 or P_2O_5 added. Lattice parameter and cell volume calculated from XRD data using Debye-Scherrer formula revealed significant gradual increase by increasing addition of MnO_2 than the standard ASTM card of magnetite due to the replacement of the small ionic radii of Fe^{2+} with high ionic radii of the Mn^{2+} , while increasing P_2O_5 added have slightly lowering effect in lattice parameters and cell volume due to the effect of P_2O_5 which act as nucleating agent and not for replacing Fe^{2+} .

Keywords: Magnetite, Glass Ceramics, Crystallization, microstructure.

In-situ synchrotron tomography of soda-lime glass batch melting reveals the influence of intergranular contacts on reaction routes

E. Gouillart,* J. Grynberg, M.-H. Chopinet, M. Toplis, M. Di Michiel, E. Boller, D. Vandembroucq

Joint Unit CNRS/Saint-Gobain Surface of Glass and Interfaces, 39 Quai Lucien Lefranc, Aubervilliers, 93303, France

Industrial synthesis of good-quality soda-lime glass is generally carried out at 1400–1500°C, despite the fact that typical compositions are completely molten at 1050°C. Such high temperatures are required to eliminate defects (typically gas bubbles and unmolten sand grains), and to homogenise the melt composition. Indeed, the reactive melting of glass batch takes place in a context of significant thermodynamic disequilibrium, and chemical interactions are limited by the local packing arrangement (i.e. the statistics of inter-granular contacts of different raw materials), and by slow diffusion in viscous liquids at later stages of the transformation. Parameters such as the grain size of raw materials are known to influence the reaction paths and the quality of glasses produced at high temperature. More insights into the influence of the microstructure of the system on the kinetics of its evolution may enable the manufacturing of higher-quality or less energy-consuming glasses. We have performed in-situ microtomography experiments of glass batch melting on the ID15A and ID19 beamlines at the European Synchrotron Radiation Facility (ESRF). In x-ray tomography, one reconstructs three-dimensional volumes of the x-ray absorption of the imaged sample from a large set of radiographies taken at different angles. Thanks to the brightness of synchrotron sources, the time-resolution of the technique makes it now possible to follow in-situ the evolution of materials from the inside, in the course of transformations at high temperature. Starting from small granular packings of sand and carbonates that are heated at a constant rate, we have observed the whole transformation of the initial granular pile into a bubble-rich liquid. Such experiments have revealed new mechanisms undocumented so far because of the lack of direct 3-D observation, such as the fragmentation of sodium carbonate grains that wrap around neighboring sand grains in order to increase the reaction surface. We also measure quantitatively the trapping of gas bubbles as liquid interfaces collapse when eutectic melts are produced in quantity. Short-range packing arrangements were found to have a profound influence on local reaction pathways, with drastically different reactions depending on the presence of contacts with sodium carbonate for sand and calcium carbonate grains; these observations hence provide important information on the generation of solid crystalline defects. These results demonstrate the potential of quantitative processing of tomography images to provide unprecedented insight into the progress of chemical and microstructural transformations of glass batches at high temperature.

Effect of oxygen partial pressure on the viscosity of iron oxide containing alkali silicate melts

Sohei Sukenaga,* Yosuke Inatomi, Yoshiaki Gonda, Noritaka Saito, Kunihiro Nakashima

Department of Materials Science and Engineering, Kyushu University

Takashi Watanabe

Department of Chemistry and Materials Science, Tokyo Institute of Technology

Takeshi Ohsugi

Department of Decommissioning and Waste Management Nuclear Science Research Institute, Tokai Research and Development Center, Japan Atomic Energy Agency

Iron oxide containing silicate melts are important materials in some of the industrial processes at elevated temperature, such as glass making and pyrometallurgical extraction (as slags). Viscosity of the melts is an important physical property for clarifying the reaction kinetics and for understanding microstructure of the melts at elevated temperature. It is well known that the oxidation state of iron ions (Fe^{2+} or Fe^{3+}) in melts changes depend on melting temperature, the basicity and the oxygen partial pressure. However, the effect of the ratio of Fe^{2+} to Fe^{3+} on the viscosity of the silicate melts has not been well understood. The aim of the present study is to clarify the effect of oxidation state of iron ions on the viscosity of iron oxide containing alkali silicate melts by changing the oxygen partial pressure.

Viscosity of $30\text{R}_2\text{O}-60\text{SiO}_2-10\text{Fe}_x\text{O}$ (mol%) ($\text{R}=\text{Li}, \text{Na}$ or K) melts has been measured by a rotating cylinder type viscometer (contact material: Pt-20 wt% Rh) with a gas-tight furnace. The measurements have been carried out as a function of systematically varying oxygen partial pressure controlled by Ar based gases ($P(\text{O}_2)=2.0\times 10^{-1}$ atm, 1.3×10^{-2} atm, 7.2×10^{-5} atm, 3.0×10^{-6} atm and 1.6×10^{-10} atm) at 1773 K. In addition, we melted the samples under each of the atmospheres for 2 h at 1773 K and then quenched on a copper plate. These quenched vitreous samples were chemically analyzed for quantifying the oxidation state of iron ions.

The ratio of Fe^{2+} to Fe^{3+} in the $30\text{R}_2\text{O}-60\text{SiO}_2-10\text{Fe}_x\text{O}$ (mol%) glasses decreased with increasing the oxygen partial pressure in all the samples. In parallel, the viscosity of the $30\text{R}_2\text{O}-60\text{SiO}_2-10\text{Fe}_x\text{O}$ (mol%) melts decreased with increasing the ratio of Fe^{2+} to Fe^{3+} . The data indicates that the increase in Fe^{2+} ions, which behave as a network modifier, would result in depolymerisation of the silicate melts. It should be also noted that the viscosity of the melts was in the order of alkali cationic radius ($\text{K} > \text{Na} > \text{Li}$) when the ratio of Fe^{2+} to Fe^{3+} in the melts was comparable; it would be due to the change in the coordination structure of Fe^{3+} in these melts.

Hydrothermal dissolution of copper slag glasses from the Mansfeld district

Thomas Pfeiffer,* Sebastian Müller, Antje Schilling, and Hans Roggendorf

Martin-Luther-Universität Halle-Wittenberg, Institut für Physik, D-06099 Halle, Germany

Slag glasses are byproducts of pyrometallurgical processes. Depending on ore, lode matter, slag formers and furnace corrosion products different glasses are produced. Depending on composition and chemical durability the materials are applied as building stones, puzzolan binders, or as secondary raw materials. In this study the dissolution behavior of copper slag glasses from the Mansfeld district (Sachsen-Anhalt, Germany) was investigated. The aim of the investigations was to convert the vitreous slag into applicable secondary raw materials. The conversion process includes the dissolution of the glass phase as a major step.

The chemical composition of the slag was (major components only, mass content in %): 47SiO_2 , 19CaO , $14\text{Al}_2\text{O}_3$, 8MgO , $4\text{K}_2\text{O}$, $4\text{Fe}_2\text{O}_3$, $1\text{Na}_2\text{O}$, 3 rest. The phase content of the slag was characterised by optical microscopy and x-ray diffraction. The crystalline content was below 5 wt%, the rest being vitreous. The slag glasses were ground to sizes between 20 and 125 μm , dispersed in NaOH solutions and treated hydrothermally in a rotating autoclave system. The concentration of the NaOH solutions was varied between 1 and 18 mole/l, the hydrothermal treatment times ranged from 4–24 h. Usually, a temperature of 200°C was applied.

After hydrothermal treatment a liquid phase and a solid residue were recovered. The liquid phase was titrated, the loss of ignition was determined and the potassium content was analysed chemically. Potassium is a highly soluble cation and it is supposed that it does not enter the solid residue. The latter assumption was of course checked. The solid residue was analysed by optical microscopy, x-ray diffraction and x-ray fluorescence. The results were evaluated with respect to kinetics and yield. The evaluation was handicapped by crystallisation processes. It is also discussed whether the crystalline materials are precipitates or altered glass.

Chemical durability of a slag glass from pig iron production - reaction products, surface alteration and kinetics

Hans Roggendorf,* Werner Lebek, Sybille Böhme, Herbert Poellmann
*Martin-Luther-Universität Halle-Wittenberg, Institut für Physik & Institut für
 Geowissenschaften, D-06099 Halle, Germany*

Slag glasses are byproducts of pyrometallurgical processes. Depending on ore, lode matter, slag formers and furnace corrosion different glasses are produced. During cooling crystallisation may occur. Slag glasses from the pig iron production are applied as latent hydraulic binder or as an additive for ordinary portland cements in the production of blast furnace cements. The reactivity of the ground slag glasses is usually lower than the reactivity of binding phases in ordinary portland cements, they are classified as puzzolanic binders. The reactivity of ground slag glasses can be enhanced by adding either basic compounds (portland cement or $\text{Ca}(\text{OH})_2$) or calciumsulfate (gypsum) compounds. Since the dissolution of the slag glasses – which is a glass corrosion process – is essential for the kinetics of the formation of their binding phases it is investigated here. Possibly, the binder reactivity of the slag glasses can be discussed as a reverse chemical durability.

The slag glasses were procured from a commercial supplier (now: Cemex, Germany) as granulated blast furnace slag. Their chemical composition was (major components only, mass content in %): 36SiO_2 , 41 CaO , $12\text{Al}_2\text{O}_3$, 9 MgO , 3 rest. The phase content of the slag glass was characterised by optical microscopy and x-ray diffraction. The slag glasses were tested either as ground original materials (size $<63\ \mu\text{m}$) or – in other tests – as remolten bulk glasses. Conditions for remelting were 2 h at 1450°C in ambient air, then casting into a hot form ($400\text{--}500^\circ\text{C}$). During remelting and casting the chemistry of the slag glass was changed: the glass is oxidised and most of the sulfur content of the original slag is lost. The cast glasses have been cut to platelets. The platelets (or 0.5 g of the ground slag glass) were corroded up to 180 d in 50 ml of a leachant (H_2O and CaSO_4 or $\text{Ca}(\text{OH})_2$ containing aqueous solutions). Usually, a corrosion temperature of 50°C was applied.

After the corrosion process an altered layer was found on the glass surface. The leachate was analysed by chemical means. The altered glass surface was analysed by optical microscopy, scanning electron microscopy (with elemental analysis), and x-ray diffraction. The results were evaluated with respect to kinetics.

A global and nondimensional approach to compute the oxides global relative glass forming ability

Roula Abdelmalek,* Boubata Nouar & Moussaoui Islam
Jijel Univ.; LIME; Eng. Sci. Fac.; Jijel; 18000; Algeria; amkroula@mail.univ-jijel.dz

The glass forming ability (GFA) is the criterion used to characterise the behavior of any material to solidify in an amorphous state (materials can be simple chemicals, chemical combinations or their melts). Many criteria (dealing with thermodynamical and/or structural and/or thermal and/or kinetic orders) have been proposed to explain the formation or the non-formation of glasses by oxides. They are all founded on crystallochemical concepts or refer to the criteria linked to the nature and the chemical bond strength of metals oxides.⁽¹⁻¹²⁾ We present a non-dimensional approach to value the glass forming ability by affecting to every oxide a coefficient (without measuring units). Obeying to the non-dimensional analysis rules, we proceed to a mathematical treatment of oxides thermodynamic and structural data⁽⁴⁻⁸⁾ introducing another characteristic: the specific thermal heat C_p that was neglected in all the other models.⁽¹⁻⁷⁾ We note this coefficient as the Global Relative Glass Forming Ability (GRGFA) and propose a model model to compute it. This new criterion confirms the prior classification of oxides but looks to be distinctive because linking the main parameters of oxides.

The obtained computed values of GRGFA permit the definitive ranking of oxides in the three oxide groups (glass formers, intermediate and modifier).

Inhibition of the corrosion of E-glass fibres by malonic acid

R L Jones* & A Z Zahir

Department of Chemistry, Curtin University of Technology, Perth, Australia.

The corrosion of E-glass fibres in acid solution is now well established and is considered a contributory factor in many instances of corrosion related failure in glass reinforced plastic materials. However the chemical mechanism and rates of corrosion are still not fully understood. The currently accepted idea is that corrosion is attributable to both the acid strength of the corroding medium and the complexing ability of the associated anion. Previous work has shown that in the case of perchloric acid the complexing ability of the associated anion can exert a passivating effect and actually slow down the corrosion process, presumably by binding on to the glass surface.

⁽¹⁾ Recent work indicates that malonic acid also is able to bind with the glass surface and, for a time, protect the surface from attack by corrosive reagents. This paper attempts to examine this passivation in more detail and determine whether or not this is a viable method of protecting the glass fibres from the corrosive effect of the common corroding acids. Results to date show that there is indeed some resistance to the corrosive process in hydrochloric and oxalic acids, but the corrosive media eventually overcomes this and, after an initial delay, corrosion does occur and the glass fibres break. However this is an interesting observation which reinforces previous work, and it is possible that some means of passivating the glass fibre surface will eventually come to light. Malonic acid is of particular interest as it is a possible breakdown product of the resin used in glass reinforced plastic.

Key words: glass fibre durability, acid corrosion, chemical passivation, corrosion prevention

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Relationships between the mechanical properties of silicate glasses and chemical composition

Russell J Hand

University of Sheffield, Department of Materials Science & Engineering, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, UK

A combination of indentation and nano-indentation have been used to measure hardness, toughness and plane strain moduli of a range of alkali-alkali earth-silicate and borosilicate glasses. For the glasses studied improved toughness values are obtained for glasses with higher magnesia contents i.e. glasses where the alkali earth oxide is probably acting as a network former. It is shown that within a given glass series increases in moduli do not translate into increases in fracture toughness, although such increases are seen over greater compositional ranges. Larger alkalis result in a higher toughness for a given Young's modulus. Possible reasons for these variations in mechanical properties with chemical composition will be examined.

On the mixed alkali effect in the 0.17[$x\text{Li}_2\text{O}(1-x)\text{Na}_2\text{O}$].0.33CaO.0.50SiO₂ glass system

Tiago De Marchi Mosca, Ana Candida M. Rodrigues
Universidade Federal de São Carlos, Departamento de Engenharia de Materiais, Rod.
Washington Luis, Km 235, 13565-905 São Carlos S.P.

The well known mixed alkali effect remains one of the challenging open questions to be solved with respect to ionic conduction in glasses. In fact, when one alkali ion is progressively substituted by another, several examples reveal a drop of up to 2–3 orders of magnitude in electrical conductivity, σ , at room temperature. It has also been observed that this decrease in electrical conductivity is followed by an increase in the activation energy, E_a . However, little, if any, attention has focused on the pre-exponential term A of the Arrhenius expression:

$$\sigma T = A \exp\left(-\frac{E_a}{k_B T}\right)$$

Using impedance spectroscopy, we have measured the electrical conductivity of glass samples of the 0.17[$x\text{Li}_2\text{O}(1-x)\text{Na}_2\text{O}$].0.33CaO.0.50SiO₂ system (where $x=0.0, 0.1, 0.2, 0.3, 0.5, 0.7, 1.0$). This glass system was chosen due to parallel crystallisation studies. The mixed alkali effect is observed, with electrical conductivity presenting a minimum for the $x=0.5$ composition, while the activation energy and the pre-exponential term of the Arrhenius equation present a maximum for the same composition.

This work discusses the influence of the pre-exponential term on the value of electrical conductivity, and makes an exploratory analysis of this pre-exponential term based on microscopic and thermodynamic characteristics.

Samples of 0.17Na₂O.0.33CaO.0.50SiO₂ glass with the addition of up to 7.5 mol% of Li₂O are also investigated. In this case, a weak but well defined decrease in the electrical conductivity is observed with the addition of up to 3 mol% of Li₂O. A further increase in Li₂O content leads to an increase in electrical conductivity. The slight decrease in electrical conductivity and the shift of the minimum to a smaller amount of Li₂O content indicate a competitive effect between the increase in alkali content and the mixed alkali effect.

New interpretation of oxide glasses properties on the basis of the constant stoichiometry groupings (CSG) concept

Oleg V. Yanush*, Tatiana S. Markova
St. Petersburg State Technological University of Plant Polymers, 4, Ul. Ivana Chernykh,
198095 Saint Petersburg, Russia

Nowadays it is evident that the short-range order structure alone cannot reproduce property-composition curves of glasses. The dominant discourse^(1,2) invokes the presence of discrete multipolyhedral network clusters – ‘superstructural units’ – which are ‘fundamental building blocks’ in glasses. Since early 80s based on vibrational spectroscopy data a new approach has been proposed to investigate the interactions of initial oxides in melts resulted in so-called constant stoichiometry groupings (CSGs) formation.^(3–5) The vibrational spectra of glasses are interpreted as a superposition of a relatively small number of unchangeable spectral forms belonging to the CSGs. The composition dependences of the concentrations of the CSGs afford an opportunity to explain, calculate and predict the compositional dependences of refractive index, density, structural thermal expansion coefficient (STEC), the fraction of four coordinated boron atoms, Kerr coefficient and other properties of binary and ternary glasses and even glasses with ‘anomalous’ composition dependence of properties. Based on the vibrational data of glasses the developed approach allows also predicting of new crystalline compounds. More than 25 binary and ternary glassforming systems have been carefully investigated using the CSG concept in the whole composition range.

The advancement of the CSG concept is possibility to design low scattering glasses built from CSGs of a single type (without concentration fluctuations) for effective Raman amplifiers. This prediction is justified for numerous silicate, borate, germanate, and phosphate glasses investigated, where in some cases the minima of light scattering losses predicted were lower than those in silica glass.

In 90s also in Russia thermodynamic modeling studies of Shakhmatkin & co-workers⁽⁶⁾ have led to the concept of salt-like groupings in glass that have the stoichiometry of the crystalline phases that exist in the system; and also the concept of polymeric-nanoheteromorphous structure of glass proposed by Minaev V.S. & co-workers.⁽⁷⁾

Remarkably that absolutely different methods (vibrational spectroscopy^(3–5) and thermodynamic modeling^(6,7)) have provided identical information about intermediate range structure of oxide glasses consisting of CSGs, or salt-like groupings (chemical groupings), or polymorphoids.

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An insight into the Germanate Anomaly: A comparative EPR and RAMAN study supported by DFT simulations

Athina Angelopoulou^{a,b*}, George Mitrikas^a, and George Kordas^a

^a*Sol-Gel Laboratory, Institute of Materials Science, NCSR "DEMOKRITOS", 15 310 Aghia Paraskevi Attikis, Greece*

^b*Department of Materials Science, School of Natural Sciences, University of Patras, 26 500 Patras, Greece*

HYSORE and Raman spectroscopy was employed to elucidate the structure of lithium-germanate glasses of the composition x mol% Li_2O – $(1-x)$ mol% GeO_2 , where $x=5, 10, 20, 30$. The paramagnetic states were induced by γ -irradiation. The cw EPR spectra were attributed to a NBOHC arising from a hole trapped at a p orbital of a non-bridging oxygen, which has been identified firstly in irradiated alkali silicate glasses as HC_1 and HC_2 . From a comparison of our signal with structural models for HC_1 and HC_2 defects in γ -irradiated alkali silicate glasses we conclude that the Ge NBOHC can be similar to the HC_1 defect centre. Evaluation of the HYSORE spectra revealed the existence of a weak coupling between the electron spin and nearby Li. Moreover, the magnetic couplings of the alkali nuclei remain almost the same with x revealing a stable alkali ionic environment. The fact that the angle β between the z principal axis of the isotropic hyperfine coupling and g tensor is always close to $40^\circ \pm 20^\circ$ indicates the presence of alkali equilibrium sites accessible for every cation. Raman investigation revealed more information regarding the structure of the germanate glasses than the EPR investigation. The explanation of the Raman spectra was accomplished by DFT calculations using the B3LYP method under the 6-311G basis set. The spectra depend strongly on the various units, such as combination of ring units, 5-fold coordination of Ge, etc. The extend of which depends on x . The exact evaluation resulted in structural models which will be presented in confirmation with the experimental results.

Fluorine containing bioactive glasses

Robert G Hill,* Delia Brauer, Mohammed Mneimne, Natalia

Karpukhina, Helen Chen Xiaojing Chen and

*Unit of Dental Physical Sciences, Barts and the London, Queen Mary, University of London,
Mile End Road, London E1 4NS UK.*

Robert Law

Department of Chemistry Imperial College London UK

Bioactive glasses are sodium calcium phospho-silicate glasses, which dissolve in physiological fluids forming hydroxycarbonated apatite(HCA). These glasses have been widely used in medicine, but are increasingly being used for re-mineralising additives for toothpastes. This paper studies the structure, dissolution behaviour and apatite forming ability of three glass series to which fluorite (CaF_2) has been progressively added. The first series is a low phosphate series of glasses with approximately equal proportions of Na_2O and CaO , the second series is a high phosphate series with approximately equal proportions of Na_2O and CaO , the third series is a high phosphate content series like series 2, but with no Na_2O .

The glasses have been characterised by XRD, high temperature DSC and solid state MAS-NMR. The dissolution behaviour of the glasses into Tris Buffer and Simulated Body Fluid has been followed using ICP-OEM and ion selective electrodes.

All the glasses were amorphous by XRD. The glass transition temperature was found to decrease with increasing CaF_2 content. ^{19}F MAS-NMR showed the fluorine to be complexed by Ca forming F-Ca(n) species in the Na free glasses and forming mixed F-Ca/Na(n) sites in the Na containing glasses. ^{29}Si MAS-NMR showed no change in the Q speciation. ^{31}P MAS-NMR showed the presence of Q^0 or orthophosphate in all the glasses.

The addition of CaF_2 to the glasses increased their dissolution rate and reduced the time to form apatite. ^{19}F MAS-NMR showed the apatite to be a fluorapatite (FAP) as opposed to a HCA. The higher phosphate content glasses formed apatite much more quickly than the lower phosphate glasses. High CaF_2 contents >13 mol% in the glass resulted in the formation of fluorite at the expense of FAP in Tris buffer and SBF. The Na free series formed FAP exceedingly rapidly, which casts doubt on the view that Na^+ ion exchange for H^+ is the first step in bioactive glass degradation.

These new fluorine containing bioactive glasses are particularly attractive for re-mineralising toothpastes, where the formation of FAP as opposed to HCA is an attractive feature.

Thermal, viscosity and thermal expansion coefficient properties for a range of phosphate based glasses

Sharifah I.S. Shaharuddin*, Ifty Ahmed, David Furniss, Andrew J. Parsons, Christopher D. Rudd

Faculty of Engineering, Division of Materials, Mechanics and Structures, University of Nottingham, Nottingham NG7 2RD, UK

Phosphate based glasses (PBG) are currently of huge interest since recent findings have shown that the durability of PBG can be increased by doping with selective metal cations. Furthermore, their degradation rates can be tailored to suit their end applications. PBGs for biomedical applications have been produced in fibre form and mostly via melt drawn techniques. Thus, data relating to viscosity temperature profile or thermal expansion property of PBG is inadequate. In order to draw fibers via preform technique, viscosity temperature correlation is crucial as it would indicate the approximate temperatures for both preform manufacture and fibre drawing.

In this study various compositions in the system $50\text{P}_2\text{O}_5-(x)\text{Ca}-(50-x)\text{Na}$ glasses, $0 \leq x \leq 50$, were investigated for their thermal properties (glass transition, T_g , crystallisation T_c , and melt temperatures, T_m), density, molar volume, linear thermal expansion coefficient and viscosity temperature correlation. The glass compositions were confirmed via EDX and the amorphous nature of the formulations investigated was confirmed via XRD. The T_g , viscosity temperature profile and density increased with increasing CaO mol%. The glass transition temperature, increased from 290 to 521°C. The viscosity temperature profiles revealed an increase in fibre drawing range from between 327°C to 529°C. These profiles also indicated the temperature regions for preform manufacturing increase from 320°C to 451°C. The density was also seen to increase from 2.5 to 2.64 g cm⁻³. Substitution of CaO at the expense of Na_2O in the glass system studied also caused a decrease in linear thermal expansion from $25.44 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ to $11.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. The effects mentioned above have been attributed to the cross-linking of Ca^{2+} cations between different phosphate chains and the higher field strength of Ca^{2+} compared to Na^+ which strengthen the glass network.

Electrical conductivity of quartz glass measured by impedance spectroscopy between 600–1100°C

D.-K. Lee

Solar Cell Research Center, Materials Science and Technology Division, Korea Institute of Science and Technology (KIST), Seoul 136-791, Korea

M. Nebe

Institute of Inorganic and Analytical Chemistry, Justus-Liebig-University, Heinrich-Buff-Ring 58, 35392 Gießen, Germany

M. Stamminger*

Heraeus Quarzglas GmbH & Co KG, Quarzstrasse 8, 63450 Hanau, Germany

J. Janek

Institute of Physical Chemistry, Justus-Liebig-University, Heinrich-Buff-Ring 58, 35392 Gießen, Germany

The electrical conductivity of quartz glass material grades with a variety of lithium and hydroxyl contents has been determined by AC impedance spectroscopy at temperatures between 600 and 1100 °C. The samples represent glass manufactured by electrical fusion and flame fusion of quartz crystals, as well as synthetic fused silica manufactured by hydrolysis of a silicon-containing precursor in an oxyhydrogen flame. The resulting plots of conductivity versus temperature yielded good Arrhenius dependencies allowing a determination of the activation energies for the electrical conduction process. The activation energies showed a change in magnitude at about 800°C. Complementing data from previous studies, the results show that the conductivity is determined primarily by the lithium content in the natural fused quartz grades. In the synthetic fused silica materials, the hydroxyl content plays the predominant role.

Tin oxide solubility in soda-lime silicate melts

P. Gateau*, C. Petitjean, P.-J. Panteix, C. Rapin, M. Vilasi

Dpt CP2S-Equipe SIRCM, IJL-UMR 7198, Faculty of Sciences and Techniques, B.P. 70239 - 54506 Vandoeuvre-lès-Nancy Cedex, France

Due to its low solubility in molten glass, the lowest among non-colouring oxides, tin dioxide is commonly used as refractory material, electrodes or as opacifier in enamels. Thus, this work deals with the influence of glass composition and temperature on SnO₂ solubility.

The solubility of tin dioxide is assessed as a function of time and temperature in simple ternary glasses: NC3S, NC4S, NC5S and NC6S (N: Na₂O, C: CaO, S: SiO₂). Further experiments were led in glasses enriched with Na₂O, CaO, Al₂O₃ or B₂O₃, in order to study the influence of network formers and modifiers on the solubility of SnO₂.

For each experiment, glass was crushed with cassiterite powder (SnO₂). From this mixture, 100 mg balls of SnO₂/glass were formed in a carbon crucible. Samples were then annealed at temperatures comprised between 1200–1400°C, for times up to 9 h. SnO₂ over-saturation in the silicate melt was controlled by SEM, while the content of dissolved oxide was measured by EPMA.

As expected, the solubility of tin oxide follows an Arrhenius law, which is characteristic of a thermally activated process. Furthermore, the limit of solubility of SnO₂ is discussed regarding the optical basicity. The sole influence of this parameter can not explain the measured evolution of tin oxide solubility. As a consequence, the discussion also deals with a potential change of the oxidation state of tin.

Effects of magnesium for calcium substitution in phosphate glasses

Delia S. Brauer^{1,*}, Sungho Lee², Kie Fujikura^{2,3}, Robert V. Law³
& Toshihiro Kasuga²

¹Dental Physical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, UK

²Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

³Department of Chemistry, Imperial College, Exhibition Road, London SW7 2AZ

Phosphate glasses dissolve completely in aqueous media, which makes them of interest for use as temporary implant materials or for controlled release of therapeutically active ions. The aim of our research was to study the effect of magnesium for calcium substitution on structure, thermal properties and dissolution of metaphosphate glasses and phosphate invert glasses.

A metaphosphate series $(45-y)\text{CaO} \cdot y\text{MgO} \cdot 50\text{P}_2\text{O}_5 \cdot 5\text{TiO}_2$ (mol%, $y=0-45$) and an invert glass series $(60-x)\text{CaO} \cdot x\text{MgO} \cdot 30\text{P}_2\text{O}_5 \cdot 10\text{TiO}_2$ (mol%, $x=0-60$) were produced by a melt-quench route. Thermal behaviour was investigated using differential thermal analysis (DTA); glass structure was investigated using Raman spectroscopy and solid-state nuclear magnetic resonance (ssNMR) spectroscopy. Dissolution behaviour was tested in Tris (tris(hydroxymethyl)aminomethane) buffer solution at pH 7.4 over up to 7 days and analysed using inductively-coupled plasma optical emission spectroscopy (ICP-OES).

Raman peak positions shifted to higher wavenumbers with increasing Mg-substitution. ssNMR spectra were complicated by presence of $Q^1(\text{Ti})$ peaks. Mg-substitution moved the Q^1 peak to more negative chemical shifts while broadening all peaks. This might be due to magnesium, an intermediate cation, partially entering the phosphate chains, forming P-O-Mg bonds.

Mg-substitution improved the processing of metaphosphate glasses, while mixed Ca/Mg invert glasses showed larger processing window windows than the all Ca or the all Mg versions, possibly due to a mixed cation effect. Mg-substitution reduced the solubility of metaphosphate glasses, while increasing the solubility of invert glasses.

In summary, Mg-substitution affected properties of metaphosphate and invert glasses in opposite ways, which might be due to its intermediate character. However, further detailed structural investigations are necessary to fully elucidate the structural role of magnesium in phosphate glasses.

Russian Glass Chemistry: From Lomonosov to Shultz

Natalia M. Vedishcheva^{*1} & Adrian C. Wright²

¹Moskovsky prospekt, 220-386, St. Petersburg, 199066, Russia

²J.J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading, RG6 6AF, U.K.

This paper briefly considers the history of Russian glass science and, in particular, its chemical aspects. Unlike in Europe, alchemy was never popular in Russia, being very little known before the end of the 17th century, when the rule of Peter the Great started. This situation strongly favoured the development of genuine chemistry, especially by the time Mikhail V. Lomonosov finished his studies and started working in the 1740s, which explains his rigorous scientific approach to both chemistry and glass properties. Lomonosov's 18th Century successor was Erik Laxman, who is the subject of the previous presentation by Kaj Karlsson, whilst the most famous glass scientist during the 19th Century was Dmitri I. Mendeleev, who considered glasses as salts of silicic acid. The question as to whether glasses are mixtures or chemical compounds was discussed, in the 1890s, by Nikolai N. Lyubavin and, in the 20th Century, the chemical constitution of glasses was first addressed by Alexander A. Lebedev (the 1920s) and then by Evgenii A. Porai-Koshits (the 1940s). Later, in the 1950s-1980s, important Russian contributions to the chemistry of glasses and glass-forming melts included those of Rudolf L. Muller, Alexander A. Appen and Mikhail M. Shultz, who studied chemical equilibria in glasses. The combined achievements of the above scientists represent an impressive legacy, contributed by Russian workers to the worldwide development of glass science.

Pliny's Lost Glass: The Search for Flexible Glass and the Formation of Research Agendas in Early Modern Europe

Vera Keller

University of Oregon, Clark Honors College, 1293 University of Oregon, Eugene, Oregon 97403, USA

For those seeking to rediscover the glories of the ancient world in early modernity, one frequently retold story encapsulated the possibilities and dangers facing invention. This was the story of flexible glass, an amazing substance, which, according to an ancient Roman tale, had been discovered during the reign of the infamous Emperor Tiberius. According to legend, Tiberius murdered its inventor and destroyed his workshop, lest the new substance reduce the value of precious metals. 'Who would not hate such a savage murderer and destroyer of art and artisan, and who reading of the affair will not boil with rage?' asked one outraged chemical writer in 1611. As other seventeenth-century commentators remarked, glass was the most perfect invention of mankind; its fragility was its only imperfection. Flexible glass thus not only presented a fantasy of perfectly restoring a decayed, ancient Rome to its pristine grandeur, but furthermore of building a newly resilient world which could never again be shattered. The story of its loss dramatized how such dreams might be dashed by private interest and secrecy - on the part of both Tiberius and the inventor, who did not share his procedure. Flexible glass was both an avidly pursued substance itself in the seventeenth century, and the story of its loss helped to shape how the pursuit of desired objects in general was conducted. This paper will recreate the search for this ancient mythical material across seventeenth-century Europe. In so doing, I will discuss what specific chemical investigations the pursuit of flexible encouraged, and more generally, how thinking about the relationship of ruler, subject, and invention helped shaped plans for the advancement of knowledge at large.

Looking for primary Roman glass production in the Western Mediterranean.

Dieter Brems*, Patrick Degryse, Monica Ganio & Sara Boyen

Department of Earth and Environmental Sciences, K.U.Leuven, Celestijnenlaan 200E, B-3001 Leuven, Belgium

Pliny the Elder's Natural History has been cited numerous times in studies of ancient natron glass production. Pliny describes the production of glass using sand from the beach near the mouth of the river Belus and the coastal strip between Cuma and Liternum near the river Volturno. After giving these precise locations for the source of glassmaking sands in the Levant and Italy, Pliny mentions that 'throughout the Gallic and Spanish provinces even, we find sand subjected to a similar process', thus indicating that glass was made from raw materials in France and Spain. However, no direct archaeological evidence has been found to support primary production in these regions. Furthermore, the suitability of these sands has never been evaluated.

In this study we investigate the possible existence of a Roman primary glass industry in the western Mediterranean, based on the occurrence of suitable sand raw materials. 185 beach sands from Spain, France and Italy are evaluated for their suitability for glass production by calculating the composition of hypothetical natron glasses made from these sands and comparing them to the composition of Roman natron glass.

The results show that suitable glassmaking sands are far from common. Only a very limited number of the analysed sands would produce a glass with major and minor elemental compositions within the ranges of Roman imperial natron glass. The rest of the sands are unsuitable for glass production in their present form, the determinant factors often being the insufficient SiO_2 , the high Al_2O_3 and Fe_2O_3 levels and either too low or too high CaO contents. The sands which would produce glasses of acceptable composition are all mainly derived from the recycling of older sedimentary successions. This reflects the importance of polycyclic chemical and mechanical weathering in the maturation of sediments. The necessary amount of CaO is brought to the sand either through calcareous fragments from minor (but important) limestones or marls in the local hinterland, or through contributions of shell fragments naturally included in the sand.

If sands contain too little CaO to produce a stable glass, pieces of shell or limestone can be added to the glass batch, as was already suggested by Pliny the Elder. Therefore a second calculation was performed in which the CaO contents of the hypothetical glasses were raised to the average CaO content of Roman glass, to model this deliberate addition of extra lime. Although the quality of most examined sands is improved, very few samples could be brought to within compositional ranges of Roman glass for

all main and minor elements.

By calculating the composition of hypothetical glasses produced from modern beach sands, we were able to define a few limited areas where suitable sand raw materials would have been available to the Roman glassmaker. This allows us to make some suggestions about the possible locations of primary Roman glass production in the western Mediterranean.

Trade routes across the Mediterranean: a Sr/Nd isotopic investigation of Roman colourless glass

M. Ganio*, S. Boyen, D. Brems, P. Degryse

Section Geology, Centre for Archaeological Sciences, K.U. Leuven, Celestijnenlaan 200E, bus 2408, BE-3001 Leuven, Belgium

K. Latruwe

Department of Analytical Chemistry, Ghent University, Krijgslaan 281 - S12, 9000 Ghent, Belgium.

Trade by sea was quite common during Roman times, as attested by the numerous shipwrecks found in the Mediterranean. Cargos were usually mixed, often composed of stone, amphorae with different contents or tableware ceramics, together with variable quantities of glass. It is less common to find a cargo mainly composed of glass. In this study major elements and Sr-Nd isotopic analysis is performed on 33 colourless glass fragments from two Roman shipwrecks discovered in the Northern Mediterranean Sea. The Iulia Felix, found off the coast of Grado (northeastern Italy) and dated to the first half of the 3rd century AD, shows a cargo mainly composed of amphorae together with a total of 140 kg of glass (cups, bottles and plates). The Ouest-Embiez 1, wrecked off the coast of Provence (southern France), is dated to the end of the 2nd-beginning of the 3rd century AD and has a cargo mainly composed of glass, with 18 tons of raw glass, and about 1800 pieces ranging from cups to window glass. Two compositional groups are defined based upon the major elements analysis, suggesting the use of different raw materials, and possibly the production of the glass samples in two separate factories. This conclusion is supported by the presence of different decolourizing agents showing the use of two different glass recipes. The first group, which shows low levels of Ca, Al, K, Ba, Ti and P, is made with a more quartz-rich (pure) sand, and Sb as decolorising agent. Its composition is similar with the 'group 1' of Jackson (2005) or with the 'group 4' of Picon and Vichy (2003). Raw glass and 'high status' dishware (cups and plates) belong to this group. The second group is produced with a less pure sand, rich in Ca and Al, and it is similar in composition with the 'group 3' of Nenna (1997) but with a higher content of MnO (>1%). Mn, the decoloriser, is positively correlated with Ba and Sr, suggesting the introduction of those three elements through a common source, probably wad or psilomelane. Sr-Nd isotopes are promising indicators for provenancing geological resources used as raw materials in glass manufacturing. The Sr isotopic composition, a proxy for the lime source, of the glass samples in analysis corresponds to the present-day seawater signal ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7092$), suggesting the use of beach sand as lime source. The two compositional groups are confirmed by the Sr content vs. $^{87}\text{Sr}/^{86}\text{Sr}$ plot. The group decolorised by Sb has a higher isotopic signature ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{average}} = 0.709045 \pm 0.000041$) together with a lower content of Sr (268–394 µg/g), while the other group shows a higher

content of Sr (458–551 µg/g) associated with a lower Sr isotopic signature ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{average}}=0.708808\pm0.000043$). This represents an unusual situation, since it is commonly accepted that beach shells, rich in aragonite, should have a higher content of Sr than limestone, together with a Sr isotopic signature very close to the modern seawater value. The anomaly can be explained by the addition of Sr through a separate source than the sand, characterized by a low Sr isotopic composition. This source introduces also the decolorizer Mn (associated with Sr and Ba). The Nd isotopic composition is typical of the heavy non-quartz fraction in the silica raw material. The Nd isotopic analysis (in progress) and the comparison with ranges of isotopic characteristics of sands from around the Mediterranean, will help provenance the glass samples of the two Roman shipwrecks and recreating their commercial trade routes.

Glass coatings on stones of copper smelting furnaces - Bronze Age originals and results of archaeological experiments

Rainer O. Werthmann

Immenhäuser Str. 16, Kassel, D-34128, Germany

In archaeological experiments at the university of Kassel, Germany, the copper smelting process in furnaces of the type used in Timna, Israel, and Fenan, Jordan, was reproduced. The materials used were close in composition to those found at the original sites: sandstone for the furnace, oxidic/ carbonatic copper ore, charcoal, iron ore as slag-forming additive. Special attention was paid to the glaze layers formed inside the furnaces containing evaporated constituents of charcoal ash, silica from the stones and traces of copper. The glass layers were investigated by scanning electron microscopy, their composition being determined at various points by electron beam microprobe. From these data, a detailed mechanism of formation could be reconstructed. The variation of the composition as a function of the temperature of formation could be shown.

The structural role of lone-pair cations in glasses

Alex C. Hannon* & Emma R. Barney

ISIS Facility, Rutherford Appleton Lab, Chilton, Didcot, Oxon OX11 0QX, UK

Oliver L. G. Alderman & Diane Holland

Physics Department, Warwick University, Coventry CV4 7AL, UK

Lone-pair cations, of which lead is a prime example, play an important role in the formation of glasses over a wide range of compositions. It has long been believed that for low PbO contents, the lead plays the role of a modifier in the glassy network, but as the PbO content increases there is a change to a network former role. This concept pre-dates the availability of modern structural probes, and the talk will first review structural studies of lone-pair cations in glasses, which give contradictory results on the validity of the traditional model. Recent combined neutron diffraction and NMR studies of the structural role of lone-pair cations in glasses will then be reported, including studies of thallium germanates, tin borates, tin phosphates, lead germanates and lead silicates.

The influence of modifiers on the tellurium environment in glass

Emma R. Barney* & Alex C. Hannon

ISIS Facility, Rutherford Appleton Lab, Chilton, Didcot, Oxon OX11 0QX, UK

Diane Holland

Physics Department, Warwick University, Coventry CV4 7AL, UK

Tellurite glasses are potential candidates for many devices including optical switching devices and laser hosts. The origins of the properties which they possess - such as high refractive indices, wide infra red transmittance, chemical durability and non-linear optical (NLO) responses - are not precisely known, but it is thought the macroscopic polarisability of the glass (electrical and optical) arises from the peculiarities in the co-ordination polyhedra of tellurium (IV) which must include one lone-pair (lp) of electrons. There is a wealth of literature to show that the addition of a modifier to a tellurite glass network results in Te coordination changes, and these changes have been linked to the NLO response. Glasses which are tellurium rich are almost entirely comprised of $[\text{TeO}_4]$ units and have strong NLO responses, the strength of which decreases rapidly in glasses with increased modifier content, due to the associated formation of $[\text{TeO}_3]$ units and non-bridging oxygens. To allow the unusual properties of TeO_2 to be utilised effectively, a clear understanding of the relationship between composition, tellurium environment and NLO properties is necessary. The titanium tellurite system has been highlighted as a possible exception to the generally understood relationship between modifier content and tellurium coordination number. Raman spectra measured on this system of glasses shows very little change in character as TiO_2 content is varied, from which it has been implied that there is no change in the tellurium environment with composition. The suggested explanation is that titanium, present in $[\text{TiO}_6]$ units, is directly substitutes for tellurium without disrupting the TeO_2 glass network. This allows the formation of $\text{O}-\text{Te}(\text{IV})-\text{O}-\text{Ti}(\text{VI})-\text{O}-\text{Te}(\text{IV})-\text{O}$ linkages (where roman numerals denote the coordination number). Supporting evidence for this idea is provided by the 25 mol% TiO_2 titanium tellurite crystal structure, which is comprised entirely of $[\text{TiO}_6]$ and $[\text{TeO}_4]$ structural units. This talk will present total scattering data that has been measured on a range of tellurites, from crystalline $\alpha\text{-TeO}_2$ and pure amorphous TeO_2 , to alkali and boron modified tellurite glasses and recently collected data from the titanium tellurite system, to discuss the effect of modifiers on tellurium environment.

Intermediate-range order in the tellurite glassforming system $\text{PbO-P}_2\text{O}_5\text{-TeO}_2$ studied by Raman spectroscopy and x-ray powder diffraction.

Inna E. Apakova, Olga Derkacheva, Tatiana S. Markova,* Oleg V. Yanush

St. Petersburg State Technological University of Plant Polymers, 4, Ul. I. Chernykh, St-Petersburg, 198095 Russia

Vladimir K. Goncharuk, Irina G. Maslennikova

Institute of Chemistry of Far-Eastern Branch of Russian Academy of Sciences, 159, Pr. Stoletiya, Vladivostok, 690022 Russia

Irina G. Polyakova

Institute of Silicate Chemistry, Russian Academy of Sciences, 29, Ul. Odoevskogo, St-Petersburg, 199155 Russia

Anatolii V. Anan'ev, Leonid V. Maksimov

Research and Technological Institute for Optical Material Science, 36-1, Ul. Babushkina, St-Petersburg, 192171 Russia

Earlier an approach to investigation of glass structure, based on vibrational spectroscopy data treatment and resulted in extraction of principal spectral components (PSCs) belonging to so-called constant stoichiometry groupings (CSGs), has been proposed to determine the products of the interaction of initial oxides in melts.⁽¹⁾ The composition dependences of the concentrations of the CSGs have afforded an opportunity to explain and calculate the compositional dependences of refractive index, and density, and some other properties of glasses in a good agreement with experimental data and even to predict successfully the existence of unknown compounds ($\text{Na}_2\text{O} \cdot 0.8\text{B}_2\text{O}_3$, $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$,⁽¹⁾ and others). Besides, the concept of CSG opens the way to elaboration of low scattering glasses as candidates for Raman amplifiers. In this paper we have chosen $(100-x)(0.5\text{PbO} \cdot 0.5\text{P}_2\text{O}_5) \cdot x\text{TeO}_2$ glass series (where x is molar percent TeO_2), in which any ternary compounds have not been investigated so far, to confirm predictive power of the CSG concept.

Application of the CSG concept to the Raman spectra has revealed the existence of the CSGs: $\text{PbO} \cdot \text{P}_2\text{O}_5$, $\text{TeO}_2 \cdot 2\text{PbO} \cdot 2\text{P}_2\text{O}_5$, TeO_2 and three others lead tellurite-phosphate groups which reach their maximal content in glasses of the system under study in vicinity of $\text{TeO}_2 \cdot \text{PbO} \cdot \text{P}_2\text{O}_5$, $2\text{TeO}_2 \cdot \text{PbO} \cdot \text{P}_2\text{O}_5$, $6\text{TeO}_2 \cdot \text{PbO} \cdot \text{P}_2\text{O}_5$ compositions. Independently formation of the same CSGs was evidenced by chemometric techniques. The composition dependences of the concentrations of the CSGs have allowed to calculate refrac-

tive index and density. X-ray powder diffraction (XRPD) of the crystallised glasses revealed five new ternary $\text{PbO-P}_2\text{O}_5\text{-TeO}_2$ compounds. Two of them, $\text{TeO}_2 \cdot 2\text{PbO} \cdot 2\text{P}_2\text{O}_5$ and $6\text{TeO}_2 \cdot \text{PbO} \cdot \text{P}_2\text{O}_5$, falls on the studied cut $(100-x)(0.5\text{PbO} \cdot 0.5\text{P}_2\text{O}_5) \cdot x\text{TeO}_2$ and form pseudo-binary systems with lead metaphosphate and TeO_2 , correspondingly. In the composition regions between these compounds (0–20 and 66.6–100 mol% TeO_2) a sequent replacement of the metaphosphate for $\text{TeO}_2 \cdot 2\text{PbO} \cdot 2\text{P}_2\text{O}_5$ and tellurium dioxide for $6\text{TeO}_2 \cdot \text{PbO} \cdot \text{P}_2\text{O}_5$ takes place in the XRD patterns as well as in the Raman spectra. All other ternary compounds lie out of the straight cut $\text{PbO} \cdot \text{P}_2\text{O}_5\text{-TeO}_2$, but composition regions, where contents of the individual crystal phases are maximal, closely correspond to CSGs stoichiometries $\text{TeO}_2 \cdot \text{PbO} \cdot \text{P}_2\text{O}_5$, $2\text{TeO}_2 \cdot \text{PbO} \cdot \text{P}_2\text{O}_5$. Analysis of Raman Intensity and Rayleigh scattering losses has shown that glasses containing small additive of tellurium dioxide are of interest to photonics technology.

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Lead tungstate-phosphate glasses: structural study, properties and crystallisation

Ladislav Koudelka,* Ivana Rösslerová Petr Mošner Zdeněk Černošek

*Department of General and Inorganic Chemistry, Faculty of Chemical Technology,
University of Pardubice, 532 10 Pardubice, Czech Republic*

Magdalena Lissová, Marek Liška

*Vitrum Laugaricio – Joint Glass Center of Institute of Inorganic Chemistry SAS, Alexander
Dubcek University of Trencin and RONA Lednicke Rovne, Studentska 2, Trencin SK-911
50, Slovak Republic*

Lionel Montagne, Laurent Delevoye

*Université Lille Nord de France – UCCS - UMR CNRS 8181, USTL, 59655, Villeneuve
d'Ascq, France*

Tungsten-oxide based materials are known for their electrochromic and photochromic properties resulting in a wide range of applications. Glasses based on tungsten oxide also belong among interesting optical materials. This contribution deals with glasses in the ternary system $\text{PbO-WO}_3\text{-P}_2\text{O}_5$ with ≤ 50 mol% P_2O_5 , which are characterized by a good chemical stability. Their structure and properties were investigated in three compositional series $(100-x)[0.5\text{PbO}-0.5\text{P}_2\text{O}_5]-x\text{WO}_3$, $50\text{PbO}-y\text{WO}_3-(50-y)\text{P}_2\text{O}_5$ and $(50-z)\text{PbO}-z\text{WO}_3-50\text{P}_2\text{O}_5$ by Raman and ^{31}P NMR spectroscopies. Basic characteristic parameters of the prepared glasses were determined. In the compositional series $(100-x)[0.5\text{PbO}-0.5\text{P}_2\text{O}_5]-x\text{WO}_3$ homogeneous glasses were prepared in the concentration region of 0–60 mol% WO_3 . Their glass transition temperature increases with increasing WO_3 content very significantly from 328 to 583°C. ^{31}P MAS NMR spectra of the glasses show on a shortening of phosphate chains by the incorporation of tungstate structural units. Most studied glasses contain tungsten atoms in octahedral WO_6 units. Clustering of WO_6 units by the formation of W–O–W bonds takes place in glasses with a high WO_3 content as observed from their Raman spectra. Crystallisation of glasses was studied by XRD and Raman spectroscopy and crystalline products were identified by both methods. Raman spectroscopy was effective also for the characterisation of glass-crystalline products. XRD characterisation of crystalline products revealed also one new crystalline lead tungstate-phosphate compound.

Glass formation and structure of glasses in $\text{ZnO-V}_2\text{O}_5\text{-WO}_3\text{-MoO}_3$ system

R. Iordanova,* A. Yordanova, L. Aleksandrov

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, “Acad. G.
Bonchev”, bld. 11, 1113 Sofia, Bulgaria.*

Y. Dimitriev

*University of Chemical Technology and Metallurgy, 8 Kl. Ohridski blvd., 1756 Sofia,
Bulgaria*

The glass formation area in the $\text{ZnO-V}_2\text{O}_5\text{-WO}_3$ system was determined by press-quenching method (cooling rate 10^2 K/s). New original glasses containing between 10–80 mol% ZnO , between 5–90 mol% V_2O_5 , and up to 30 mol% WO_3 were obtained. Homogeneous glasses of the composition $(100-x)[a\text{ ZnO: b V}_2\text{O}_5\text{: c WO}_3]x\text{MoO}_3$, were obtained up to 70 mol% MoO_3 . Characterisation of amorphous samples was made by x-ray diffraction (XRD), differential thermal analysis (DTA), infrared spectroscopy (IR) and x-ray photoelectron spectroscopy. According to DTA data, the raising of ZnO content leads to increase of glass transition (T_g) and crystallisation (T_c) temperatures. The glasses located in the central part of the glass formation area possess highest thermal stability ($\Delta T = T_c - T_g$). Quenching of compositions located outside of glass formation area resulted in separation of ZnO , ZnWO_4 and ZnMoO_4 crystal phases. Structural model of the glasses was suggested on the basis of IR and XPS spectra. The addition of ZnO to V_2O_5 causes a transformation of layered vanadate network to metavanadate (VO_5), pyrovanadate (VO_4) and ortovanadate one. V_2O_5 and MoO_3 possess similar chain structures and create random networks in wide concentration range with participation of MoO_6 and VO_5 units. Three-dimensional WO_3 structure is not suitable to join with V_2O_5 and MoO_3 in amorphous network.

Keywords: glass, structure, ZnO , MoO_3 , V_2O_5 , WO_3

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Short- and intermediate-range order of phosphorus-selenium glasses

David Price

CEMHTI, 1d ave de la Recherche Scientifique, ORLEANS Cedex 2, 45071 FRANCE

Aleksei Bytchkov

CEMHTI, Orleans and ILL, Grenoble, France

We present state-of-the-art neutron and x-ray diffraction data that provide a definitive picture of the short- and intermediate-range structure of P-Se glasses spanning both glass regions. Specific goals were (1) to obtain detailed information about the development with increasing of intermediate-range order on the length scale around 10 Å, based on the behavior of the first sharp diffraction peak; and (2) to obtain a reliable statistical picture of the short-range order, using the information about types and concentrations of local structural units provided by recent NMR measurements to interpret the trends observed as the P concentration is varied. Particular attention is given to the fine structure of the first peak in the pair distribution function and to a feature in the structure factor at 7.5 \AA^{-1} , highlighted by Sergi *et al.* as a signature of molecular units.

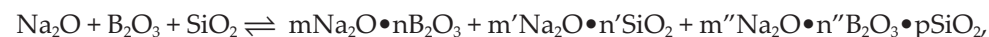
The Vitreous State: A Product of Chemical Equilibria

Natalia M. Vedishcheva*¹ & Adrian C. Wright²

¹Moskovsky prospekt, 220-386, St.Petersburg, 199066, Russia

²J.J. Thomson Physical Laboratory, University of Reading,
Whiteknights, Reading, RG6 6AF, U.K.

Experimental studies of the vitreous state performed within the last few decades by a variety of methods have resulted in the accumulation of a large body of experimental data on the structure and properties of binary, ternary and multi-component glasses. The most common interpretation of these data is based on a consideration of the short-range order in the glass structure, as characterised by the presence of different basic structural units with varying numbers of bridging oxygen atoms, such as B(n) or Si(n). More recent progress in structural studies has been marked by the determination of the intermediate-range order, e.g., for borate glasses, at the level of superstructural units that comprise combinations of basic structural units whose type and numbers are strictly determined. In the case of other systems, the latest stage of structural studies involves the connectivities in vitreous networks, which implies the types and numbers of neighbours for a given basic structural unit. However, no information about these levels in the glass structure allows either structural changes due to variations in the glass composition or synthesis conditions to be predicted, or structure-property relationships to be unambiguously established. This is due to the fact that the structural models known to the authors completely neglect the role of the network-modifying cations that form characteristic metal-oxygen polyhedra. As a result, these models do not conform to the principles of mass balance, charge balance and that of the minimum Gibbs energy of a given system. The present paper shows that this problem can be successfully solved, if glasses are considered as products of chemical interactions between oxide components that proceed according to such equilibria as



where m, n and p are the coefficients determining the stoichiometry of the binary and ternary compounds that can be found in the phase diagram of a given system. This approach takes into account the presence of the network-modifying cations in glasses and considers structural changes in terms of the Gibbs energy of a given system. The approach is based on determining the chemical structure of glasses, which implies their content of various chemical groupings. As the approach allows both the structure and a variety of glass properties to be calculated, structure-property relationships are established quantitatively. The approach also explains quantitatively the relationship between the short- and intermediate-range order and shows which of them predominates in determining glass properties.

Thermodynamic modelling and high-temperature Raman spectroscopy of silicate melts

Olga N. Koroleva
Russia, Miass, IMIN UrB RAS

The work is devoted to study of silicate melts structure depending on composition and temperature by means of thermodynamic modeling and experimental methods. The model of associated solutions⁽¹⁾ was used for thermodynamic calculations of Q^n -distribution in glasses and melts of binary and ternary silicate systems. According to thermodynamic modeling the equilibrium between structure units of silicate system ($M_2O \leq 50\%$) shifts to the right with increasing temperature in sodium and potassium silicate melts. Q^n -distribution of lithium silicate melts behaves oppositely, and spectroscopic data confirm this result. By means of thermodynamic modeling it was shown that in the system $(40-x)\%K_2O \times x\%Li_2O \times 60\%SiO_2$ distribution of modifier cations between Q^n -species becomes more random with increasing temperature. According to the idea about acid-base interaction in melts there is ordering of this distribution with decreasing temperature. Such behavior is agreed with results of Raman spectroscopy for glasses.

At the same time the other theoretical method was used to create a thermodynamic model of silicates. The base of this model is Gibbs energy minimization approach.⁽²⁾ Moreover a database for silicate melts was collected and evaluated. To test the model the obtained data compared to results of high-temperature Raman spectroscopy.

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Whether the term 'polyamorphism' is correct for non-crystalline substance?

V. S. Minaev*, S. P. Timoshenkov, V. V. Kalugin
National Research University Moscow Institute of Electronic Technology, dom 5, proezd 4806, Moscow, Zelenograd, Russian Federation

Walf *et al* (1992) note to possibility of actual macroscopic polymorphism in the amorphous state called 'polyamorphism'. In the glassy state well below T_g , cooperative phenomena can occur and sometimes appears as a 'quasi-thermodynamic' phase transformation between isocheimal structural polymorphs or 'polyamorphs' (Yarger, Angell *et al.*, 1996). a-Si, a-Ge, a-H₂O show abrupt change from a low-density amorphous (LDA) to a high-density amorphous (HDA) state while the transition proceeds gradually in SiO₂, GeO₂, BeF₂, GeSe₂ (Durandurdu *et al.*, 2002). So there are no even two polyamorphs, which was observed in glassy water. Could we speak about polyamorphism as about multitude of different amorphous states? In case of water we can conditionally accept the existence of two polyamorphs and call this diamorphism (also conditionally). Yarger, Angell *et al.* (1996) thinks that it's impossible to give the current experimental data to discern the mechanism of structural transitions in SiO₂, GeO₂, BeF₂, and other tetrahedral network glasses. The concept of polymeric-polyamorphoid structure of non-crystalline substance (1,2) proposes such mechanism. In according to this concept individual chemical substance is a copolymer of fragments (polymorphoids) of different polymorph modifications (PM), without translational symmetry (long-range order), but characterised by strictly defined intermediate- and short-range orders inherent to one of the PMs taking part in glass formation. In the non-crystalline substance the fast cooling of melt or high pressure changes the concentration ratio of polymorphoids (CRP) in direction of that polymorphoids, which was formed at the conditions corresponding to their place in the P-T phase diagram. As a result, there are, for example, quartz- or cristobalite-like glass (Golubkov, 1992). In these glasses polymorphoids ratio of quartz and cristobalite is continuously changing in a wide range and getting close to pure quartz and cristobalite. Amorphous substance has not "poly", but "innumerable" polyamorphs. The conditions ($P=1 \cdot 10$ Kbar, $T=77-114$ K) for obtaining high-density amorphous water – HDA ($d=1 \cdot 31$ g·cm⁻³) are close to the conditions of crystalline ice VI ($d=1 \cdot 37$ g·cm⁻³) formation. The HDA decompression to 1 atmosphere leads to falling of density to $1 \cdot 17$ g·cm⁻³ (Mishima, 1986). In accordance with P-T diagram and density changes a huge amount of Ice VI polymorphoids that were in HDA before the decompression transforms into polymorphoids of Ice IX ($d=1 \cdot 19$ g·cm⁻³) and Ice I ($d=0 \cdot 92$ g·cm⁻³). The last was in glassy H₂O originally. Due heating HDA ($d=1 \cdot 17$ g·cm⁻³) at the temperature 77–125 K it transforms to LDA (Yohary *et al.*, 1996) with density $0 \cdot 94$ g·cm⁻³ (polymorphoids of Ice IX has been transformed to Ice I polymorphoids) and changing of CRP respectively. Thus, polyamorphism of non-crystalline substance is incorrect label of the phenomenon of

different PM's polymorphoids CRP continual change. In process of this phenomenon polymorphoids of one PM can prevail over polymorphoids of another PM with the corresponding approximation of properties to the properties of these PMs.

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In situ - analyses of glasses and supercooled melts in microconfinement

Lothar Wondraczek*, Markus A. Schmidt, Nicolai Granzow, P. St. J. Russell

University of Erlangen-Nuremberg, Department of Materials Science, Martensstrasse 5A, Erlangen, 91058, Germany

Infiltration of microstructured capillaries and photonic crystal fibers was recently demonstrated as a unique way to fabricate all-solid fiber waveguides from unusual combinations of materials. Interestingly, the technique also offers the possibility to study, in situ, the properties of supercooled melts and consolidation of glasses in microconfinement under variations of pressure and temperature. In this context, this talk will consider the behaviour of various types of glass (chalcogenide, tellurite and phosphate) under microconfinement. Effects on rheology, glass transition, structure and structural anisotropy will be discussed.

Elemental speciation in nuclear waste glasses

Sergey V. Stefanovsky*

SIA Radon, 7th Rostovskii lane 2/14, Moscow 119121 Russia

Juris J. Purans

Institute of Solid State Physics, Kengaraga 8, Riga, Latvia

The reliability of vitreous waste forms depends on the speciation of the elements within the forms. An appropriate technique for determining valance state and local environment (coordination number, distances between the target and surrounding ions) of the waste elements is x-ray absorption spectroscopy (XAS).

Up to now most of XAS studies of the elements in waste glasses were performed for Mn, Fe, U whereas such major fission products as Cs and Sr were studied to a much less extent. Since 1989 numerous XAS measurements of Cs, Sr, Co and Fe in borosilicate and aluminophosphate glasses were performed in the framework of collaborations between SIA Radon and the Institute of Solid State Physics. This paper briefly summarizes the results of these works.

XAS study showed that at relatively low Cs₂O content (~1–2 mol%) in Na-Cs borosilicate glasses, Cs ions are present in a slightly distorted twelve-fold coordinated oxygen environment where 9 oxygens are positioned at a distance of 0.295 nm and 3 – at a distance of 0.310 nm. The closest Si atoms are positioned at a distance of ~0.331 nm. With the increase of Cs₂O concentration in the glass both the coordination number (CN) and the average Cs–O distances reduce, whereas, the Cs–Si distances increase. With that said, both the first and the second coordination cells are split into two sub-cells and in the glass with 15 mol.% Cs₂O the first cell has a configuration of distorted hexagonal bipyramid with five Cs–O distances of 0.281 nm and three of 0.258 nm. Two Cs–Cs distances at 0.39–0.41 nm and 0.52 nm may be due to various modes of linking of CsO₈ polyhedra: with shared edges and vertices. In Na-Cs aluminophosphate glasses, Cs ions at concentration of 4–5 mol.% have average CN close to 8 and the first coordination cell is distorted: five Cs–O distances are equal to 0.285 nm and three equal to 0.300 nm. Increase of Cs₂O content results in a slight decrease of the Cs–O distance and increase of contribution of the second coordination cell with respect to the first one.

Sr²⁺ ions in both borosilicate and aluminophosphate glasses have a CN in the first cell close to 8. The first cell is split into two subcells where 6 and 2 oxygens are positioned at distances of 0.252 nm and 0.274 nm in borosilicate and 0.258 nm and 0.288 nm in aluminophosphate glasses, respectively. With the increase of SrO content in borosilicate glasses to ~6–7 mol.% a relative intensity of the second Sr cell (Sr–Si) decreases

and then increases with an increase of SrO content to ~13 mol.%. In aluminophosphate glasses a contribution due to the second cell gradually reduces at decreasing of SrO content from ~5 to ~22 mol.% demonstrating difference in the structure of glasses and various type of chemical differentiation of the components in glasses.

Extensive studies of Co environment in sodium tetraborate, sodium borosilicate glasses and multicomponent borosilicate glass simulating actual waste glass showed that the cobalt in these glasses exists in a divalent form and Co²⁺ ions form tetrahedral and octahedral complexes with Co–O distances in the first cell of 0.197–0.198 nm and 0.212–0.215 nm, respectively. The contribution due to the second cell in the structure of borosilicate glasses is rather minor. In the structure of aluminophosphate glasses Co is present as Co(II) and Co(III) and is mostly four-coordinated.

Investigation of the solubility of lanthanides and minor-actinides in $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-Al}_2\text{O}_3\text{-CaO}$ glasses

Abdessamad Kidari*, Magali Magnin, Jean-Luc Dussossoy & Isabelle Giboire

Commissariat à l'énergie atomique, Département d'Etudes du Traitement et du Conditionnement des Déchets, Bâtiment 208, B.P.17171, Bagnols sur Cèze Cedex, F-30207, France

The processing of high burn-up UO_2 fuel yields highly radioactive liquid wastes with higher concentrations in minor actinides. Glass formulations capable of assimilating a higher waste content than the current R7T7 $\text{B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ glasses are under development. On a non-radioactive laboratory scale, it is acknowledged that actinides can be replaced by lanthanide elements with identical oxidation states, similar coordination environments and close ionic radii. They are regarded as effective substitutes: non-radioactive formulations should reflect the glass forming ability, melt behaviour and structural features of their radioactive counterparts. This study compares the solubility and distribution of americium and neodymium in $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-Al}_2\text{O}_3\text{-CaO-La}_2\text{O}_3$ glasses. It assesses the substitution of americium by neodymium from a structural point of view. The tendency toward devitrification of Nd and Am-bearing melts has been determined for varying La_2O_3 to Nd_2O_3 and fixed La_2O_3 to Am_2O_3 ratios, thus for both slowly cooled and quenched glass melts. Homogenous glasses and apatite containing glass-ceramics were probed by means of x-ray diffraction, Raman spectroscopy, scanning electron microscopy and chemical analyses. These experiments provide key information on the effects of $\text{La}_2\text{O}_3\text{:Nd}_2\text{O}_3$ and $\text{La}_2\text{O}_3\text{:Am}_2\text{O}_3$ ratios and concentrations on the connectivity of the amorphous networks and the stoichiometry of the apatite phases.

Chemical mechanisms during vitrification of model containment HLW glass.

A. Monteiro,* S. Schuller
CEA, DTCD/SECM/LDMC, Marcoule, Bagnols sur Cèze, 30 200, FRANCE

M.J. Toplis, R. Podor, J. Ravaux, N. Clavier

High-level radioactive wastes (HLW) obtained after reprocessing of spent Uranium oxide fuel are commonly incorporated in alumino-borosilicate containment glass. In the French industrial process (cold or hot crucibles), the complex mixture of oxides and nitrates resulting from calcination of actinides and fission product solutions (calcine) is vitrified by chemical reaction with a glass frit. The physical and chemical interactions occurring at high temperatures between these compounds produce a complex succession of intermediate steps: impregnation, supersaturation, phase separation, crystallization, dissolution. The kinetics of these reactions depend on several different factors, such as low solubility limits in the glass (important for elements such as Mo, rare earth elements, Ru), temperature, time, and geometry of the glass frit. The competing effects of these factors ultimately affect the homogeneity of the final glass. In order to determine the kinetics of reaction and the mechanisms occurring during glass synthesis, low temperature diffusion, DTA-TGA analyses and in-situ high temperature Scanning Electron Microscopy (SEM) have been used to investigate the interaction between a model glass frit ($\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-Al}_2\text{O}_3$) and a model calcine ($\text{Na}_2\text{O-Al}_2\text{O}_3\text{-MoO}_3$). Five sets of calcine+frit simplified have been studied. For each set the final glass should be of identical composition, but the $\text{Na}_2\text{O/Al}_2\text{O}_3$ ratios of the individual starting components are variable. In-situ SEM is used to follow crystal formation in real time during glass synthesis. The microstructure of glasses formed is examined by XRD and different crystalline phases are characterized. The results show that the nature of crystalline phases is influenced by the $\text{Na}_2\text{O/Al}_2\text{O}_3$ ratios in the calcine. The combination of these techniques provides new information on the reaction process during glass synthesis and allows us to determine the kinetics of the dominant reactions.

Modeling radiation-induced alteration of the network topology of alkali borosilicate high-level waste glass

Leslie Dewan, Linn W. Hobbs,* Jean-Marc Delaye

MIT, Nuclear Science & Engineering, Bldg 13-4054, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA

High-level nuclear waste glasses are subject to radiation-induced degradation over very long time scales. In such glasses, bond-breakage and atom displacements occur by both radiolysis (principally from energetic beta-decay electrons) and ballistic mechanisms involving collision cascades initiated by energetic fission nuclei and recoil of alpha-emitting actinide nuclei. This study investigates collision-cascade-induced alteration of the glass network in a simplified sodium borosilicate model nuclear waste glass, using molecular dynamics (MD) codes and efficient topological assessment algorithms. Collision cascades were initiated ballistically (5 keV initial kinetic energy, dissipated elastically) and carried out using atomistic codes and both two-body Buckingham and three-body Born-Mayer-Huggins-Ziegler potentials. Network topologies of the initial and resulting altered glass structures were determined by enumerating the primitive-ring-based local cluster atom complement at each atom site and depicting these anaglyphically. The topological description is seen to provide a revealing assessment of network structural changes in the simulated radiation environment that can be related to alkali segregation and observable macroscopic changes, such as swelling, viscosity changes, and radiation-induced devitrification.

Vitrification of high molybdenum waste

Barbara Dunnett,* Nick Gribble, Rick Short, Edward Turner

National Nuclear Laboratory, Sellafield, Seascale, Cumbria CA20 1PG

Carl Steele, Andrew Riley

Sellafield Ltd., Seascale, Cumbria, CA20 1PG, U.K.

In the UK, the Sellafield Waste Vitrification Plant (WVP) currently immobilises highly active liquors produced from reprocessing of spent nuclear fuel into a borosilicate glass. Future challenges for WVP include the washout of solids from the base of the waste storage tanks in preparation for decommissioning, which will result in high molybdenum feeds to the plant. Molybdenum has a low solubility in the standard alkali borosilicate frit used on WVP, but laboratory experimental work has led to the development of a new calcium borosilicate glass formulation which can incorporate up to 10 wt% molybdenum oxide without any detrimental phase separation.

Vitrification of high molybdenum feeds using the new formulation has also been carried out, using non-active simulants, on the Vitrification Test Rig (VTR) which is a full scale working replica of a WVP processing line. This paper discusses the results of both the laboratory and full scale trials.

Spectroscopic investigation of glasses produced by microwave heating

Martin C. Stennett*, Paul A. Bingham, Sue D. Forder and Neil C. Hyatt
*University of Sheffield, Department of Engineering Materials, Sir Robert Hadfield Building,
 Mappin Street, Sheffield, S1 3JD, UK*

Dielectric (or microwave) heating is a fast, clean and economical synthesis technique which has been demonstrated to be applicable for processing a wide range of inorganic solids. The ability to absorb microwave radiation is a key requirements for materials to be suitable for microwave heating. Many oxide and non-oxides couple strongly to microwave fields making the process suitable for the synthesis of a range of ceramics and glasses. Microwave heating has a number of key advantages over conventional heating. Microwave heating is a rapid process and unlike conventional heating the charge is heated from the inside out. This can minimise undesirable decomposition, oxidation and reduction reactions, the loss of volatile materials, and other kinetically slow processes which can occur during conventional melting. In this work, the vitrification of iron phosphate glasses have been investigated. Iron phosphate glasses have potential application as immobilisation matrices for radioactive waste. The aim of this study was to investigate the feasibility of preparing base and waste loaded glasses, by microwave heating, and to characterise the microwave glasses with respect to conventionally melted glasses with identical compositions. Microscopic techniques were used to investigate the composition and phase assemblage of the glasses and the complimentary techniques of Fe-K edge X-ray absorption and ^{57}Fe Mossbauer spectroscopy were used to probe the iron valance and coordination environment.

Structural Features of High- Fe_2O_3 and High- $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ SRS HLW Glasses

Sergey V. Stefanovsky*
SIA Radon, 7th Rostovskii lane 2/14 Moscow 119121 RUSSIA

Kevin M. Fox and James C. Marra
Savannah River National Laboratory, Building 773-A, Aiken, SC 29808 USA

Selection of appropriate high level waste (HLW) glass composition is one of the key elements of the vitrification process. Savannah River National Laboratory (SRNL) has identified a small number of simulated, multi-component waste glass compositions that, while amorphous via XRD, have unusually poor chemical durability. The cause of the reduction in durability is not known, but is suspected to be amorphous phase separation. Three glasses containing major aluminum, boron, iron, lithium, sodium, and silicon oxides at various ratios and minor different waste oxides both as-prepared and heat-treated were examined with XRD, SEM/EDS and optical microscopy, FTIR, Raman and XAS spectroscopic methods.

Both the as-prepared and heat-treated glasses were found to be X-ray amorphous. SEM photomicrographs demonstrate homogeneity of the as-prepared glasses at least at a level of $\sim 50\text{--}100$ nm. Surface of the glasses after etching is coated with a mesh of micron-sized cracks, the rim is strongly depleted with Na_2O and enriched with SiO_2 i.e. this is a typical surface layer remaining on the surface of glass after leaching. Chemical composition of the core is similar to that of the bulk of unaltered glass. No phase separation was found. FTIR spectra of the as-prepared glasses within the range of $4000\text{--}400$ cm^{-1} are composed of bands within the range of $3600\text{--}3200$ cm^{-1} and $1650\text{--}1600$ cm^{-1} due to stretching and bending modes in molecules of absorbed and structurally bound water and hydroxyl groups, weak bands at $2950\text{--}2800$ cm^{-1} due to oscillations of hydrogen bonds and bonds located lower than 1600 cm^{-1} due to oscillations of bonds forming anionic motif of the structure of glasses. The strongest absorption in both FTIR and Raman spectra takes place within the range of $980\text{--}1150$ cm^{-1} due to superposition of vibrations of bridging Si–O–B bonds linking SiO_4 and BO_4 tetrahedra in a common network. FTIR and Raman spectra of the glasses heat-treated at 500°C consist of the bands in same ranges as spectra of initial glasses but most of the bands are split due to structural ordering in the glass network pointing to chemical differentiating and onset of pre-crystallization processes.

XANES data show that Fe is mainly trivalent. Fourier Transform of Fe K edge EXAFS in glasses demonstrate a minor second coordination cell of Fe ions in all three glasses. The first coordination cell in all the glasses is split into two components. Computer simulation indicates two Fe–O distances – shorter at $\sim 1.72\text{--}1.76$ Å and longer at $\sim 1.90\text{--}$

1.94 Å in the structure of the glasses. Coordination number of Fe on oxygen is 4 or nearly 4 and Fe ions are located in a distorted tetrahedral environment.

In the whole, it may be concluded that the glasses are homogeneous, no crystalline phases or liquid-liquid phase separation were found both in as-prepared and heat-treated and etched glasses, boron is present in both trigonal and tetrahedral oxygen environment, aluminum is mainly tetrahedrally coordinated, iron is predominantly trivalent and tetrahedrally coordinated. Possible reason of low chemical durability of the glasses is relatively low fraction of tetrahedrally coordinated boron and low concentration of Al_2O_3 forming $[\text{BO}_{4/2}]^-\text{Me}^+$ and $[\text{AlO}_{4/2}]^-\text{Me}^+$ tetrahedral units fixing alkali ions and thus reducing their leaching.

Investigation of the effect on long-term aqueous durability with variations in the composition of UK vitrified HLW product

Mike T Harrison^{*1}, Carl J Steel² and Andrew D Riley²

¹ NNL, Central Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG

² Sellafield Ltd, Sellafield, Seascale, Cumbria, CA20 1PG

The Waste Vitrification Plant (WVP), operated by Sellafield Ltd, converts Highly Active Liquor (HAL) from the reprocessing of spent nuclear fuel into vitrified High Level Waste (HLW) product for safe interim storage, and ultimate disposal in a deep geological repository. One of the important aspects to understand in relation to disposal of HLW glass is its behaviour over long timescales under aqueous conditions. To this end, a series of laboratory-based leach tests on the expected range of WVP glass compositions has been initiated, with some of the preliminary results described in this paper.

The aqueous dissolution behavior of a range of simulated UK vitrified HLW glasses has been investigated using static leach tests at different surface area to volume ratios for durations up to 16 weeks. Both Magnox and Blend glass compositions have been investigated at a range of waste oxide incorporations. The experiments demonstrated the complex dissolution behaviour of UK HLW glass with the results depending on the test conditions used. However, a number of general observations can be made, such as the improvement in dissolution behaviour with increased waste loading and as the proportion of Oxide waste in 'Blend' HLW glass is increased.

The Glass Dissolution Rate Equation Revisited

Denis Strachan

Pacific Northwest National Laboratory

Thirty years ago, a rate equation for the dissolution of glass in water, based on transition state theory, was developed. Because most data were collected at pH values above 7, the equation was well developed for what became known as the “basic leg” of the equation. We recognized that the “acid leg” existed, but very few data were obtained at acid pH values. This resulted in what appear to be inconsistencies. The intrinsic rate constant that is defined as being independent of pH and temperature is supposed to depend on the composition of the glass. An inverse dependence of the rate on pH is needed to explain the increase in rate as a function of increasing pH, even though the active species, H_3O^+ , is no longer the dominant species above pH = 7. I will discuss new versions of the rate equation that removes these inconsistencies and fits the existing data as well or, perhaps, better than the existing bifurcated approach currently taken.

Crystallisation Study of an Aluminosilicate Glass Containing both Rare Earths and Molybdenum.

J. Marra & N. Chouard*

DOE Office of Environmental Management, Office of Technology Innovation and Development, 1000 Independence Ave., SW Washington, DC 20585, USA

Vitrification is utilized world-wide to immobilize high level radioactive waste resulting from reprocessing of commercial and defense-related used nuclear fuel. Borosilicate glass is the immobilization matrix preferred by most countries. In the U.S., high level radioactive wastes resulting from reprocessing of used fuel for defense purposes have presented numerous glass chemistry challenges. The solubility of many high level waste components can limit waste loading within the glass resulting in the need to produce more glass. Additionally, some troublesome components can limit glass melting rate further increasing the cost and schedule to immobilize the waste.

Proposed advanced fuel cycle reprocessing flowsheets and processes present similar glass chemistry challenges. The solubility of components resulting from higher fuel burnup can limit waste loading in glass. Similarly, proposed additives to facilitate separations can limit waste loading. Finally, concentrating the radionuclide content in the waste can impact waste loading through chemical species solubility and glass heat load limitations.

In this presentation, troublesome waste components resulting from defense and commercial used fuel reprocessing will be identified. The impacts of these troublesome components on glass chemistry and properties will be discussed. Finally, approaches to facilitate incorporation the species in glass will be presented.

Viscosity of Simulated High Level Waste Vittrified Residues

Carl Steele^{*1}, Barbara Dunnett², Andrew Riley¹, Katy Ferguson², Nick Gribble² and Rick Short²

¹Sellafield Ltd., Seascale, Cumbria, CA20 1PG, U.K.

²National Nuclear Laboratory, Sellafield, Seascale, Cumbria CA20 1PG

In the UK, the Sellafield Waste Vitrification Plant (WVP) experience shows that melter performance and lifetime is strongly dependent on liquor feed composition. A predictive knowledge of the glass properties yielded by a certain feed composition is highly desirable to understand the optimum regime or regimes to run the melter. This would allow WVP to mitigate the detrimental effects of a tuning period to melter operation and life, after the start of a melter run or the introduction of a new feedstock. The process can be optimised pre-emptively to a specific glass to maximise lifetime and performance. In addition, throughput could be increased with an improved understanding of glass properties.

It is important that the vitrified product melt viscosity is in a range that allows it to be poured from the melter and does not result in long pour durations or the inability for the glass to be poured.. Viscosity measurements have been carried out on a range of simulated vitrified products with a variety of waste loadings. and the viscosity was found to increase with increasing waste loading. A comparison of the viscosity values obtained in house has been made for similar glasses measured on other viscometers and possible reasons for differences identified.

Research has recently been initiated with Sheffield University to attempt to create a more representative model of melter behaviour to provide plant support by mathematically modelling the meso and macro scopic scales using computational fluid dynamics methods. An empirical approach has also been adopted using neural network logic to predict changes in glass viscosity due to compositional variation. Some preliminary results will be presented from this research.

Viscous Flow and Viscosity of Melts and Glasses

Michael I. Ojovan

University of Sheffield, Department of Materials Engineering, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, UK

An overview is given of oxide glasses and melts viscosity. Although the glass-liquid transition is accompanied by explicit discontinuities in the derivative parameters such as the specific heat or thermal expansion coefficient, the viscosity is a continuous function of temperature. An unresolved issue for the viscosity remains the apparent changes in activation energies with temperature.⁽¹⁾ Viscous flow has low activation energies at high temperatures and high activation energies at low temperatures but a wide transition temperature range where the viscosity has a modified, non-Arrhenius behaviour. The most common models of transition viscosity are that of Vogel-Fulcher-Tamman and Avramov-Milchev.⁽¹⁻³⁾ The viscosity of melts and glasses is exactly described by a two exponential formula,⁽³⁾ which is derived assuming that broken bonds in an amorphous material (termed configurons) weaken its bond lattice and facilitate viscous flow at higher temperatures: $\eta(T) = aT[1 + b\exp(B/RT)][1 + C\exp(D/RT)]$. Here a is a geometrical coefficient of a configuron, $b = \exp(-S_m/R)$, $B = H_m$, where H_m and S_m are the enthalpy and entropy of configuron motion and $C = \exp(-S_d/R)$, $D = H_d$, where H_d and S_d are the enthalpy and entropy of configuron formation. This equation can be used over practically all temperature ranges and gives the correct Arrhenian-type asymptotes at high and low temperatures namely $\eta(T) = abT\exp(B/RT)$ and $\eta(T) = abCT\exp[(B+D)/RT]$ respectively. At low temperatures the concentration of broken bonds is low, because of that the activation energy of viscosity takes the full (high) value $Q_H = B + D = H_d + H_m$. Situation changes at high temperatures when the activation energy is only due to the energy needed to transfer a molecule or a configuron from its original position to the adjacent vacant site. Because of that at high temperatures the activation energy of viscous flow is low: $Q_L = B = H_m$.

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Thermal Behaviour of Iron Aluminium Phosphate Glasses Containing UO₂.67

D.S. Rodriguez¹, P. A. Arboleda¹, D. O. Russo¹, F. Soldera^{1†}, C. J. R. González- Oliver¹ and J. Ma. Rincón^{2*}

¹Centro Atómico de Bariloche (CAB), S. C. de Bariloche, Argentina

²CSIC, IETcc, The Vitreous and Ceramics Lab/Group, Madrid, Spain

[†]now in Saarbrücken, Germany

A summary about the thermal behaviour (viscosity variation, dilatometry and crystallization trend) of several glasses of iron aluminium phospho- silicate is presented as well as new data related to the densification process of glassy particles agglomerated from such compositions which include significant amounts (6-19 wt%) of uranium oxide (UO₂.67). The sintering study of vitreous powders allows to classified these glasses in order to prevent the relative capability for the immobilization and stability of the uranium oxide in these glassy or glass-ceramic matrices.

High-Temperature Density and Heat Capacity of a Simulated High-Level Radioactive Waste Glass

Toru Sugawara^{*1}, Takafumi Shiono¹, Satoshi Yoshida¹, Jun Matsuoka¹, Akira Inagaki² and Eiji Ochi²

¹ The University of Shiga Prefecture, Hikone, Shiga, Japan

² Japan Nuclear Fuel Limited, Rokkasho-mura, Kamikita-gun, Aomori, Japan

Density and heat capacity of radioactive waste glass are essential parameters in order to calculate heat and mass transfer in a glass melting furnace. We have measured high-temperature density and heat capacity of simulated radioactive waste glass (48.5SiO₂-14.8B₂O₃-10.0Na₂O-3.1CaO-5.2Al₂O₃-3.1ZnO-3.1Li₂O-12.4waste oxides, wt%).

Density in glass transition range (753-813K) was determined by combining room temperature density of annealed glass and thermal expansivity measured by TMA. Densities of glass melt between 1073 and 1273K were measured by weighing a Pt crucible with the waste glass melt in a molten NaCl. Heat capacities of glass and glass melt up to 1673K were measured by differential scanning calorimetry and drop calorimetry.

Density and heat capacity of glass melt extrapolated to low temperature are consistent with those of glass at T_g measured by TMA and DSC, respectively. Density of glass melt ranges from 2.73 g/cm³ at 753K to 2.48 g/cm³ at 1273K. No temperature dependence was observed in thermal expansivity of melt. The glass transition takes place when the heat capacity approaches 99% of the Dulong-Petit limit. At the glass transition, the heat capacity of melt is 53% higher than that of glass. It decreases down to 24% with increasing temperature. These features are in agreement with those of soda-lime borosilicate melt reported previously.

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X-ray CT imaging of the vitrified glasses containing pseudo-radioactive wastes: structure and chemical reactions of glass beads and wastes in cold cap

Keita Watanabe^{*1}, Tetsuji Yano¹, Kenji Takeshita¹, Akira Inagaki² and Eiji Ochi²

¹Tokyo Institute of Technology, Meguro-ku, Tokyo, JAPAN

²Japan Nuclear Fuel Limited (JNFL), Rokkasho-mura, Kamikita-gun, Aomori, JAPAN

Glass is the suitable host materials for the encapsulation of radio-active nuclear wastes because of its long-term stability, high chemical durability and large solubility capacity of encapsulation. In Liquid Feeding Ceramic Melter (LFCM), high-active liquid wastes are supplied into the glass melter from the top in the form of nitrates aqueous solution with borosilicate glass beads. They are heated and react to form the glass melt in “Cold Cap” region. For the stable operation of LFCM, which uses Joule heating system, this “Cold Cap” plays quite important thermal and/or chemical roles in melter.

In this study, the laboratory-scale electric resistance furnace was developed for the formation of ‘pseudo-Cold Cap’, to which the glass beads and pseudo-radioactive nuclear waste solution are introduced with the controlled feed rate as same as those in the practical LFCM system. Transparent silica glass cell is used as the crucible for the vitrification, and moved downwards in the heating zone with the controlled temperature gradient of the furnace at the designated speed determined in relation to the feed rate. Inside the cell, vitrification reactions of the wastes with glass beads proceeds. The formed pseudo-Cold Cap in silica cells are quenched rapidly, and subjected to the analysis by X-ray CT scanning system.

Figure 1 shows the cross-section images of the quenched sample in a silica cell by X-ray CT scanner. In the upper part (Fig. 1(a)), the glass beads still possess spherical shape with the bright layer (unreacted wastes with higher density than glass beads) on their surface, and changed into the inter-connected shape holding bright domains inside at lower (higher-temperature) part. At much higher-temperature zone (Fig. 1(b)), foam structure was clearly seen while the bright domains still exist inside the glass region.

This work was a part of the research supported by Japan Nuclear Fuel Limited with Grant-in-Aid by the Ministry of Economy, Trade and Industry.

Old Kingdom Egyptian faience: some new perspectives

Linn W. Hobbs^{*,1,2,3} Drew Whisenant^{1,2} and Leslie Dewan^{1,3}

¹Center for Materials Science on Archaeology & Ethnology

²Department of Materials Science & Engineering

³Department of Nuclear Science & Engineering

Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA

Egyptian faience is essentially a glass-ceramic comprising finely-divided quartz held together by an ostensibly soda-lime silicate interstitial glass covered by a glaze layer incorporating transition-metal ion coloration. This material was produced continuously from the pre-dynastic era (*post* 4000 BCE) continuously until the Roman period (30 CE), though with evident evolution of both chemistry and processing routes. The generally accepted view is that both interstitial glass and the glaze layer are the result of either cementation or (especially in earlier examples) efflorescence glazing in which alkali additions (soda, potash from plant ash or carbonates, lime from carbonates) react with crushed quartzite upon heating to 800–1000°C to form a glassy silicate phase. The overall alkali content of the final glass (0.5–3% Na, 0.1–1.5% K, 0.5–3% (Ca + Mg)) is insufficient to account for a glass transition at these temperatures, but reaction pathways involving the initially locally high alkali content have been invoked to rationalize the envisaged processing route. Glaze analysis has focused more on alkali network-modifier and transition metal cations and minor crystalline phases than on other network-forming elements (besides Si) that are also present (specifically P and Al) and can provide alternative lower-temperature processing routes to a vitreous product. This presentation will review prior understanding and report on ongoing investigations of early dynastic faience by analytical electron microscopy and multi-component network modeling using topological connectivity approaches.

Glass furniture in St Peterburgh

John P Smith

Before Baccarat in France and Osler in England produced items of glass furniture for the Eastern market large items of furniture using coloured glass were being produced in St Petersburg (c1800). Also coloured glass beads or tubes were used to make vivid wall coverings and pictures, particularly in Orangebaum Palace. The author, who has written extensively on Osler and other glass furniture makers, visited St Petersburg around 1990 and took a large number of photographs. I have only just received this form for submission and hope that it is not too late. I attended the conference last year.

Lomonsov, the Russian chemist, amongst his many other activities was responsible for developing a range of coloured glass, largely for the Imperial Glass Works. (I have further details at home and can quote chapter and verse).

There is a well documented occasion when in 1806 (from memory) the Czar gave the Czar the Shah of Persia a large bed, made partially of blue glass, surrounded by fountains, which was delivered with difficulty by Russian soldiers, most of whom died on the trip. (I have a drawing and firsthand account).

The palaces in St Petersburg still contain furniture effectively veneered with coloured glass, some clear some opaque. Together with chandeliers and torchieres. (I have photos and close-ups taken in situ).

To make pictures and wall hangings very thin tubes of coloured glass were made, and strung together like beads, the best remaining are in the palace of Orangebaum, about 40 kilometres outside St Petersburg, was which well restored but I understand is no longer in such good condition as it is too far off the tourist track. (Again I have good photographs).

I could briefly talk about other glass furniture made in Europe later in the 19th century.

Finally, when the St Petersburg underground was built in the 1970's (?) all the stations were decorated to greater glory of Soviet Russia, one station has many columns, all clad in cast glass decorative panels.

The prince and the popper: Prince Rupert's Drops and natural history in the early Royal Society

Anna Marie Roos

University of Oxford, Faculty of History, Old Boys' School, George Street, Oxford, OX1 2RL, U.K.

Prince Rupert's Drops are teardrop shaped beads formed by dropping molten glass into cold water. Brought to England by Prince Rupert of Bavaria (1619-82), the nephew of Charles I of England, the origins of the drops' explosive nature and remarkable tensile properties were a matter of great debate in the early Royal Society. After a demonstration of their composition, fabrication, and physical properties, this paper will elucidate their role in Restoration court life and satire, Robert Hooke's early microscopic observations, and to what extent their explosive power affected the formation of pre-Newtonian theories of the tides.

Dynamic processes in a silicate liquid from above the melting point to below the glass transition

Marcio Luis Ferreira Nascimento¹, Vladimir Mihailovich Fokin², Edgar Dutra Zanotto^{*1}, Alexander S. Abyzov³

¹Vitreous Materials Laboratory, Department of Materials Engineering,
Federal University of São Carlos 13595-905 São Carlos-SP Brazil, www.lamav.ufscar.br

²Vavilov State Optical Institute, ul. Babushkina 36-1, 193171 St. Petersburg, Russia

³National Science Center, Kharkov Institute of Physics and Technology,
Academician Street 1, 61108 Kharkov, Ukraine

We critically analyze extensive literature data, including our own, on three important kinetic processes - viscous flow, crystal nucleation and growth - in lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$) in a wide temperature range, from above T_m to $0.98T_g$, where $T_g \approx 727$ K is the calorimetric glass transition temperature and $T_m = 1307$ K is the melting point. We found that crystal growth mediated by screw dislocations is the most likely growth mechanism in this system and calculated the controlling diffusion coefficients $D_{\text{eff}}^{\text{U}}$. We completed the analyses by looking at the ionic diffusion coefficients of Li^{+1} , O^{2-} , and Si^{4+} estimated from real experiments as well as from MD simulations, which were then employed to estimate the effective volume diffusion coefficients, $D_{\text{eff}}^{\text{U}}$, resulting from their combination within a hypothetical $\text{Li}_2\text{Si}_2\text{O}_5$ "molecule". The similarity of the temperature dependencies of $1/\eta$, where η is shear viscosity, and $D_{\text{eff}}^{\text{U}}$ corroborates the validity of the Stokes-Einstein/Eyring equation (SEE) at high temperatures around T_m . Using the equality $D_{\text{eff}}^{\text{V}} = D_{\text{eff}}^{\text{U}}$ and the SEE equation we estimated the jump distance, $\lambda \sim 2.70\text{\AA}$, and showed that the $D_{\text{eff}}^{\text{U}}$ have the same temperature dependence but exceed $D_{\text{eff}}^{\text{V}}$ by about 8 times. The difference between $D_{\text{eff}}^{\text{V}}$ and $D_{\text{eff}}^{\text{U}}$ suggests that the first determines bulk processes of mass transport whereas the second relates to the mobility of the structural units on the crystal/liquid interface. The $U(T)$ curve thus evaluated agree with experimental data until the temperature is lowered down to the so-called decoupling temperature $T_d^{\text{U}} \approx 1.1\text{--}1.2 T_g$, when $D_{\text{eff}}^{\text{V}}$ begins to decrease with decreasing temperature faster than $D_{\text{eff}}^{\text{U}}$. We demonstrate for the first time that a similar decoupling occurs between $D_{\text{eff}}^{\text{V}}$ and $D_{\text{eff}}^{\text{r}}$ (independently estimated from nucleation time-lags), but at a lower temperature $T_d^{\text{r}} \approx T_g$. For $T > T_g$ the values of $D_{\text{eff}}^{\text{r}}$ exceed $D_{\text{eff}}^{\text{V}}$ only by 2 times. The different behaviors of $D_{\text{eff}}^{\text{r}}(T)$ and $D_{\text{eff}}^{\text{U}}(T)$ are likely caused by a difference in the mechanisms of critical nuclei formation and of growth of macro-crystals, and also due to their different interfaces. In summary, we have shown that at low under-coolings one can employ viscosity data for quantitative analyses of crystal growth rates, but mass transport for crystal nucleation and growth in deeply supercooled liquids are not controlled by viscosity. We discuss the origin of decoupling based on spatially *dynamic heterogeneity* of glass-forming melts.

Keywords: glass, crystal growth, nucleation, viscosity, diffusion, dynamic heterogeneity.

Controlled crystallization of xenotime- and monazite-type crystals in glass-ceramics

C. Ritzberger, E. Apel, V. M. Rheinberger and W. Höland*
Ivoclar Vivadent AG, R&D Department, Bendererstr. 2, Schaan, Li-9494, Liechtenstein

Glasses derived from the chemical 45-60 wt% SiO_2 – 8-20 Al_2O_3 – 5-30 Y_2O_3 – 1-10 P_2O_5 system with additives of B_2O_3 , Na_2O , K_2O , Li_2O , CaO and F up to 5 to 10 wt.-% were formed by melting producing glass frits. Glass-ceramic powder compacts were developed during heat treatment of the glass grains in a temperature range of 800°C up to 1050°C. Special glass-ceramic compositions will be demonstrated to show the precipitation of xenotime- (YPO_4) and monazite-type (LaPO_4 , TbPO_4) crystals in the glass matrix. The microstructure of the glass-ceramics with main crystals of monazite and xenotime and secondary phases are demonstrated by SEM studies. The glass-ceramics are characterized by CTE of 9.5 to $10.6 \times 10^{-6} \text{ K}^{-1}$ (100 – 400 °C). According to biomaterials standards for dental products, the glass-ceramics show good chemical durability (in acidic acid) and translucency (measured as contrast ratio value of 68).

Dependence of crystallization processes of glass-forming melts on prehistory: a theoretical approach to a quantitative treatment

Jörn W. P. Schmelzer

University of Rostock, Institute of Physics, Wismarsche Str. 43-45, Rostock, Germany

Crystallization processes in glass-forming melts are observed most frequently in a range of temperatures overlapping the glass transition interval.^(1,2) In the glass transition interval, the characteristic cooling and/or heating times are of the same order of magnitude as the relaxation times to the corresponding meta-stable states of the glass-forming melts.⁽³⁾ By this reason, the values of pressure and temperature alone do not determine uniquely the state of the glass-forming melt in this range and additional structural order parameters like fictive temperature and fictive pressure have to be introduced into the description as performed for the first time by Tool.⁽⁴⁾ In addition to pressure and temperature, these structural order parameters determine from a thermodynamic point of view the bulk properties of the glass-forming melts and surface properties of the interface crystal-melt and the characteristic relaxation times, diffusion coefficients, respectively, the viscosity. By this reason, they can be expected to affect significantly nucleation and growth processes in the vitrification range. However, such effects are so far widely ignored in the general theoretical treatment of crystal nucleation and growth. Another problem is how fictive pressure and temperature can be determined uniquely once they are employed as structural order parameters.

The present contribution is directed to the analysis of this circle of problems with the following main topics. First, a general thermodynamic definition of fictive pressure and fictive temperature is given being independent on any models of structural order parameters. Second, for the case the relaxation behaviour of the system is determined by only one independent structural order parameter, an analysis of relaxation processes is given based on thermodynamics of irreversible processes. It is shown how – based on thermodynamics of irreversible processes – one can give a straightforward explanation of relaxation behaviour proportional to the square root of time ($\sim t^{1/2}$) and the origin of the Kohlrausch relaxation law. Finally, it is discussed how differences in the structure of the glass-forming melt, reflected by differences in the values of the structural order parameter, may affect crystallization processes. Consequently, differences in the crystallization behaviour in dependence on prehistory have to be expected and can be treated quantitatively in terms of the thermodynamic approach utilized.

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Vitrification and crystallization in the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system

Salaheddine Alahraché*, Michael Deschamps, Mathieu Allix, Matthew Suchomel, Domingos De Sousa Meneses, Dominique Massiot and Guy Matzen.

CEMHTI-CNRS, Site Haute Température, 1D avenue de la Recherche Scientifique, 45071 Orléans cedex 2, FRANCE

By means of an aerodynamic levitator equipped with two CO_2 lasers, we prepared an $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ rich glass with the minimum amount of SiO_2 (4 wt%). The use of this powerful vitrification technique allowed us to overcome the high melting temperature of the oxide mixture and its high tendency to crystallize. To elaborate this glass in a classical furnace, at least 20 wt% of SiO_2 should be added to melt the yttria-alumina mixture and to avoid crystallization. Once prepared by the former method, we studied the nucleation and the crystals growth of the YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$) under the action of heat, using DSC and XRD followed by Rietveld analysis. Furthermore, by means of ^{27}Al solid-state NMR, we studied the local Al environment in the starting glass as well as in the YAG crystals. We found by ^{29}Si NMR that Si^{4+} ions of the matrix are incorporated in the YAG crystals, which consequently reduces the lattice parameter of these crystals. This shrinkage was followed in time by XRD for two different crystallization temperatures. From the data obtained by X-ray synchrotron we determined the amount of the Si^{4+} incorporated in the YAG crystals as well as the site of substitution.

The influence of sulfur on nucleation and crystal growth in $\text{Na}_2\text{O-SiO}_2$ glasses

Joachim Deubener*, Hansjörg Bornhöft, Susanne Krüge

Clausthal University of Technology, Institute of Non-Metallic Materials, Zehntner Strasse 2a, Clausthal-Zellerfeld 38640, Germany

Sulfur solubility at near ambient pressure is of importance for glass technologists due to the role sulfur compounds are playing to fine and color glass melts. According to sulfur speciation sulfur is exclusively dissolved in silicate melts as sulfate at high oxygen fugacities and as sulfide at low oxygen fugacities. While the sulfur solubility in technical soda-lime-silicate glasses is in principle low (< 0.3 wt% S) it can reach up to 4 wt% in model glasses of the sodium metasilicate - sodium disilicate join under oxidized conditions. Additionally, a striking change in the crystallisation kinetics from a surface to a volume dominated nucleation mechanism has been reported in sulfur-free melts, if the Na/Si ratio is increased from the disilicate to the metasilicate composition. Despite this compositional dependence consequences of the sulfur solubility on the melt dynamics (e.g. viscosity), glass transition and the crystallisation kinetics are only scarcely known. To bridge this gap we prepared sulfur-bearing glasses by adding sodium sulfate to the batch as well as sulfur-free melts of the same Na/Si ratio. The composition of the glasses was analyzed by X-ray fluorescence. Nucleation and crystal growth rates were determined from optical images of cross-sections of glasses subjected to single and double stage heat treatments by counting number densities and sizes of crystals in the volume of the glass. DSC runs were performed to gain knowledge on glass transition and crystallisation temperature as well as their heating rate dependence. Together with the viscosity of the melts as determined by beam bending these data are used to discuss the effects of sulfur on the transformation kinetics in silicate melts.

Effect of agitation on crystallization behavior of calcium silicate melts

Noritaka Saito*, Kakeru Kusada, Sohei Sukenaga, & Kunihiro Nakashima

Department of Materials Science and Engineering, Kyushu University, 744, Motoooka, Nishi, Fukuoka 819-0395, Japan

We investigated the effect of agitation on the crystallization behavior of $\text{CaO-SiO}_2\text{-R}_2\text{O}$ ($\text{R} = \text{Li, Na, or K}$) melts by in-situ measurements of their electrical capacitance. It is well known that the electrical capacitance of liquids is generally much higher than that of solids because of the differences in their respective polarization mechanisms. We exploited this difference as a sensitive indicator of the crystallization of molten silicates in an experimental furnace equipped with an electrical-capacitance measurement system. The system comprised a Pt-based alloy crucible and a rotating rod, both connected to a capacitance meter (LCR meter).

As expected, at a particular temperature, the electrical capacitance of the molten silicates abruptly dropped by two or three orders of magnitude depending upon the chemical composition, thus clearly indicating crystallization. It was also found that for rotating-rod measurements (with agitation), the temperatures at which the capacitance abruptly dropped were higher than those without the shear stress. This suggests that shear stress accelerates the crystallization of molten silicates. Moreover, the crystallization temperature of 10mol% R_2O -containing melts decreased linearly with respect to the cationic radius of the alkaline additive. The temperatures are inconsistent with and much lower than the liquidus temperatures of these systems, which indicates that the degree of supercooling depends on the alkaline additives.

Crystallisation of ZnO from supercooled melts and glasses

Y. Dimitriev¹, R. Iordanova², M. Milanova², M. Hassan¹

¹ *University of Chemical Technology and Metallurgy, Blvd. " Kl. Ohridski", bl. 8, 1756 Sofia, Bulgaria*

² *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, " Acad. G. Bonchev" str, bl. 11, 1113 Sofia, Bulgaria*

The aim of this study is to achieve the crystallization of ZnO as a primary phase from multicomponent supercooled oxide melts and after heat treatment of non-traditional glasses. Different compositions containing 75-80 mol% ZnO were selected. Transitional metal oxide V_2O_5 , WO_3 and MoO_3 were added to decrease the melting temperature below 1400°C. In order to improve glass formation tendency B_2O_3 and Bi_2O_3 were used up to 20 mol%. Bulk translucent greenish samples were obtained by quenching between two copper plates. Depending of the compositions they are X-ray amorphous or mixtures of glass and crystals. SEM observations shown that micro-sized ZnO crystals with different morphology were dispersed in amorphous matrix. According to DTA data glass transition temperature (T_g) is in the range 350-450°C and crystallization (T_c) temperature is near 650 °C. The synthesized materials are potential candidates for preparation of new functional materials.

Effect of sodium, potassium and zinc substitutions in lithium disilicate glass and glass-ceramics

N. Karpukhina^{*1}, H. A. Abo-Mosallam², R. G. Hill¹, R. V. Law³

¹Dental Physical Sciences, Queen Mary University of London, United Kingdom

²Glass research Department, National Research Centre, Egypt

³Department of Chemistry, Imperial college London, United Kingdom

The effect of low cation substitutions on structure and thermal properties of the lithium disilicate glass with 1mol% of P_2O_5 was investigated. The rationale was to understand how the nature of the nucleating phosphate phase changes with different substitution in the composition. Three series of glasses with up to 9mol% of sodium, potassium and zinc oxides instead of lithia were prepared and characterised by DSC and solid-state NMR. The crystallised glasses were in addition characterised by the X-ray powder diffraction.

Sodium substitution reduces glass transition temperature, T_g , of the lithium disilicate glass. Similar but smaller changes were observed on potassium substitution. Introducing the zinc oxide did not affect T_g . On sodium substitution the lithium cations charge balancing orthophosphate species in the glass are substituted by sodium but not by potassium or zinc ions as shown by ^{31}P MAS-NMR. This shows that potassium and zinc are accommodated in the silicate network but not in the phosphate. This results in formation of the solid solution of $(Na, Li)_3PO_4$ with high sodium fraction on crystallisation in the sodium substituted series of glasses. Whereas Li_3PO_4 phosphate phase crystallises in the potassium and zinc series aiding precipitation of the lithium disilicate.

On crystallisation in the zinc substituted series the silicate network effectively breaks down into three different crystalline phases, the lithium zinc silicate (Q^1 phase), lithium disilicate (Q^2 phase) and silica (Q^4 phase), as observed from the ^{29}Si MAS-NMR and XRD. The ratio of the lithium zinc silicate increases with increasing the zinc content. Similar depolymerisation of the silicate glass network is observed on crystallisation in the potassium substituted series. Lithium metasilicate, lithium disilicate, mixed potassium lithium disilicate and silica are formed with, however, lower degree of crystallinity than in the zinc series. Mostly lithium disilicate phase with small fraction of the sodium disilicate and silica found in the sodium substituted series.

Phase separation and crystallization mechanism in $LiNbO_3$ - SiO_2 glasses

Hélène Vigouroux^{*1,2}, Evelyne Fargin¹, Alexandre Fargues¹, Bruno Le Garrec², Marc Dussauze³, Vincent Rodriguez³, Frédéric Adamietz³, Renaud Podor⁴, Dominique Vouagner⁵, Dominique De Ligny⁵, Bernard Champagnon⁵, Sergei Lotarev⁶, Vladimir Sigaev⁶

¹CNRS, Université de Bordeaux, Institut de Chimie de la Matière Condensée de Bordeaux, 87 avenue du Dr. A. Schweitzer, Pessac, F- 33608, France

²CEA-CESTA, 15 avenue des Sablières, 33114 Le Barp, France

³Institut des Sciences Moléculaires – UMR 5255 CNRS, Université Bordeaux, 351 cours de la Libération, 33405 Talence, France

⁴Institut de Chimie Séparative de Marcoule, UMR 5257 - ICSM Site de Marcoule, Bâtiment 426, BP 17171 -30207 Bagnols sur Cèze cedex

⁵Université Claude Bernard Lyon-1, LPCML-UMR 5620 CNRS, 12 rue Ampère12, 69662 Villeurbanne, France

⁶Mendeleev University of Chemical Technology of Russia, Miusskaya pl.9, 125047 Moscow, Russia

Transparent glass ceramics are becoming prospective candidates for various applications like in nonlinear optical materials.⁽¹⁾ Transparent Glass ceramics with second order non linear optical properties can be elaborated through bulk precipitation of nano or submicroscopic size crystallites.

Crystallization study has been performed through Differential Scanning Calorimetry on the $35Li_2O$ - $25Nb_2O_5$ - $40SiO_2$ composition glass. Both qualitative nucleation and growth rate curves have been obtained. According to these curves, glass samples were appropriately heat treated, leading to transparent or translucent glass ceramics, which exhibit second order nonlinear optical properties. Depending on heat treatments, surface and/or bulk crystallization of the exclusive $LiNbO_3$ crystalline phase were observed. Second harmonic Generation (SHG) measurements have revealed an original bulk SHG signal measured on a crystallized glass obtained after a longer duration of growth treatment. As the composition of this crystalline phase is different from the one of the initial glass, an important phase separation can be expected.⁽²⁾

For a better understanding of the bulk crystallization mechanism and optimize both SHG response and transparency, the phase separation has been studied by Scanning Electronic Microscopy (SEM) analysis performed on the nucleated sample heat treated at the maximal temperature of nucleation. This has revealed that spinodal decomposition could be at the origin of phase separation, as suggested by Prapitpongwanich *et al.*⁽³⁾ Both Raman Spectroscopy in-Situ and MEB in-situ have been carried out on $LiNbO_3$ - SiO_2 glass sample to investigate and determine the nature of the

phase separation during the heat treatment. Furthermore, viscosity measurements as a function of temperature (of heat treatment range) will be also analyzed to complete the analysis of phase separation and crystallization process.

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Nucleation and crystallisation of As_2Se_3 undercooled melt

Marek Liska*, Jana Holubova, Eva Cernoskova, Zdenek Cernosek,
Maria Chromcikova, Alfonz Plsko

A. Dubcek University of Trencin, VILA, Studentska 2, Trencin, SK-911 50, Slovakia

The isothermal nucleation of As_2Se_3 undercooled melt followed by the constant heating rate crystallization and consequent melting was followed by DSC. The melting enthalpy was used to quantify the degree of conversion. The non linear regression analysis of conversion dependence on isothermal nucleation temperature and time was performed in frame of the classical nucleation theory.

Fluctuation Inhomogeneities of Glasses and Melts Studied by Light Scattering Spectroscopy and High Temperature Acoustic Methods

Leonid V. Maksimov*, Anatolii V. Anan'ev, Viktor N. Bogdanov, Oleg V. Yanush

Research & Technological Institute of Optical Material Science, Laboratory of Glass Ceramics, 36 Bld.1, Ulitsa Babushkina, Saint Petersburg 192171, RUSSIA

The problem to be discussed concerns relationship between fluctuation inhomogeneities in inorganic glasses and their macroscopic properties significant for their elaboration and usage in the widest application area extending from optics (fiber, graded-index, laser one, etc.) and optoelectronics to nuclear physics (detection of ionizing radiation, immobilization of radioactive waste), medicine (dental technique, artificial bones), agriculture (ecological friendly glassy fertilizers), and others. Review of the problem is based on generalization of light (Rayleigh, Mandel'shtam-Brillouin – RMBS –, and Raman) scattering data combined with the data of high temperature acoustics. To analyze experimental results the well-known phenomenological model of “freezing” equilibrium fluctuations of density, concentration and anisotropy in a glass melt in the process of glass melt cooling, and also the model of constant stoichiometry groups and the doped ion segregation model developed by the authors are used. Data for single component (SiO_2 , B_2O_3 , GeO_2 , P_2O_5), binary (alkali and alkaline silicate, borate, germanate, phosphate, and others), ternary (alkali borosilicate, alkali niobategermanate, alkali niobatephosphate, and others), and multicomponent glasses including commercial ones is presented and discussed. It includes composition dependences of Landau-Placzek ratio (ratio of intensity of Rayleigh scattering intensity to the intensities of Mandel'shtam-Brillouin doublet), intensities of Raman bands and static compressibility at the glass transition temperature. The latter was found from temperature and frequency dependencies of ultrasonic velocity in glasses and their melts taken in the 20-1300 C temperature range. Using Macedo-Schroeder's formalism the contributions of “frozen-in” density and concentration fluctuations into Rayleigh scattering are estimated separately from optical and acoustic data. Multicomponent glasses characterized by optical homogeneity exceeding that of silica glass were elaborated. Non-random spatial distribution of dopants including rare-earth ions in a glass host (doped ion segregation) causes excessive Rayleigh scattering losses and enhancement of dopant-dopant interaction. Therefore, it opens the way to optimize operation parameters of laser and up-converting glasses by the proper choice of glass host composition. Raman scattering study of niobate glasses shows that the existence of groups with stoichiometry of the well-known electrooptical (EO) crystals and crystal-like orderliness in the glasses is a necessary condition of high EO sensitivity. Thus, the combination of light scattering and acoustic methods opens the

way to make relationship between microinhomogeneities of glasses and their macroscopic properties clearer. The study was partially supported by the Russian Foundation for Basic Research. (Grant 10-03-00323)

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Leonid V. Maksimov, Anatolii V. Anan'ev, Viktor N. Bogdanov, Oleg V. Yanush*

Research & Technological Institute of Optical Material Science, Laboratory of Glass Ceramics, 36 Bld.1, Ulitsa Babushkina, Saint Petersburg 192171, RUSSIA

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scopic properties clearer. The study was partially supported by the Russian Foundation for Basic Research. (Grant 10-03-00323)

The role of cation bond valence in phase separation of binary silicate melts and glasses

G. Mountjoy

*School of Physical Sciences, University of Kent, Canterbury CT2 7NH,
United Kingdom*

In their 2002 article Hudon and Baker⁽¹⁾ surveyed quantitative measures of phase separation in binary silicate melts such the consolute temperature (i.e. the upper temperature of immiscibility). It was suggested that this follows a notable trend in relation to the ionic radius of cation M. We propose that the bond valence (b.v.) of cation M (i.e. the average valence per M–O bond) reveals trends in phase separation of binary silicate melts. For example, the relation between consolute temperatures and b.v. is shown in Figure 1 below. It is seen that phase separation is least for b.v. ~ 0 , and is greatest for b.v. ~ 0.5 . This motivates an interpretation that phase separation occurs due to the mismatch in bond valence between the cation M and the oxygens in the silicate network. This effect has been seen in previous molecular dynamics modelling of $x\text{CaO}-(1-x)\text{SiO}_2$ glasses,⁽²⁾ as illustrated in Figure 2 below for $x=0.1$. Phase separation occurs because bonding of isolated Ca to non-bridging oxygens is unfavourable, as such Ca–O–Si bonds do not have balanced bond valance.

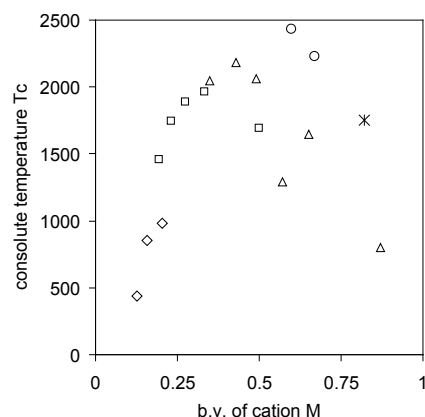
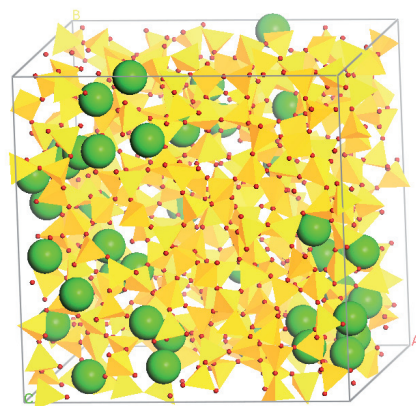


Figure 1. consolute temperature vs. b.v. Figure 2. phase separated CaO–SiO₂ glass.



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Microstructure of multicomponent borosilicate glasses containing MoO₃

Elena Kashchieva*¹, Ivan Petrov², Reni Iordanova³, Yanko Dimitriev⁴

¹*Department of Physics, University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria*

²*Bulgaria Department of Physics, University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria*

³*Bulgaria Institute of General & Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria*

⁴*Bulgaria Department of Silicate Technology, University of Chemical Technology & Metallurgy, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria*

Molybdenum oxide (MoO₃) is known to be only slightly soluble in borate and borosilicate glasses and to induce liquid phase separation in super cooled melts during the cooling.^(1,2) The goal of this study is to verify the tendency for metastable immiscibility and crystallization in multicomponent glasses in the system SiO₂–B₂O₃–Na₂O–ZnO–Nd₂O₃–MoO₃. The content of MoO₃ varies from 5 to 20 mol%. The local structural changes were studied by IR spectroscopy. The MO₄ and BO₃ units determining the appearance of metastable phase separation were identified in the amorphous partially depolymerised silicate network with participation of SiO₄ tetrahedra. Various microheterogeneous structures with complex morphology related to the initial stages of phase separation were observed by TEM and SEM. It was established that depending on the duration and temperature of additional heat treatment the processes of crystallization and immiscibility occur simultaneously or sequentially. Discussions concerning the reasons for immiscibility and obtaining of homogeneous glassy materials were made based on crystallo-chemical, thermodynamic and kinetic considerations.

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Influence of CoO addition on phase separation and crystallization of glasses of the ZnO-Al₂O₃-SiO₂-TiO₂ system

I. Alekseeva^a, A. Baranov^b, O. Dymshits^{a*}, V. Ermakov^b, V. Golubkov^c,
M. Tsenter^a, A. Zhilin^a

^aResearch and Technological Institute of Optical Materials Science, 36/1 Babushkin Street,
Saint-Petersburg 192171 Russia;

^bNational Research University of Information Technologies, Mechanics and Optics,
Kronverkskiy pr., 49, 197101, Saint-Petersburg, Russia;

^cI.V. Grebenshikov Institute of Silicate Chemistry, Russian Academy of Science, Odoevskogo
str., Saint-Petersburg 199155, Russia.

The evolution of structure, phase composition and spectroscopic properties of CoO-doped (up to 5 mol%) titania-containing zinc aluminosilicate glasses in the course of glass-ceramics formation has been studied using Raman scattering, small angle X-ray scattering, X-ray diffraction analysis and optical absorption spectra. Cobalt oxide entered phases formed during heat-treatments, i.e., amorphous phase, enriched in ZnO, Al₂O₃ and TiO₂ and crystalline phase of ZnAl₂O₄ gahnite. Though after high-temperature heat-treatments a part of Co(II) ions remained in amorphous zinc aluminotitanate phase, the absorption of these glass-ceramics was mainly defined by tetrahedrally coordinated Co²⁺ ions located in ZnAl₂O₄ gahnite nanocrystals. In glass-ceramics, the residual high silica amorphous phase contained a small quantity of [TiO₄] centers, which content decreased with CoO addition. Addition of CoO to the parent glass influenced kinetics of its phase separation, nature and quantities of phases precipitated during heat-treatments.

ASAXS as a tool to investigate phase separation in glasses as shown in case of cuprous halide photochromic glasses

A. Hoell¹, S. Haas², D. Tatchev³, A. Heinemann⁴, G. Goerigk¹ & M. Müller⁵

¹Helmholtz Zentrum Berlin, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany.

²Humboldt-Universität zu Berlin, Physikalische Chemie, D-12489 Berlin, Germany.

³Bulgarian Academy of Sciences, Institute of Physical Chemistry, Sofia, Bulgaria.

⁴Helmholtz Zentrum Gestacht, c/o TU-Muenchen, D-85747 Garching, Germany.

⁵Otto-Schott-Institut, Friedrich-Schiller-Universitaet Jena, D-07743 Jena, Germany.

Cuprous halide nanocrystals, embedded in a glassy matrix are of interest with respect to their photochromic behaviour. A silver-free photochromic glass was prepared using a 14.2Na₂O-6.0Al₂O₃-26.6B₂O₃-53.2SiO₂ base glass doped with small amounts of Cl, Br, Cu, Cd, and Sn ions. During isothermal heat treatments at T=600°C up to 60 min, small liquid droplets of CuX precipitate resulting in CuCl_{0.4}Br_{0.6} nanocrystals after cooling. It is known, that both Cd and Sn ions have a large influence on the photochromic properties and on the sizes of the nanocrystals.⁽¹⁻²⁾ But the structural arrangement of the Cd and Sn ions in- or outside the nanocrystals is not known. In order to investigate the influence of Cd and Sn on the precipitation process and to understand the growth and growth delay processes, anomalous small angle x-ray scattering (ASAXS) experiments have been performed.⁽³⁻⁴⁾

The obtained results from an extensive ASAXS study at all accessible x-ray absorption edges will be presented. The x-ray energy has been tuned near and below the K-absorption-edges of Cu, Br, Cd and Sn giving rise to a variation of the atomic scattering factor of the corresponding element. A Mathematica package for simultaneous nonlinear regression has been developed for the data analysis. In this fit program the theoretical energy dependent values $f'(E)$ and $f''(E)$ of the 11 elements the glass is made of has been used. Only meaningful physical and chemical parameters were fitted, such as compositions, mass densities and volume fractions. Analytical and non analytical constraints were included to reduce the number of parameters.

The result of the simultaneous nonlinear regression of all curves measured at these four different absorption edges and assuming two different models for the particles will be presented and discussed. Both models, poly-disperse core-shell and diffusion zone surrounding spherical shaped crystal model, lead to the same structural conclusions. The crystalline core consists of the elements Cu, Cl and Br, mainly. These three elements form the CuCl_{0.4}Br_{0.6} nanocrystals that are responsible for the photochromic mechanism. Cd and Sn are concentrated in a shell surrounding the nanocrystals. The nanocrystals do not contain Cd and Sn.

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Spectroscopic studies of photochromic glasses

Andreia Ruivo,* Vesselin Petrov, César A.T. Laia & F. Pina

FCT/UNL, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516
Monte da Caparica, Portugal

Photochromic glass materials, which change of colour on exposure to sunlight, are known for several years, and had numerous applications.^(1,2) The composition of these systems is rather complex, but normally involve silver halides and copper cations that undergo photoinduced redox reactions, producing metallic silver clusters (AgO). Elucidation of the photochemical mechanisms of these materials were studied some decades ago, however issues such as photoluminescence of those materials, energy transfer and direct observation of the primary photoreaction are still lacking. In this work several photochromic borosilicate glasses were synthesized in order to access those issues. It was found that some of the glasses displayed blue photoluminescence, which are dependent of the presence of PbO. Copper also plays a role, since Cu⁺ is red photoluminescent in those glasses. By increasing Cu⁺ concentration it is possible to obtain several photoluminescence colours. With silver halides the photoluminescence is not completely suppressed, but the photochromic process becomes dominant. Halide ions are essential for the photochromic effect, but they act as luminescent quenchers. Energy transfer from the glass matrix to the silver halide is a strong possibility for the primary photoreaction. Laser flash photolysis was used to study the kinetics involved on the primary processes. Thermochromism is also observed on these glasses, offering the possibility to develop an optical temperature sensor. The role of electron and energy transfer on the photochromic process will be discussed and confronted with the present literature knowledge.

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Interdisciplinary studies of ancient glass from Dichin, Bulgaria.

Tom Smith

University of Nottingham Department of Archaeology, Archaeology and Classics building,
University Park, Nottingham, NG7 2RD, England

Lack of reliable historical accounts and archaeological excavations with secure contexts means that the Balkans region is largely not understood during the transition to Late Antiquity. Recent excavations at Dichin, Bulgaria, have provided potential for clarifying interpretation of the locality and the region. Bone, grain and ceramic evidence determined Dichin featured two phases of occupation, from AD 410-490 and AD 540-580. Poulter⁽¹⁾ interprets the sites irregular layout as a suggestion to a foederati garrison, which ties in with the peace treaty of AD 382 and the settling of Goths in Balkan Peninsula. Rehren & Cholakova's⁽²⁾ study of the glass artefacts concluded high quality wares were being imported, and several lower quality wares were being produced locally. The sample was too small to offer further insight. My current research focuses on analysing a larger sample size of the Dichin glass, focusing on a variety of contexts, forms and colours. Chemical analysis and composition data infers the technology used, and characterises the artefact into an ancient group, that suggests an area of primary production. This in turn allows economic conditions on a local and regional scale to be inferred, and also offers a unique insight into the output of the primary glass producers. Material culture is considered a proxy between past and 'present' identities of garrison. The primary focus of this paper is to present and discuss more so the material analysis of the glass, with the archaeological theory taking a supporting role.

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A temporal assessment of the educational philosophies reflected in the historical artefacts at the Welsh School of Architectural Glass, Swansea.

Marilyn Griffiths

Swansea Metropolitan University, Mount Pleasant Campus, Swansea, SA1 6ED

This research attempts to glean an understanding of the pedagogical philosophies, which fostered the growth and success of the Welsh School of Architectural Glass, Swansea and to establish the foundations of an archive of work for future education in decorative Architectural Glass.

Since the beginning of the Welsh School of Architectural Glass department seventy five years ago, there have been many changes in the world of glass technology and architecture. Many schools and colleges that offer the same or similar courses to Swansea have merged into other courses, closed or are on the verge of closing. It is intended that this research will make a significant contribution to the understanding of how the Welsh School of Architectural Glass has survived thus far and to assist the School in looking towards future growth. A number of points need to be considered in depth, namely :- a) Understanding of the teaching philosophies that may have prevailed over the past 75 years of the course; b) An overview of the influences and cross fertilisation of ideas from other branches of the visual arts; c) Financial constraints that may have impacted on the department over the years; d) Changes in policies in Higher Education at Governmental and local levels, and; e) Changes in the industries in glass technologies and in the world of Architecture.

Historical content and context serves to create a wholeness to education, and the artefacts that have accumulated over the years will contribute to inform the practice of current and future staff and students. The sharing of past skills and knowledge provide enhanced access and deepens understanding by challenging perceptions and intellectual frameworks.

A scoping exercise to ascertain the number of cartoons, designs, photographs, glass panels and other ephemera as yet unknown needs to be systematically conducted. Educational papers such as prospectus, curricular descriptors, exam papers and other various teaching related documents would prove invaluable to this research.

Many of these designs and cartoons have suffered some damage over the years through handling and insensitive storage. To enable this rich teaching resource to be safely accessed it must be logically recorded, professionally stored as far as possible and eventually made available for staff to use. Networking with other establishments such as Ely Stained Glass Museum, The Glynn Vivian Art Gallery and The National

Museum of Wales, Cardiff, to ascertain best practice in this field is therefore important. Swansea Metropolitan University's own archive will naturally be useful and collaboration with this department will also be necessary.

Historically, the School has had an impact on the development of stained glass. It was, William Grant Murray's (the instigator of the course) ambition to forge a name for Swansea in this field and through the guidance and teaching of Howard Martin and others who followed in his wake, the name of Swansea is recognised as the place to study glass. As so many past students of the department have become extremely successful and highly respected nationally and internationally in the field of Architectural Glass, it is important for Swansea socially, economically and culturally that the School continues to survive.

Optical spectroscopy of cobalt in oxide glasses

Myrtille Hunault, Georges Calas and Laurence Galois

IMPMC, University of Paris, CNRS and IPGP, Case 115, 75252 Paris Cedex 05, France

Colouring glasses using cobalt impurities has been used since centuries in glassmaking, giving the well-known intense blue colouration of glasses. Alkali borate glasses containing cobalt are compared to silicate glasses using optical absorption spectroscopy. We pay special attention to the variations in the molar extinction coefficient, in order to get quantitative information on the local surrounding of Co^{2+} cations in these glasses. The influence of the nature of the alkali (Li, Na, or K) on colouration for a given alkali content is also investigated.

In borate glasses, the concentration of 4-coordinated cobalt increases with the alkali content and with the size of the alkali ion. The evolution of the absorption spectra agrees well with the literature. However, the amount of tetrahedrally coordinated cobalt reaches only the half of the cobalt concentration in the glass. This indicates that most Co^{2+} behave then as a “silent” species in borate glasses.

X-ray absorption spectroscopy (EXAFS and XANES) data indicate that alkali-poor borate glasses contain mostly octahedral Co^{2+} occurring within regular sites. These data are discussed in the light of Ni-bearing alkali borate glasses. Silicate glasses have been investigated in a broad range of soda-lime glasses used for designing modern stained-glasses. This comparison confirms the importance of the “silent Co^{2+} species” in the coloration of oxide glasses.

Glass formation in lithium phosphate glasses with anionic substitution

Nerea Mascaraque*, Alicia Durán, Francisco Muñoz

Instituto de Cerámica y Vidrio(CSIC), Kelsen 5, 28049, Madrid (Spain)

Lithium phosphate glasses have attracted much attention in the last years for their potential application as solid state electrolytes for rechargeable lithium batteries. Solid electrolytes have several advantages compared to liquid ones: they are non contaminant, do not have flammable organic compounds and a separator is not needed to prevent physical contact between both electrodes. Bates and co-workers developed a new amorphous lithium phosphorous oxynitride (LiPON) suitable to be used as electrolyte in thin-film lithium secondary microbatteries. The substitution of oxygen by nitrogen in phosphate glasses produces an increase in electrical conductivity as well as in chemical stability, which have enhanced their research in devices for energy applications. This improvement of conductivity is also possible with fluorine/oxygen and sulphur/oxygen substitutions. However, the main drawback of lithium phosphate glasses with S^{2-} ions substituting oxygen is their very low chemical stability. This work presents a study on the synthesis of lithium phosphate glasses where oxygen is substituted by nitrogen and either fluorine or sulphur, with the aim of enhancing both electrical conductivity and chemical durability.

In $\text{Li}_2\text{O-LiF-P}_2\text{O}_5$ and $\text{Li}_2\text{O-SO}_3\text{-P}_2\text{O}_5$ glasses, the nitridation produces total loss of fluorine and sulphur during the ammonolysis of the melt. Then, a two melting steps process has been carried out. A glass with composition $55\text{Li}_2\text{O.45P}_2\text{O}_5$ is first nitrated and the oxynitride glass is re-melted with fluorine or sulphur compounds under a nitrogen flow. This method allowed the preparation of glasses with higher fluorine contents than when non-nitrated glasses are used, keeping the initial amount of nitrogen. In this new synthesis route, the most interesting point is the obtaining of glasses with high lithium content where nitrogen and fluorine coexist. Similarly, we studied the synthesis of glasses within the systems $\text{Li}_2\text{O-P}_2\text{O}_5\text{-PON-SO}_3$ and $\text{Li}_2\text{O-P}_2\text{O}_5\text{-PON-P}_2\text{S}_5$, where oxygen can also be substituted by nitrogen. However, the second melting of an oxynitride phosphate glass with Li_2SO_4 gives rise to loss of nitrogen by reaction with sulphur.

Glass batch reactions observed at the granular scale

J. Grynberg*, E. Gouillart, M.H. Chopinet, M. Toplis

Surface du Verre et Interface, UMR125, 39 quai Lucien Lévy, Aubervilliers 93300, France

The reactive melting of glass raw materials at high temperature has been thoroughly studied from the point of view of possible chemical reactions. Little is known, however, about physical transformations at the granular scale, such as the rearrangements of grains in the course of solid-solid reactions, or due to capillary forces and bubbles motion. As such transformations of the microstructure impact on the kinetics of the chemical reactions, more insights into the evolution of the microstructure are needed to understand the persistence of defects (unmolten grains and bubbles) during glass melting. We report here how the first steps of the transformation of the reactive packing of glass raw materials can influence the final glass homogeneity. Small batches of quartz and sodium carbonate grains were submitted to different heating treatments and quenched at 900°C. Observations of complete centimeter-scale samples are performed with Scanning Electron Microscopy (SEM). Dedicated image processing methods were developed in order to extract the unmolten grains and bubbles from the SEM images. We show that the number of defects in the glass melt is related to the initial grains sizes, and to the thermal history to which the batch is submitted. We observe important rearrangements of the grains because of a remarkable affinity of sodium carbonate for sand under 750°C, when materials are still in the solid state. We also study the spatial distribution of unmolten sand grains and the composition of the first liquids. Different transformations of the microstructure and therefore different reaction paths are identified in our experiments. We propose a simplified model at the granular scale to account for such observations.

Structure of amorphous iron phosphate FePO_4

Bushra Al-Hasni* and Gavin Mountjoy

University of Kent, School of Physical Sciences, Ingram Building, Canterbury, Kent, CT2 7NH, UK

A full complete study of amorphous iron phosphate prepared by two methods thermal decomposition and ball milling using a series of experiments has been performed. This including x-ray and neutron diffraction, small angle scattering, x-ray absorption spectroscopy, FTIR, Differential thermal analysis (DTA), Mossbauer spectroscopy and X-ray Fluorescence. The FTIR spectra consist of a number of strong extensively convoluted bands that characterized from all phosphate glasses. The glass transition temperature was determined at 550°C and the crystallization at 600°C. The Mossbauer spectrum of amorphous FePO_4 prepared by thermal decompositions indicated the presence of 100% of Fe^{3+} in tetrahedral environment. The Fe environment in amorphous FePO_4 prepared by two methods is similar. The Fe is coordinated to four oxygen atoms with mean separation of 1.96 Å. The small angle scattering showed that there is a large scale structure in the amorphous FePO_4 prepared by thermal decomposition. In addition, modelling these structures was helpful to support experimental results and get a better understanding by providing a valid three-dimensional model structure. The models gave reasonable agreement with the experimental results.

Local structure in Pb^{2+} containing silicate and germanate glasses

Oliver L. G. Alderman*, Diane Holland

University of Warwick, Department of Physics, Gibbet Hill Lane, Coventry CV4 7AL, UK

Alex C. Hannon, Emma R. Barney & Steve Feller

The latest diffraction data on binary lead silicate and germanate glasses are presented. The measurements represent part of an in-depth, multi-technique approach toward understanding the structural role of Pb^{2+} in oxide glass systems. The existence of short Pb-O bonds in both systems indicate that asymmetric Pb sites, associated with stereochemically active lone pairs, are present. For the lead silicate glasses with >60mol% PbO, both silicon NMR and diffraction results support the existence of a lead-oxide sub-network, that is, oxygen coordinated solely to lead. In the germanate system, a change in germanium to oxygen coordination number with composition is observed. This number goes through a shallow maximum and can be related to measured thermo-physical properties such as density and glass transition temperature. Comparison is made to the $\text{Na}_2\text{O-GeO}_2$ system in which a higher average Ge-O coordination is reached at lower modifier content.⁽¹⁾ Unlike the sodium germanate system; in the lead germanate glasses Pb competes for the added oxygen, such that the average coordination O-Ge is below two for all concentrations of PbO. Comparison is made between germanate and silicate compositional analogues. Only a small linear shift in Pb-O bond length distributions is observed between the two systems.

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Amorphous structure in thallium germanate binary glasses

Nattapol Laorodphan*, Emma Barney, Andy P. Howes, John V. Hanna,
Ray Dupree and Diane Holland

University of Warwick, Department of Physics, Gibbet Hill Road, Coventry, CV4 7AL, UK

Thallium, in its +1 oxidation state (Tl^+) in glass, introduces interesting non-linear optical properties due to its stereo-chemically active lone-pair of electrons. This affects not only the environment of Tl^+ ion but also that of the glass network former. The structure of thallium germanate glasses has been investigated using several techniques. We here report the solid-state nuclear magnetic resonance (NMR) and Raman spectroscopy results. Thallium has two NMR-active isotopes, ^{203}Tl and ^{205}Tl , with 29.5% and 70.5% natural abundance respectively. Both isotopes have nuclear spin $I = 1/2$, high gyromagnetic ratios and magnetic moments and very similar Larmor frequencies 57.12 and 57.63 MHz relative to ^1H at 100 MHz. These factors make thallium NMR both difficult and informative. ^{205}Tl NMR of amorphous samples gives very broad lines (~1,000 ppm) which increase with thallium content and large chemical shift range of a few hundred to approximately 2,000 ppm. Broadening reflects interaction between neighbouring ^{203}Tl - ^{205}Tl nuclei and therefore ^{203}Tl enriched glass and crystalline samples at the composition equivalent to $\text{Tl}_2\text{Ge}_4\text{O}_9$ are also investigated. Raman spectra of the glasses show changes in Raman shift in the 400–600 cm^{-1} and 700 - 1,000 cm^{-1} regions, corresponding to the change in germanium environment, and in the 200-300 cm^{-1} region for thallium environment. It is believed that glass structure mimics local structural units in crystal phases at the equivalent composition. Thus, data have also been obtained on $\text{Tl}_2\text{Ge}_6\text{O}_{13}$, $\text{Tl}_2\text{Ge}_4\text{O}_9$, $\text{Tl}_2\text{Ge}_2\text{O}_6$ and $\text{Tl}_8\text{Ge}_6\text{O}_{14}$ crystalline samples.

Structure-property relationship of ionic sulfophosphate glasses

S. Reibstein^{1*}, K.H. Nielsen¹, N. Da¹, S. Krolikowski¹, D. De Ligny², B.Champagnon², S. Sirotkin², J.-P. Simon³, O. Grassme^{1,4}, G. Peters⁵, L. Wondraczek¹.

¹Chair of Glass and Ceramic, Department Material Science and Engineering, University Erlangen-Nuremberg, 91058 Erlangen, Germany

²Laboratoire de Physico-Chimie des Matériaux Lumineascent, Université de Lyon, Université Claude Bernard Lyon 1, UMR 5620 CNRS, 69622 Villeurbanne, France

³European Synchrotron Radiation Facility and Laboratoire de Thermodynamique et Physicochimie Metallurgiques, CNRS, Institut National Polytechnique et Université Joseph Fourier Grenoble, BP75, 38402 St. Martin d'Hérès, France

⁴Siemens AG, 91058 Erlangen, Germany

⁵Institute of Anorganic Chemistry, Christian-Albrechts-University Kiel, 24098 Kiel, Germany

Sulfophosphate glasses are receiving continuous attention from academic as well as industrial perspectives. A facile fabrication of sulfophosphate glasses is founded in the high solubility of SO₃ in supercooled ortho- and pyrophosphate melts. Distinct properties such as a glass transition temperature T_g well below 400°C, specific corrosion behavior or mechanical stability are from special interest. It is believed for this specific type of glasses that those and many other properties can be related in an almost archetypical way to the atomic and topological structure. However, only little attention has been paid to structural characterization of sulfophosphate glasses, albeit their non-intuitive ease of fabrication. Here, we will discuss structural data (NMR, Raman and SAXS spectroscopy), and we will try to establish first relations to macroscopic behaviour.

Durability of UK Nuclear Waste Glasses in neutral and high pH solutions

Nathan J. Cassingham,^{*} Niel C. Hyatt and Paul A. Bingham
University of Sheffield, Department of Materials Science and Engineering, Sir Robert Hadfield Building, Mappin Street, Sheffield, S1 3JD, United Kingdom

Vitrification of high-level nuclear waste (HLW) has been a major focus internationally for decades. Current UK glasses utilize an alkali borosilicate glass with 25 wt% waste loadings. Final geological disposal strategies have suggested the HLW waste packages will be in close proximity of intermediate level nuclear waste (ILW) packages which create high pH solutions. These high pH solutions, at long times, may interact with the UK HLW waste packages. It is known that high pH solutions increase the rate of corrosion in glasses. This presentation discusses our study of long term dissolution experiments of UK simulated HLW glasses in both high purity H₂O and a buffered Ca(OH)₂ solution under a CO₂ free environment. Here, results will be presented for two distinct surface area to volume ratios of a UK simulated HLW blend (25 wt% Magnox and 75 wt% ThORP waste calcine) glass at a 25 wt% waste loading.

Encapsulation of β -tricalcium phosphate in a sodium aluminophosphate glass matrix

A T Grigg^{*1}, A J Marsden¹, S Feller², Dr D Holland¹

¹Department of Physics, University of Warwick, Gibbet Hill Rd, Coventry, CV4 7AL

²Coe College, 1220 First Avenue NE, Cedar Rapids, Iowa 52402, USA

Polycrystalline β -tricalcium phosphate (β -TCP) is of interest to the nuclear industry due to the ability of active metal cations to substitute onto the abundant and varied calcium sites. To complete the waste storage process, the β -TCP powder is encapsulated in a sodium aluminophosphate (NAP) glass matrix. It is this encapsulation that is examined in this work.

Samples were made at various β -TCP:glass ratios, by melting β -TCP and NAP glass in an alumina crucible at 1500°C, before using a roller quencher to cool at 10⁶ KS⁻¹. Amorphous samples were successfully made at ratios from 10:90 to 80:20 β -TCP:NAP. ²⁷Al NMR data have been collected at 14.1 T, and ²³Na and ³¹P at 11.75 T. The ³¹P and ²⁷Al data in particular show a trend from a very broad peak typical of NAP glass, to a narrower peak consistent with a disordered β -TCP spectrum. X-ray diffraction data have been collected on all samples, showing broad patterns characteristic of an amorphous structure. At higher β -TCP concentrations however, some narrower crystalline peaks are visible in positions consistent with α -TCP, a high-temperature phase of TCP retained due to rapid cooling. Differential thermal analysis (DTA) data have also been collected on all compositions, showing crystallisation events at two temperatures around 500°C. It has been established that the phase change at higher temperature is due to crystallisation of heavily sodium-aluminium doped β -TCP. Further data collection and analysis are in progress. Preliminary Raman data will also be presented.

Gamma irradiation effects in glasses intended for the immobilisation of nuclear waste

Owen McGann

University of Sheffield, Department of Materials Science & Engineering, Sir Robert Hadfield Building, Mappin Street, Sheffield, South Yorkshire, S1 3JD, UK

Over the past 50 year the process of vitrification has become an accepted route for the immobilisation of high level nuclear waste, and is increasingly being considered for the immobilisation of intermediate and low level wastes. During the lifetime of the waste forms the glass that comprise the bulk of their material will be exposed to a significant dose of radiation. Gamma radiation effects the waste forms in a distinct manner, effecting the bulk material instead of just regions local to the radionuclides, and producing effects dependent upon the glass composition. Consequentially the effect of gamma irradiation upon a glass intended for nuclear waste immobilisation is of great interest, as it could have a significant effect upon the long term stability of a final vitrified waste form. This presentation will provide an overview into the mechanisms by which gamma irradiation effects glasses, and will go on to discuss experimental results from a study carried out to explore the effect of gamma irradiation upon a range of prospective nuclear waste form glasses, in terms of electronic, mechanical and structural changes that have taken place during gamma irradiation, and exploring the dependency of such effects on the composition of the glass and the dose of gamma irradiation.

Understanding the effect of refractory spinel phases on HLW glass processing

James Stevens

University of Sheffield, Department of Materials Science and Engineering, Sir Robert Hadfield Building, Mappin Street, Sheffield, South Yorkshire S1 3JD, England

Refractory spinel phases are known to form during the calcination and vitrification of wastes arising from nuclear fuel reprocessing. Limiting the size of the spinel crystals is important to reduce the depth and viscosity of a sludge layer that forms on the floor of the melter and which interferes with melt pouring. The general chemical formula for spinel present in both simulated calcine and vitrified simulated waste has been investigated and comparative data for spinel crystal identification as a function of waste loading has been provided by Raman spectroscopy. The fraction of spinel crystal in the vitrified waste has been analysed. A preliminary thermodynamic model of both the calcination and vitrification processes has been developed.

Ni environment and its structural role in MgO-Al₂O₃-SiO₂ glasses and glass-ceramics

Aymeric Dugué^{1,*}, Laurent Cormier¹, Olivier Dargaud², Georges Calas¹ and Laurence Galois¹

¹*Institut de minéralogie et de physique des milieux condensés, Université Pierre et Marie Curie, 4 place Jussieu, F-75005 PARIS, France*

²*Saint-Gobain Recherche, 39 quai Lucien Lefranc, F-93303 AUBERVILLIERS, France*

Ni-doped glass-ceramics have been recently extensively studied because of their broad emission in the infrared region and they are considered as promising materials for tunable solid-state lasers.⁽¹⁻²⁾ Transparent glass-ceramics have the advantages of both crystalline (good optical and mechanical properties) and glass (good formability) materials. Transparent Ni²⁺-doped MgO-Al₂O₃-SiO₂ glass-ceramics can be prepared with nanocrystalline spinel MgAl₂O₄ containing Ni²⁺. In recent years, studies have been focused on improving the infrared emitting ability and understanding the crystallization sequence of this glass-ceramics.⁽²⁻⁴⁾

The goal of this study is to determine the environment of Ni in the glass and the modifications occurring during the nucleation processes. The structure around nickel in glasses is probed by neutron diffraction with isotopic substitution. Ex-situ samples of Ni-doped glass-ceramics have been studied by X-ray diffraction coupled with Rietveld refinements and by diffuse reflectance spectroscopy in order to determine the weight proportions of the crystalline phases and the major coordination of nickel. A deep investigation has been done on the cation distribution in the spinel phase.⁽⁵⁾

Our results show that initially nickel is 5-fold coordinated and 4-fold coordinated to a lesser extent. The spinel phase appears to crystallize in highly Ni-doped glasses.⁽⁶⁾ An important modification of the coordination of nickel is observed during the spinel crystallization, resulting in 6-fold and 4-fold coordinations. The proportions of these coordinations are determined by the cation distribution in the spinel phase. The results of our study also show that the amount of 6-fold coordinated nickel reaches a maximum during the annealing process before to decrease.

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Color prediction software for designers and the glass industry: a tool for art, design and conservation.

Peter Sundberg*¹ and Päivi Jokela²

¹Glass Research Institute (Glafo) POBox 5157, SE-350 05 Växjö, Sweden

²Linnaeus University, SE-351 95 Växjö, Sweden

Coloration in glass is conveniently achieved by transition elements, and glasses coloured by manganese, cobalt, copper, chromium and iron are used in our study. A set of 100 coloured glass samples were prepared to calibrate the system. As long as the same glass system is used, it is quite straightforward to use multivariate data analysis to predict (1) the amount of colorants needed for a given colour (absorption spectra), or alternatively (2) the colour obtained from a given set of colorants.

A severe complication arises as most of these elements can co-exist in several oxidation states, each contributing differently to the coloration. Furthermore, the balance between these colorants is not constant. Even if the same colorant is used, the obtained glass colour can vary due to mutual interactions between the colorants present in the system and also due to different melting conditions or different glass compositions. The science behind this will be outlined and shown with illustrative examples using a multivariate approach.

The main focus in perceptual colour research has been on surface colours and most existing color systems, such as Natural Color System (NCS) and Munsell, are established using opaque colours. Our working hypothesis is to adopt the Natural Color System (NCS) representation also for transparent materials. Thus in the current study, the perceived colours in our calibration set are determined by trained observers in a standardized setting. A status report will be given on our work to correlate the measured CIELab colour coordinates with the perceptive coordinates in the Natural Color System.

The overall aim is to design and develop a unique virtual tool, which can be used to facilitate the communication in the glass production chain: from designer via glass scientists to the glass production. For the conservationist, the tool will show how to produce a new glass with desired colour properties. What is more, the tool may allow the use of coloured waste glass cullet in the production of coloured glasses in a pot furnace.

Melting History of In-flight melted Soda-Lime-Silica Glasses using Oxy-Fuel Combustion Burner

Tetsuji Yano^{1*}, Daiki Morishima¹, Jun Taguchi¹, Yusuke Miyake¹,
Takafumi Sato¹, Keizo Satoh², Masanori Iwamoto², Yasunori Ebihara²,
Satoru Inoue³

¹Dept. of Chemistry and Materials Science, Tokyo Institute of Technology, JAPAN

²TOYO Glass Co. Ltd., JAPAN

³National Institute for Materials Science, JAPAN

In-flight melting (IFM) method is the innovative glass melting process to enable large reduction of energy for melting. Granular powders, which are prepared by spray-dry method from the water slurry of the glass raw materials, are injected into the hot zone formed by oxy-fuel combustion burner and/or plasma flame. Quite short residence time of millisecond order in hot zone enables vitrification of granular powder, and glass droplets are accumulated and form the glass melt under the flame. Short completion of the vitrification process reduces the energy consumption which has been used for heating the batch blanket in the ordinary Siemens-type furnace.

In this study, soda-lime-silica glass prepared by IFM process using oxy-fuel combustion burner in the 1 ton/day-scale melter are investigated in detail. 16Na₂O-10CaO-74SiO₂ glass in mass% were obtained using above glass melter in different energy levels. The glass melts were sampled below the oxy-fuel burner flame, and subjected for the investigation. Gas in the residual bubbles, dissolved gas species in the glass samples were analyzed using MS, FT-IR spectrometers and gas chromatograph analysers to clarify the correlation between the IFM glass properties and melting history.

In the presentation, the analyzed results and trends are shown correlating with the IFM condition, and characteristics of IFM glasses will be discussed from the points of view of the IFM vitrification process in hot flame.

Drainage and a life time of a single bubble rising through a molten glass

H. Kočárková*¹ & F. Pigeonneau¹ & F. Rouyer²

¹*Surface du Verre et Interfaces, UMR 125 CNRS/Saint-Gobain, Aubervilliers, France*

²*Laboratoire de Physique des Matériaux Divisés et des Interfaces, FRE 3300, Université Paris-Est, Marne la Vallée, France*

For better understanding of a stability of glass foams, an experiment with a single bubble rising towards a level of a molten glass was compiled. Life time of the bubble was determined and an evolution of thickness between the bubble and the fluid interface was measured *via* interference method under various conditions such as viscosity range, bubble size, gas inside the bubble and chemical composition of glass.

Thickness evolves exponentially with time for all tested chemical compositions, thinning rate is a function of the fluid viscosity and Bond number (characteristic of physical properties: size of the bubble, density and surface tension of the two liquids), but not a function of the chemical composition of glass. A thermo stabilizing effect, which prolongs the life time of the bubble, is observed only for the high temperature (above 1300°C).

New tin oxide electrodes for high temperature applications

Julien Fourcade* and Olivier Citti

Saint-Gobain, SEFPro, 9 Goddard Rd, Northborough, MA 01532, USA

Tin oxide electrodes are commonly used for the melting of lead crystal glass and alkali free borosilicate glasses for electronic applications. Solubility of tin oxide in such glasses is rather low and the lifetime of electrodes is usually judged acceptable. In recent years, new glasses such as arsenic and lead free glasses, as well as higher strength glasses have appeared. Manufacturing of these new glasses usually requires the use of higher temperature. At high temperature, stannic oxide tends to be reduced into the more soluble and more volatile stannous oxide according with the following reaction: $\text{SnO}_2(\text{s}) = \text{SnO}(\text{g}) + 1/2\text{O}_2(\text{g})$ This reaction remains limited up to 1400°C in air and in oxidized melts. Nevertheless, when electrodes are used in more reduced silicate melts and/or at temperature above 1550°C, reduction mechanisms start to significantly impact the corrosion resistance of the material and the lifetime of tin oxide electrodes can be dramatically decreased. Authors have developed a new tin oxide material for electrodes with enhanced stability at high temperature and/or in more reducing conditions. The new material was designed to extend the lifetime of electrodes in silicate melts without affecting their electrical properties.

New highly resistive zirconia fused cast products for alkali free glass melting

Isabelle Cabodi, Michel Gaubil, Christel Morand

*Saint-Gobain C.R.E.E, SEFPRO, Building 550, avenue alphonse Jauffret, Cavaillon
BP20224 84306 Cedex, France*

The High Zirconia Fused Cast (HZFC) products are widely used to melt alkali free glasses. As these glasses are extremely resistive, there is a need for a new range of HZFC products with a very strong electrical resistivity (ER), especially for glassmakers that wish to melt higher resistive glasses or to use higher electrical power in their furnaces. Indeed, the ER of refractory materials, especially those that support heating elements, need to be improved in order to avoid electric losses which can initiate locally thermal breakdown and as a consequence a rapid degradation of materials. To improve the products' ER, the common approach has been so far to improve the ER of the glassy phase (alkali free) and/or to increase the glassy phase content. Going further in this direction of increasing glassy phase content could become hazardous for the glass defects potential and corrosion resistance of the materials. Then we developed a new approach, combining a highly resistive glassy phase with a significant increase of the ER of the Zirconia network itself. The electrical properties of this product are discussed through new electrical corrosion tests results. The glass contact properties remain in accordance with the glass quality level. Glass defect topics will be also discussed.

The analysis of *in-situ* 17th century painted glass from Christ Church Cathedral, Oxford

Rebecca B. Scott^{1*}, Andrew J. Shortland², Matthew Power³ and Kelly Domoney²

¹*Department of Earth and Environmental Sciences, Katholieke Universiteit Leuven, Belgium*

²*Department of Earth and Environmental Sciences, Katholieke Universiteit Leuven, Belgium*

³*Department of Engineering and Applied Science, Cranfield University, Shrivenham*

⁴*Christ Church Cathedral, Oxford*

The stained and painted glass in Christ Church Cathedral, Oxford has had a varied and in some cases turbulent history. This is especially true of the High Lime, Low Alkali (HLLA) painted glass of the 17th century. During this period, a scheme of around 20 windows all painted by the Van Linges replaced the pre-existing Medieval stained glass windows. The Van Linge scheme took around 10 years to complete and survived in the windows for only a short time, before being removed in the Civil War. Some of the Van Linge windows survived and were re-instated into the Cathedral, along with windows by other 17th century artists such as William Price. The Victorian tastes did not favour the painted glass of the 17th century as is attested to by many contemporary authors, and during the 1870s renovations to the building much of the painted glass was removed. Two examples survive in the cathedral today, 'Jonah before Nineveh' and the figural image of 'Bishop King', both attributed to the Van Linges. An ongoing research project has focussed on investigating the history of the cathedral windows with particular focus on the painted glass of the 17th century. This paper focuses on one of the *in-situ* windows, 'Jonah before Nineveh'. Handheld X-ray Florescence (HH-XRF) was used to analyse the window in a non-destructive manner to determine the extent to which the window was the work of a 17th century artist. The results showed that not only was the window of a HLLA composition, but also, two distinct HLLA compositions could be determined, indicating that the window had been repaired during the later 17th century.

A Vision Fulfilled?

Alun Adams

Swansea Metropolitan University, Mount Pleasant Campus, Swansea SA1 6ED, Wales

2010 saw the 75th Anniversary of the Welsh School of Architectural Glass and the publication (not coincidentally) of the book by the late Maurice Broady on Swansea's architectural glass tradition. Martin & Thomas, Celtic Studios, and the teaching of stained and architectural glass in Swansea are all interlinked. These links within the broader context of stained glass in Wales will be presented and discussed as will the assertion that the 'Vision' of those who founded the taught programme has been fulfilled.

Alun Adams is Co-ordinator of the Architectural Glass Centre, the commercial arm of the Welsh School of Architectural Glass at Swansea Metropolitan University. A former student at the School he specialised in the history of stained glass with particular interest in Arts and Crafts and in issues and techniques of restoration and conservation. He was for 10 years a lecturer at the School. He is stained glass adviser to the Cathedrals and Churches Commission of the Church in Wales, and has been involved in an advisory capacity on projects with the National Museum of Wales. He has written a number of articles/papers on aspects of the history of stained glass in Wales, and was co-author with David Dungworth on the glass at Margam Castle, Port Talbot. Most recently he was joint editor with Elspeth Broady of "A Vision Fulfilled: The Story of Celtic Studios and Swansea's Architectural Glass Tradition".

Recovery of the lost technology of Bright Copper Ruby

Peter Wren Howard

Independent Glass Technologist, 87 Enville Street, Stourbridge, West Midlands DY8 1XW

European Glassmakers of the early medieval period had a palette of colours that was based on the presence in their glass formulations of significant percentages of Iron and Manganese. The presence of these two metals in the glass form a colouring system that can be varied across the spectrum depending on the redox balance in the glass, from a light blue at extreme reduction, through green, yellow, sepia, pink to purple, at its most oxidised. Results of research in this system, done in collaboration with the Department of Mineralogy of the Natural History Museum have been previously published.

On a visit to Chartres Cathedral in April 2005 the author was very surprised to find that the colours in the stained glass windows of the Cathedral which was built between 1196 and 1224 AD in no way resembled those of the technology available to European glassmakers of that period. In particular there is extensive use of a bright mid red colour which is the same colour throughout the cathedral, showing no streaks, and no tendency to show brownish dark shades of red. As red glass is notoriously difficult to produce, and the degree of consistency that had been achieved, it became apparent that this was the work of real masters of the art from 800 years ago who must have been using some technique that is unknown today.

Researching the history of glassmaking revealed that this bright red Copper ruby glass when made up as an enamel was known as "Rouge Clair" and was applied to gold artifacts in special cases and was so highly prized that special mention was made of it in inventories of royal and aristocratic households. Knowledge of the technique was lost in the mid 14th century at the time of the Black Death.

The author has conducted a number of research glass melts and has succeeded in replicating the clarity of the red produced by Copper in glass 800 years ago, and gone on to demonstrate that using the same technology, extremely low concentrations of Copper in glass can be made to form a pure pink glass, without any trace of the yellow cast that low concentration Copper normally gives.

Structural properties related to transition elements in oxide glasses. Application to glass coloration

Georges Calas*, Laurence Galois, Laurent Cormier and Guillaume Ferlat

University Pierre and Marie Curie, Institute of Mineralogy and Physics of Condensed Matter, Tour 23/4, 4 Place Jussieu, Paris 75252, France

Transition elements play an important role in physical and chemical properties of glasses. Since the discovery of glass making, the coloration caused by transition elements has always been one of the most attractive properties of glasses. Still now, transition metal ions constitute the most important source of glass coloring agents. Coloration varies, for a given transition element, as a function of chemical and physical parameters such as glass composition or melting/fining conditions. At the same time, the electronic transitions responsible for light selective absorption and glass coloration provide unique information about the local structure and chemical bonding of glasses. This presentation aims to review optical absorption data at the light of complementary information provided by a broad range of spectroscopic and scattering methods (e.g., XANES, EXAFS, neutron scattering with isotopic substitution), providing a unique harvest of results of scientific and technological significance: unusual coordination numbers, distribution of site geometry, sensitivity to the chemical bond, medium-range organization, heterogeneous spatial distribution... Complementary information is provided by numerical modeling, for instance underlining that 5-coordination is a commonly present coordination state for transition metal ions. Some of these structural characteristics are inherited from the peculiar dynamics of silicate melts, and this implies to revisit the electronic transitions responsible for glass coloration. As transition elements can be connected to the various structural subsets of glasses, they are useful color indicators of the complex structure of these materials. Vice versa, the variation of colors may be rationalized as a function of glass composition and melting conditions.

The complex behaviour of iron in oxide glasses: a multi-spectroscopic investigation

Paul A. Bingham

Department of Materials Science and Engineering, The University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, UK.

The local structural environment and oxidation state of multivalent elements in oxide glass can strongly affect their physical properties and hence it is important to gain a detailed understanding of the factors governing their behaviour. Here, the behaviour of Fe in oxide glass matrices has been considered since iron is almost ubiquitous in practical glasses, yet its behaviour is far from fully understood.

The effects of bulk glass composition and iron concentration, and the presence of iron in multiple valences and multiple coordinations can be barriers to obtaining a detailed and quantitative understanding of its behaviour in glasses as functions of glass composition and preparation conditions. Here these barriers have been (partially) removed by studying Fe²⁺ and Fe³⁺ separately and in isolation, and the results show clear differences in the behaviour and local structural ordering of Fe²⁺ and Fe³⁺, termed collective and selective behaviour, respectively.

Results from a combination of optical absorption and luminescence spectroscopies and Fe K-edge XANES and EXAFS of SiO₂-R₂O-R'O glasses doped with 0.2 mol% Fe₂O₃ (broadly indicative of technical silicate glasses) are discussed. It is concluded that, whilst Fe²⁺ exhibits collective behaviour and can be a useful probe ion for investigating average or bulk glass structure, Fe³⁺ exerts strong local ordering effects, exhibiting selective behaviour, and may be less useful for probing bulk compositional effects. This local ordering of Fe³⁺ takes the form of a transition from [4]Fe³⁺ to [6]Fe³⁺ as functions of alkali and alkaline earth cation type. For the first time, this transition has been measured and quantified by XANES and EXAFS and the results are in agreement with previous results from optical spectroscopy.

Photoionisation of transition metal ions in glasses

Doris Möncke^{1*}, Doris Ehrt²

¹National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute,
Vassileos Constantinou Ave. 48, 11635 Athens, Greece

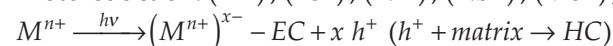
²Otto-Schott-Institut für Glaschemie, Friedrich-Schiller-Universität, Fraunhoferstr. 9, 07743
Jena, Germany

Understanding the principles of photoionisation in glasses is imperative for many applications since irradiation induced defects are detrimental to high quality optics, whereas strong photochemical reactions are desired in photosensitive glasses.

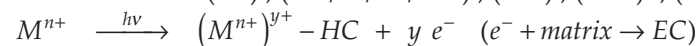
Defects can be classified according to their origin into intrinsic or extrinsic defects. Intrinsic defects arise from irradiation-induced breakdown of the glass matrix. Short-lived radicals or transient defects may either recombine or transform into more stable defect centres, which consist of negatively charged electron centres (EC) and positively charged hole centres (HC).

Extrinsic defects are formed by the photoionisation of polyvalent dopants:

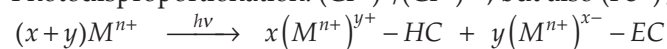
Photoreduction: $(\text{Ti}^{4+})^{\cdot-}, (\text{Fe}^{3+})^{\cdot-}, (\text{Ni}^{2+})^{\cdot-}, (\text{Nb}^{5+})^{\cdot-}, (\text{Mo}^{6+})^{\cdot-}, (\text{Ta}^{5+})^{\cdot-}, (\text{W}^{6+})^{\cdot-}$



Photooxidation: $(\text{V}^{4+})^+, (\text{Mn}/\text{Fe}/\text{Co}/\text{Ni}^{2+})^+, (\text{Zr}^{3+})^+, (\text{Nb}^{3+})^{++}, (\text{Mo}^{5+})^+, (\text{Mo}^{3+})^{+++},$



Photodisproportionation: $(\text{Cr}^{3+})^{\cdot-}/(\text{Cr}^{3+})^{+++}$, but also $(\text{Fe}^{3+})^{\cdot-}/(\text{Mn}^{2+})^+$



The formation of extrinsic defects either increases the amount of reversibly charged intrinsic defects or replaces intrinsic defects of like charge.

Defect formation is a dynamic process. The mechanisms and rates of defect formation depend on many factors such as the glass matrix, irradiation parameters, concentration, and species of the dopants and might even change during the irradiation process.

In this work, photoionisation of various transition metals was studied at different dopant concentrations in fluoride-phosphate, metaphosphate, and boro-silicate glasses after irradiation with lasers, X-rays or UV-lamps.

Defects often absorb strongly in the UV and VIS region and for this reason they can be characterized by optical spectroscopy. Many defects, including intrinsic defects, are also paramagnetic and the combined analysis by EPR and optical spectroscopy is very effective for the unambiguous identification of the induced defects.

The environment of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Dy^{3+} ions in oxide glasses

A.C. Wright*, R.N. Sinclair, J.L. Shaw, R. Haworth, C.K. Howard

University of Reading, Department of Physics, J.J. Thomson Physical Laboratory,
Whiteknights, Reading, Berks RG6 6AF, U.K.,

The neutron diffraction isotopic substitution technique is employed to investigate the environment of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions in a soda-lime-silica glass and that of both $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Dy^{3+} ions in a sodium borosilicate glass. In the case of the Dy^{3+} ions, a special form of the isotopic substitution method, the null technique, is used, in which the neutron scattering length for Dy is set to zero by selecting the appropriate combination of isotopes. This enables the changes in the structure of the base glass, caused by adding Dy_2O_3 , to be studied in greater detail. The neutron diffraction data were obtained using the D4c diffractometer at the Institut Laue-Langevin (ILL; Grenoble, France) and, in each experiment, data were recorded for three samples; the base glass, the base glass incorporating natural Fe_2O_3 or Dy_2O_3 and a similar glass containing ^{57}Fe or ^0Dy , where ^0Dy denotes Dy with a zero scattering length. The data are Fourier transformed to yield the real-space total correlation function, $T(r)$, and the first co-ordination shells of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Dy^{3+} ions are investigated via a peak fit to the isotopic difference correlation function $DT(r)$. Conclusions are drawn with respect to both the structure of the base glass and the environment of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Dy^{3+} ions.

Photoluminescence of rare earth and transition metals in glasses and glass ceramics

Doris Ehrh

Otto-Schott-Institut, Friedrich-Schiller-Universität Jena, Fraunhoferstr.6, D-07743 Jena, Germany

In the last years many studies were carried out in the field of glasses and glass ceramics for special photonic devices and their potential applications. Photoluminescence of these materials is an important and sensitive optical property which is known since a long time. But its nature is very complicated and depends on different affects. The aim of this paper is to summarize a few of our systematic work which was carried out in our institute in Jena in collaboration with a lot of colleagues from different institutions over a long time.

In the last years systematic studies and developments were carried out in the fields of active Nd^{3+} (f^3), Er^{3+} (f^{11}), and Yb^{3+} (f^{13}) laser and amplifier glasses. Yb-FP glass samples are used in the high performance POLARIS laser system. Various fluoride and oxide glasses, which are also important for potential practical applications, with high intrinsic UV transmission were doped with luminescent species of various electronic configurations, s^2 : As^{3+} , Sb^{3+} , Sn^{2+} , Pb^{2+} ; d^0 : Ti^{4+} , Nb^{5+} , Mo^{6+} , Ta^{5+} , W^{6+} ; d^{10} : Zn^{2+} , Ag^+ , Cu^+ ; d^5 : Mn^{2+} ; f^n : Ce^{3+} (f^1), Pr^{3+} (f^2), Sm^{3+} (f^5), Eu^{3+} (f^6), Eu^{2+} (f^7), Tb^{3+} (f^8), Dy^{3+} (f^9), Ho^{3+} (f^{10}), Er^{3+} (f^{11}) and Tm^{3+} (f^{12}). Static and time resolved photoluminescence behaviour in the ultra-violet and visible range was investigated depending on glass matrices and concentration of luminescent species.

Some glasses were transformed in glass ceramics by thermal treatment. The change of photoluminescence was studied. In some cases a change of the coordination number was detected by the change of photoluminescence.

Our main goal is very old, like to the time of Lomonosov, to investigate the influence of glass composition on properties and to prepare glasses with specific properties.

Nd^{3+} environment and solubility in multicomponent silicate glasses

Odile Majerus^{1,*}, Daniel Caurant¹, Isabelle Giboire^{1,2}, Arnaud Quintas¹, Marion Lenoir¹, Pascal Loiseau¹, Jean-Luc Dussossoy², Thibault Charpentier³

¹Laboratoire de Chimie de la Matière Condensée de Paris – ENSCP site, CNRS UMR 7574, ENSCP (Chimie Paristech), 11 rue Pierre et Marie Curie, 75005 Paris, France.

²DEN/DTCD/SECM/LDMC, Laboratoire d'Etudes et Développement des Matrices de Conditionnement, CEA Marcoule BP 17171, 30207 Bagnols sur Cèze, France

³DSM/IRAMIS/SCM/LSDRM, Laboratoire de Structure et Dynamique par Résonance Magnétique, CEA Saclay, 91191, Gif-sur-Yvette, France

Understanding the structural role and solubility of neodymium oxide in multicomponent silicate glasses is of great interest for the formulation of nuclear waste containment glasses, because rare earths are abundant fission products and Nd^{3+} ions are considered as good simulants of highly radiotoxic Am^{3+} and Cm^{3+} actinides ions. Because of their size, ionic bonding character and intermediary field strength, big rare earths such as neodymium exist in highly coordinated and distorted polyhedra in oxide materials. In silicate glasses, Nd^{3+} ions are poorly soluble and their solubility increases with the addition of alkali and/or alkaline earth oxides, that bring the non-bridging oxygens necessary to form their coordination sphere. In multicomponent glasses such as aluminoborosilicate glasses of interest as glassy wasteforms, neodymium oxide competes with intermediary oxides such as Al_2O_3 , ZrO_2 , and to some extent B_2O_3 for the bonding to the oxygens provided by alkali/alkaline-earth oxides. Moreover, new structural roles may appear for neodymium depending on the composition in these complex systems. In this contribution, we will focus on the incorporation of Nd^{3+} ions at non-doping levels (about 4 mol% Nd_2O_3) in aluminoborosilicate glasses with different compositions in the SiO_2 - Al_2O_3 - B_2O_3 - Na_2O - CaO - ZrO_2 system. The environment of Nd^{3+} ions in these complex glasses has been examined by the mean of optical absorption spectroscopy and L_3 -edge EXAFS, and has been compared with the Nd^{3+} environment in simple alkali silicate, alkali borate, aluminosilicate and alkali borosilicate glass compositions. Furthermore, the competition between Nd_2O_3 and other oxides is assessed by studying the local structure in aluminoborosilicate glass series with increasing Nd_2O_3 or La_2O_3 content, using a multispectroscopic approach (notably with ^{11}B , ^{23}Na and ^{27}Al MAS NMR in La-bearing glasses). The Nd^{3+} distribution of sites is not significantly modified in this series, with only an increase of the local disorder as Nd_2O_3 content increases. The increase of the Nd_2O_3 content modifies the polymerization degree and the BO_4/BO_3 ratio of the aluminoborosilicate network but not the AlO_4 units. Interesting relationships will be drawn between the glass composition, the local structures and the crystallization tendency of a Nd-rich silicate apatite phase.

Ultraviolet, visible, ESR, and infrared spectroscopic studies of CeO₂ – doped lithium phosphate glasses and effect of gamma irradiation

M. A. Marzouk^{a*}, H. A. ElBatal^a, A. M. Abd Elghany^b, F. M. Ezz Eldin^c

^aGlass Research Department, National Research Center, Dokki, Cairo, Egypt

^bSpectroscopic Department, National Research Center, Dokki, Cairo, Egypt.

^cNational Institute for Radiation Research & Technology, Nasr City Cairo, Egypt.

UV-visible and FTIR spectroscopic properties of some prepared undoped lithium phosphate and CeO₂-doped glasses of the same composition were measured before and after successive gamma ray irradiation. The undoped lithium phosphate glass exhibits strong ultraviolet absorption which is correlated with the presence of trace iron impurities within the raw materials used for the preparation of such glasses. The undoped glass shows after gamma irradiation with 2 M rad, the broadness of the UV band with the resolution of two peaks at about 242 nm and 300 nm and the appearance of a small broad band centered at 514 nm. On further exposure to 5 M rad, the base glass exhibits a spectrum consisting of a broad UV absorption with two peaks at about 243 and 384 nm and three visible bands at about 404, 514 and 915 nm. CeO₂ – doped samples reveal the broadness of the UV absorption and the appearance of two bands at about 235 and 312 nm. Gamma irradiation on CeO₂ – doped glasses produces an extra induced visible band and show obvious shielding effect especially within the visible region but the UV absorption remains unaffected with two peaks at about 240 and 316 nm. Infrared absorption spectra of the prepared glasses reveal characteristic IR vibrations due to characteristic phosphate groups according to the glass composition and the effects of CeO₂ or gamma irradiation are observed to be limited. E.S.R spectra of the unirradiated CeO₂ – doped glass show no specific signals while gamma irradiation produces characteristic resonance indicating the appearance of Ce³⁺ ions.

Keywords: UV-visible – IR; spectra, Lithium phosphate glass; CeO₂; Gamma irradiation; E.S.R.

Structural investigation of rare earth doped borosilicate glass and gel

Estelle Molières^{*1}, Frédéric Angeli¹, Patrick Jollivet¹, Dominique de Ligny², Gérard Panczer², Anne Soleilhavoup³, Thibault Charpentier³, Odile Majérus⁴, Daniel Caurant⁴, Philippe Barboux⁴

¹CEA, DEN, LCLT, 30200 Bagnols-sur-Cèze, France

²LPCML, 10 rue Ada Byron, 69622 Villeurbanne, France

³CEA, DSM, LSDRM, 91191 Gif-sur-Yvette, France

⁴LCMCP-ENSCP, Chimie Paristech-CNRS, 11 rue Pierre et Marie Curie, 75231 Paris, France

Within the packaging of high-level nuclear waste in France, it is envisaged to increase the loading rate in actinides and fission products in borosilicate glass matrices. Rare earth are part of these fission products and simulate some minor actinides. Under these conditions, the glass chemical composition affects its chemical durability. In contact with water, a layer called 'gel' is formed at the glass surface. This gel is amorphous and presents a different structure compared with the pristine glass and it is depleted in soluble elements. Our aim is to get a better insight into structural changes coming from aqueous alteration. A glass serie was synthesized with different rare earth contents (lanthanum, europium, neodymium) and altered under static conditions at two pH (7 and 9,5). One glass was also enriched with oxygen-17 for Nuclear Magnetic Resonance (NMR) experiments. In addition, 0.15 mol% of europium III was added in glasses in order to use Eu as a structural probe for luminescence experiments. Glasses were characterized by complementary spectroscopies: ¹⁷O MQ MAS NMR, ²⁹Si and ¹¹B MAS NMR, Raman and Fluorescence. Leaching experiments under static conditions were carried out in basic and neutral medium. A glass was also altered in the same conditions but in ¹⁷O enriched water. The resulting gels were studied by NMR spectroscopy, Raman, SEM, SIMS, SAXS and Fluorescence and the leachates were analysed by ICP-AES to quantify the released elements into the solution. Rare earth addition resulted in structural changes in the glass network. We observed a clear boron coordination evolution as well as a polymerisation variation. Moreover, we highlighted a contribution due to lanthanum insertion from ¹⁷O MQ MAS NMR. In addition, substantial structural changes between gel and glass were observed. Differences appeared between glasses with and without rare earth. Moreover, the ion europium III environment modification was also determined.

Evolution of P environment in $^{45}\text{S}_5$ Bioglass during the first stage of HA formation

Athina Angelopoulou^{a,b*}, Valérie Montouillout^{c,d}, Dominique Massiot^{c,d}, and George Kordas^{a,b}

^a*Sol-Gel Laboratory, Institute of Materials Science, NCSR "DEMOKRITOS", 15 310 Aghia Paraskevi Attikis, Greece*

^b*Department of Materials Science, School of Natural Sciences, University of Patras, 26 500 Patras, Greece*

^c*CNRS, UPR3079 CEMHTI, 1D avenue de la Recherche Scientifique, 45071 Orléans cedex2, France*

^d*Université d'Orléans, Faculté des Sciences, Avenue du Parc Floral, BP 6749, 45067 Orléans cedex 2, France*

Advanced solid state NMR methods have been applied for the study of $^{45}\text{S}_5$ Bioglass of the composition $46\cdot1\text{SiO}_2\text{--}2\cdot9\text{P}_2\text{O}_5\text{--}26\cdot6\text{CaO--}24\cdot4\text{Na}_2\text{O}$ and one with partial substitution of Na_2O with K_2O . The glasses were immersed in Simulated Body Fluid (SBF) for 2, 24 and 43 h in order to investigate the ionic environment kinetics during the first stage of hydroxycarbonate apatite (HA) formation. In the presence of SBF ion, exchange occurs in the bioactive glass surface where the cations Na^+ and Ca^{2+} from the glass exchange with H^+ from the surrounding SBF solution. Therefore, the investigation of environment kinetics started with Na^+ ions. The ^{23}Na MAS NMR spectra of the bioglasses were quite enlightening. On $^{45}\text{S}_5\text{--Na}$ MAS spectrum, the apparition of a very narrow signal could be observed, probably due to a hydrated phase contribution. This signal was very clear after a treatment of 43h in SBF. Concerning, the $^{45}\text{S}_5\text{--Na/K}$ Bioglass the signal was not so obvious. Specifically, a narrow signal could be observed after a treatment of 24h in SBF. However, it was quite difficult to characterize it at 43h since it did not seem to rise. Additionally, ^{23}Na MQMAS NMR was employed to determine the Na ionic environment. Though, such information was not possible to extract from this study. HA formation requires the precipitation of calcium–phosphate-rich layer (CaP) which occurs on the surface though reactions of calcium and phosphate ions from the glass together with those from body fluids. Therefore, the investigation of phosphorus environment, through ^{31}P MAS and $^1\text{H}\text{--}^{31}\text{P}$ CP-MAS NMR methods, could probably provide more characteristic information in correlation with the Na^+ ionic phase contributions. On the CP-MAS spectrum, the signal due to phosphorus in close vicinity with proton is observed. In the ^{31}P MAS spectrum the hydrated phase has been correlated with the dried one, due to phosphorus far from proton. The proportion of hydrated to dried phase contribution has been calculated for the $^{45}\text{S}_5\text{--Na}$ and $^{45}\text{S}_5\text{--Na/K}$ glasses. The main difference between the bioglasses is a “stabilization” observed in the kinetic of hydrated phase in case of $^{45}\text{S}_5\text{--Na/K}$ after 24h in SBF. The explanation of the NMR spectra was accomplished by DFT calculations using the B_3LYP method under the 6-311G basis set. The exact evaluation resulted in structural models which will be presented in confirmation with the experimental results.

Crystallization of niobium containing bioactive phosphate glass

Agnese Stunda*, Liga Berzina-Cimdina

Riga Technical University, Riga Biomaterials Development and Innovation Centre, Building 3/3, Pulka iela, Riga, LV1039 Latvia

Calcium phosphate materials are widely studied as bone substitution materials. Bioactivity of material is highly dependent on phase composition. Amorphous phase (glass) is the most soluble comparing to the same composition crystalline state. Crystallization of glass allows obtaining a composite material of various phases with necessary chemical and physical properties. Controlled crystallization of glass also provides opportunity to obtain various microstructure of glass-ceramic. The aim of this study was to research crystallization processes of glass in system $\text{Na}_2\text{O--CaO--Nb}_2\text{O}_5\text{--P}_2\text{O}_5$. Analysis of bulk glasses showed that crystallization of glass in this system is heterogeneous – crystallization evidently starts from surface. To obtain homogenous glass-ceramic the glass before crystallization was ball-milled in fine powder and then compacted if a form of pellet. Characteristic temperatures were obtained from differential thermal analysis. Some crystallization rates were compared $1^\circ\text{C}\cdot\text{min}^{-1}$, $2^\circ\text{C}\cdot\text{min}^{-1}$ and $5^\circ\text{C}\cdot\text{min}^{-1}$. Glass transition temperature T_g was 630°C , 635°C and 644°C and nucleation was at approximately 690°C , 696°C and 713°C accordingly. The DTA maximums corresponding to nucleation were flat though given nucleation temperatures are $\pm 5^\circ\text{C}$. At $1^\circ\text{C}\cdot\text{min}^{-1}$ the crystallization maximums was at 751 and 788°C , at $2^\circ\text{C}\cdot\text{min}^{-1}$ - 763°C and 802°C and at $5^\circ\text{C}\cdot\text{min}^{-1}$ it was at 778 and 831°C . The temperature gap between nucleation and first crystallization peak was $\sim 65^\circ\text{C}$ and increased with heating rate only by few degrees, while temperature difference between first and second crystallization peak was growing more rapidly with increasing heating rate (37°C , 39°C and 52°C accordingly). The size and the shape of DTA peaks also varied – at $1^\circ\text{C}\cdot\text{min}^{-1}$ the intensity of nucleation maximum was almost the same as intensity of first crystallization peak, but second crystallization peak was almost two times more intensive. At $2^\circ\text{C}\cdot\text{min}^{-1}$ the intensity of first crystallization maximum was twice larger and second crystallization maximum was three times larger than nucleation maximum. At $5^\circ\text{C}\cdot\text{min}^{-1}$ the intensity of first crystallization maximum was similar to the intensity of second crystallization peak. However the phase analysis showed that crystalline phases are quantitatively and qualitatively similar in all heating rates. At the beginning tricalcium phosphate (whitlockite) and calcium diphosphate slowly appears, than rapidly crystallizes niobium phosphate bronze ($\text{Na}_4\text{Nb}_8\text{P}_4\text{O}_{32}$). The electron micrograph analysis showed that calcium phosphate crystals are needle shaped while phosphate bronze fill the rest of volume.

Dielectric properties of SiO₂-TiO₂-Al₂O₃ thin films prepared by sol-gel method for humidity sensors.

Alfonz Plško^{*a}, Katarina Faturikova^b, Marek Liška^c, Jana Pagačova^d,
Iveta Papučova^d, Jana Šulcova^d

^aAlexander Dubcek University of Trencin, Studentska 2, Trencin SK-911 50, Slovak Republic

^bInstitute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska cesta 9, Bratislava SK-845 36, Slovak Republic

^cVitrum Laugaricio – Joint Glass Center of IIC SAS, TnU AD, FChPT STU and Rona, Alexander Dubcek University of Trencin, Studentska 2, Trencin SK-911 50, Slovak Republic

^dFaculty of Industrial Technologies TnU AD, J. Krasku 492, Puchov SK-020 32, Slovak Republic

Abstract

Thin films prepared by sol-gel method have wide range of use in humidity sensors area. Mostly their dielectric properties, which vary according to the air humidity, are used. These variations are determined by absorption and desorption of water molecules from environment on the sensor surface. These sorption processes are limited by the state of surface layers, which is influenced by their composition, thermal treatment and chemisorption of water from air humidity during annealing of layers from thermal treatment temperature to room temperature. We were observing the influence of precursor sols composition and water chemisorption on dielectric properties of SiO₂-TiO₂-Al₂O₃ layers prepared by sol – gel method. The composition of prepared layers was in the range of SiO₂-TiO₂-Al₂O₃ 0:0,95:0,05; 0,32:0,63:0,05; 0,475:0,475:0,05; 0,63:0,32:0,05; 0,95:0:0,05 mol% ratios. Thin films were deposited onto Al₂O₃ substrates with comb-type Au electrodes by dip-coating method. Thin film samples were heated at 500°C for 50 min. The process of chemisorption was carried out by controlled annealing prepared sensors in relative humidity 0,13 % , 52,9 % and 97,6 % environments. The dielectric properties of the films were evaluated using impedance spectroscopy. Complex impedance spectra of thin films sensors at relative humidity 0,13 % in the frequency range 1 kHz to 1 MHz were measured and evaluated by using equivalent circuits. The best fitting for experimental set of data was achieved with one parallel RC circuit in series with one parallel circuit R with CPE (constant phase element). The observed influences of preparation conditions, such as layers composition and water chemisorption process during layers annealing are discussed from the –OH groups concentration changes on the surface of thin layers point of view, which has direct impact on dielectric properties and their water absorption and water desorption process.

On the binding of halogens in binary alkali-silicate melts

A.Kiprianov^{*(1)}, N.Karpukhina⁽²⁾, N.Pankratova⁽¹⁾, I.Ponomarev⁽¹⁾

⁽¹⁾St.Petersburg State University, Russia,

⁽²⁾Queen Mary University of London, UK

The first question one have to solve while planning new oxyhalide glass compositions – is about the quantity of halogen that can be bound with the alkali-silicate matrix: “how much of the fluoride or chloride is possible to add to the batch and how much of this would remain in the final material?” Considering the glass melting temperature and high halides volatility, the answer is not obvious.

The aim of the work was to determine the amount of halogens remaining in binary silicate glasses of different compositions after melting and to define the factors driving/controlling the halogen losses on melting. The report contains experimental results (as-batched and as-analysed compositions) of series of oxyhalide alkali silicate glasses $x \text{ Me}_2\text{O} - (100-x) \text{ SiO}_2 + z \text{ wt. \% Hal}$ (Me = Li, Na, K; Hal = F, Cl; $18 \leq x \leq 32 \text{ mol \%}$; $0 \leq z \leq 15 \text{ wt. \%}$) and the statistical model predicting in the first approximation quantity of the halogen remaining in the glass.

It is experimentally shown that the quantity of the fluorine remaining in binary glass after synthesis linearly follows its quantity added to the batch before melting. As for the chlorine, the trend is far from linear, the curves demonstrate pronounced maximum indicating the increase of the chlorine losses after some critical concentration. At the same time, comparison of the lost quantities of alkaline metal and chlorine results in conclusion that the primary losses occur in the form of the alkali chloride.

To assist the interpretation of the results modeling of the binary silicate network was attempted. Firstly, we assumed the variety of groupings of $[\text{SiO}_{4/2}]$ and $([\text{SiO}_{3/2}] \text{ ONa})_n$ $n \geq 1$ present in the melt as a result of even statistical distribution. Secondly, only those integrated associates containing three and more polar silicate groups can bind with one chlorine atom. The simple mathematical method was used to estimate the probability of formation of the integrated associates in three component systems $\text{M}_2\text{O}-\text{MHal}-\text{SiO}_2$. The calculated curves are in a good agreement with the experimental data.

The used formal statistical approach was also applied to binary lithium silicate glasses. Good correlation between well known Vogel's data demonstrating phase separation phenomena in $\text{Li}_2\text{O}-\text{SiO}_2$ system and the calculated probability of formation of $2 \cdot [\text{SiO}_{3/2}] \text{OLi} - 6 \cdot [\text{SiO}_{4/2}]$ associates is shown.

Vitrification and Durability: Strategies for Vitrifying Wastes Containing Challenging Anions

James M Schofield, Paul A Bingham and Russell J Hand*

Immobilisation Science Laboratory, Department of Engineering Materials, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, UK

Wastes containing anionic species such as halides and sulphates represent a major challenge for vitrification routes, because such species tend to have low solubilities in many silicate and borosilicate glasses and to result in salt layer formation during glass melting. We have undertaken work on a range of wastes containing chlorides and sulphates and have successfully developed calcium aluminosilicate glass compositions, based on a 51.4 mol % CaO, 7.17 mol % Al₂O₃ and 41.43 mol % SiO₂ base glass that can incorporate up to 17.5 mol% of a simulated actinide chloride waste stream. Additionally in our work on glasses with improved sulphate retention we have shown that cationic field strength can be correlated with sulphate solubility. This paper will review this work with the aim of drawing wider conclusions for suitable strategies for the vitrification of wastes containing challenging anionic species.

Surface structures of iron-phosphate glasses with high chemical durability

Tetsuji Yano^{1*}, Naoto Akagi¹, Shuichi Shibata¹, Takeshi Okita², Kanae Matsuyama², Shinya Miyamoto², Ippei Amamoto³, Hirohide, Kofuji³

¹*Dept. of Chemistry and Materials Science, Tokyo Institute of Technology, JAPAN*

²*Power Systems Company, Toshiba Corp., JAPAN*

³*Japan Atomic Energy Agency(JAEA), JAPAN*

Surface structures of iron phosphate glasses (IPG) are investigated in order to know the origin of their high chemical durability using X-ray photoelectron spectroscopy. Extremely high chemical durability of glass is one of the requirement conditions for the encapsulation of the high-level radio-active wastes (HLW) for the long-term. Taking into account of the volume reduction of the waste materials, high loading capacity of HLW is also required. IPG has been gathering attention as the candidate material to satisfy these conditions, and the relation between such properties and glass structure has been investigated.

In this study, several IPG samples in which a part of iron oxide are replaced by other transition metal oxides are prepared and subjected to the chemical durability test. Surface structures are investigated before and after the durability test and the information on the structural changes are obtained.

The iron-phosphate glass with the composition of 5M₂O_x-25Fe₂O₃-70P₂O₅ (mol%) and those containing 25mass% pseudo-nuclear wastes were melted using alumina crucibles in air, where M=3d transition metals. The prepared glasses were cut into disc, polished to have mirror planes and finally annealed before the chemical durability test. Chemical durability test is based on MCC-1 procedure; the tested samples are immersed into water in the sealed Teflon vessels and kept at 90 °C for 1 week, and then the solutions were analyzed using ICP spectrometer. The sample surfaces were also subjected to the analysis using X-ray photoelectron spectroscopy. Surface composition, chemical states of the constituent elements were derived from the samples before and after the chemical durability test.

The replacement using chromium oxide showed a large improvement of chemical durability, ~10⁻² g/m²/day, which is more than one magnitude smaller than those of other IPG samples. Fe/P atomic ratio of surface changed to ~0.4 irrespective of the glass composition. However, M/P ratio increased for M=Cr while decreased largely for M=other transition metal ions. Enrichment of chromium ions on surface is the key factor for the large improvement of chemical durability of Cr₂O₃-Fe₂O₃-P₂O₅ glass

system

This study was carried out under a contract with METI (Ministry of Economy, Trade and Industry) as part of its R&D supporting programme for developing geological disposal technology.

Investigation of the effect on long-term aqueous durability with variations in the composition of UK vitrified HLW product

Mike T Harrison^{*1}, Carl J Steel² and Andrew D Riley²

¹ NNL, Central Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG

² Sellafield Ltd, Sellafield, Seascale, Cumbria, CA20 1PG

The Waste Vitrification Plant (WVP), operated by Sellafield Ltd, converts Highly Active Liquor (HAL) from the reprocessing of spent nuclear fuel into vitrified High Level Waste (HLW) product for safe interim storage, and ultimate disposal in a deep geological repository. One of the important aspects to understand in relation to disposal of HLW glass is its behaviour over long timescales under aqueous conditions. To this end, a series of laboratory-based leach tests on the expected range of WVP glass compositions has been initiated, with some of the preliminary results described in this paper.

The aqueous dissolution behavior of a range of simulated UK vitrified HLW glasses has been investigated using static leach tests at different surface area to volume ratios for durations up to 16 weeks. Both Magnox and Blend glass compositions have been investigated at a range of waste oxide incorporations. The experiments demonstrated the complex dissolution behaviour of UK HLW glass with the results depending on the test conditions used. However, a number of general observations can be made, such as the improvement in dissolution behaviour with increased waste loading and as the proportion of Oxide waste in 'Blend' HLW glass is increased.

Mask-etching as a tool to determine chemical resistance of glass surfaces

Ksenia V. Shandarova*, Gundula Helsch and Joachim Deubener
*Clausthal University of Technology, Institute of Nonmetallic Materials, Building 2a,
 Zehntnerstr., Clausthal-Zellerfeld 38678, Germany*

Etching with different kinds of mask materials is well known from microfabrication, e.g. photolithography of integrated circuits. In this technique a resist mask is applied to a silicon wafer and microstructures are generated subsequently by etching the unmasked parts. We adopt this method to determine the chemical resistance of glass surfaces as well as of mask materials in alkaline solutions of various pH-levels. Therefore, a thin sol-gel layer (20-35 nm), that plays the role of a mask, is partially removed from the glass surface to generate unprotected surface in form of lines of width $\approx 250 \mu\text{m}$ before curing. After mask preparation coated glasses were immersed into alkaline solution at 75°C and the increase of the depth at the line bottom as a function of corrosion time was measured. Benefits of this approach are extreme small ratios of the glass surface to the volume of the alkaline solution ($<0.1 \text{ cm}^2 : 25 \text{ ml}$) and convection at the line bottom which keeps pH of the solution during the test almost constant: a prerequisite condition to determine steady state corrosion rates. As long as the coating remains resistant to the affecting solution, only the unprotected glass surface on the line bottom is dissolved. As a result a steady increase of the depth takes place which is measured frequently by a profilometer and defined as the corrosion speed in nm/h. It was found that this parameter varied according to pH-level of the solution, its temperature and the glass composition (e.g. using a oxide mask of 25 nm on float glass in 1 M NaOH solution at 75°C the speed of corrosion was $\approx 80 \text{ nm/h}$ at the tin bath surface and $\approx 95 \text{ nm/h}$ at the air surface). Besides determination of the corrosion rates of glass surfaces this approach can also be used to test the protective properties of the mask material itself. As the mask ceases to protect the glass surface, synchronous corrosion starts to occur not only on the unprotected line bottom, but also on the masked surface. Thus, total dissolution of the mask material in the solution ("life time") is indicated by the onset of zero corrosion speed, i.e. depth at the line bottom is constant with time, which defines the protective character (= mask thickness/life time) of the coating under such conditions. Using mask-etching the corrosion resistance of different flat glass surfaces such as soda-lime-float glass, boro-float glass and alumoborosilicate glasses as well as the protective character various mask materials against alkaline solutions of pH-levels in the range from 5 to 12 were determined.

Interfacial reactions and diffusion characteristics of binary alloys with silicate glass-ceramics

Lee A. Gerrard, Brian L. Metcalfe & Ian. W. Donald
Material Science Research Division, AWE, Aldermaston, Berkshire, UK

Seals between glass-ceramics and metals are formed by initially softening the glass, by heating, while in contact with the metal. This is followed by a controlled crystallisation of the glass, creating the glass-ceramic, and on cooling the two components are joined. However, sealing of glass-ceramics to metals can result in undesirable interfacial reactions between constituents of the glass-ceramic and diffusing metal species. These interactions can have serious consequences on the lifetime behaviour of seal systems. Thus, it is necessary to study both the interfacial reactions and the diffusion characteristics of such systems.

Joining studies of pure metals (Fe, Ni and Cr - the major constituents of stainless steels) have previously been undertaken using Lithium Zinc Silicate (LZS) glass-ceramics. The results showed no evidence for interfacial reactions with Fe and Ni with only minor for Cr. However, substantial ion diffusion for Fe was observed into the glass-ceramic, much less for Cr and a negligible amount for Ni.

It has now become necessary to increase the complexity of the system to study the behaviour of binary alloys. In the present study an LZS glass-ceramic has been utilised in addition to both Ta_2O_5 and Nb_2O_5 (1-6.5 mol%) loaded LZS glass-ceramics, which modifies the coefficient of thermal expansion (CTE). Selected binary alloys (Fe64/Ni36, Fe55/Ni45, Ni80/Fe20, Ni90/Cr10 and Fe87.5/Cr12.5) were chosen to complement the previous studies.

Extensive reactions were observed at the glass-ceramic to metal interface and also along grain boundaries within the Fe/Ni alloys; whereas superior seals were observed for the high Ni-content alloys. Extensive Fe diffusion, potentially Fe^{2+} , was observed in the glass-ceramic from the high Fe content binary alloys. In contrast, alloy surface layers of CrO_x were observed, using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX), for the alloys containing Cr.

Crizzling glasses: problems and solutions

Stephen Koob

Chief Conservator, The Corning Museum of Glass, One Museum Way, Corning, NY 14830,
USA

Numerous glasses in museum or private collections suffer from atmospheric deterioration or “crizzling”. The two primary factors are poor composition and storage in radically fluctuating humidity. Better storage conditions can slow down, but not stop the deterioration, and many glasses have been removed from exhibition or display because of their compromised and fragile conditions. A new safe and simple treatment using an acrylic polymer can restore some of these to a presentable condition, and with controlled temperature and humidity, this stability can be maintained.

Room temperature corrosion of museum glass: an investigation using high resolution SIMS

Sarah Fearn

Dept. of Materials, Imperial College, London, SW7 2AZ, UK

Glass is often regarded as a stable durable material and the wide range of contemporary applications of glass reinforce this belief. However, there is nothing inherent in the glassy state that confers stability and the problem of glass corrosion has been well documented by many workers.^(1,2) The glass corrosion still affects commercial float glass production and glasses used to contain high level nuclear waste, but one area in particular where glass corrosion is very common is in the museum. Display and the safe storage of many antique glasses is made very difficult as the composition of these glasses renders them very vulnerable to attack from atmospheric moisture^{3,4}. In order, therefore, to conserve these artefacts it is essential to fully understand the composition of the corroded glass and the corrosion mechanism.

In this work, compositional changes due to the ageing environment have been obtained using high resolution SIMS. By monitoring the compositional changes with time it is possible to identify ambient environments that cause the most and least alteration to the glass composition.

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Glass dissolution

Denis Strachan

Pacific Northwest National Laboratory

For most countries with nuclear power, disposal of nuclear waste from the reprocessing of used nuclear fuel represents a technological problem. The common solution to this problem is to immobilize the waste in glass, either borosilicate or phosphate, in large steel canisters and place these canisters in a geologic repository at depths of 1 km or more. Assuring the public and the regulator that this is a safe method for current and future generations is major part of the development of a repository. In the US, “future generations” means those people who might be living approximately 1 km from the repository horizon one million years from the time the repository is closed. Thus, mere extrapolations of laboratory data, irrespective of the time over which those data are collected become irrelevant.

Other than physical intrusion into the repository at some future date, e.g. drilling a well, water transport is the only way that stored hazardous elements can reach the accessible environment. Since extrapolations of data laboratory-based dissolution tests cannot be used, the effort has been to understand the chemical mechanism by which glass and water interact. In this talk, I will cover some of the background that took us from the relatively short-term needs, for example of soda and beer bottles, to the current understanding. This involved the development of a parameterized constitutive equation that allows us to calculate the release of the hazardous components over relevant times and conditions. These equations have resulted in our ability to follow a science-based approach to assuring the public and the regulator of safe disposal. Oddly enough, glass artifacts discarded by people who lived up to 4000 years ago can be used to validate this approach to the assessment of repository performance.

Durability of bioactive glasses

Leena Hupa

Process Chemistry Centre, Åbo Akademi University, Turku Finland

Bioactivity of certain glass compositions is based on selective leaching of their surface followed by formation of a layer structure of silica and hydroxyapatite crystals. In vivo the bioactive glasses bond chemically to bone via a hydroxyapatite layer. The layer formation is studied often in aqueous solutions buffered within the body fluid range. Today, bioactive glasses are used mainly as powdered fractions. However, novel clinical applications in which the glasses are used as sintered porous implants or fibres are being actively studied. In different applications, the desired reactivity of the glasses might range from very bioactive to almost inert compositions. Consequently, detailed understanding of the reactivity and durability of the glasses in different environments is highly essential. The solution composition, temperature, exposure time, surface area to volume ratio, flow of the solution, and conditions of the surface all affect the dissolution of the glass. In this presentation, the influence of the composition of bioactive glasses on their reactivity and durability in different in vitro conditions will be reviewed. Further, the feasibility and relevance of various laboratory methods – including standard methods such as ISO 719 is discussed. A newly developed method for in-situ time-dependent evaluation of the dissolution behaviour of glasses will be demonstrated

Glass of the alchemists. A retrospect on an exhibition at The Corning Museum of Glass 2008

Dedo von Kerssenbrock-Krosigk

Museum Kunstpalast, Glasmuseum Hentrich, Ehrenhof 4-5, Dusseldorf 40479, Germany

In 2008, an exhibition at The Corning Museum of Glass was dedicated to the “Glass of the Alchemists.” It focused on 17th and early 18th century glass production in Central Europe and on the British Isles, when new glass qualities—e.g. lead crystal in England, Kristallglas and gold ruby glass in Central Europe—emerged almost simultaneously. The principal argument of the exhibition and its accompanying catalogue was that alchemy provided much of the knowledge that glassmakers required to succeed in this technological revolution. Fairly recent studies by historians of science show that alchemy should not be merely considered as a vain and preposterous quest for making gold, but rather as a material science that preceded chemistry and that was at times highly successful in its endeavours. A short presentation and summary will be provided, as well as some information on further research in this field (as far as it has come to the contributor’s attention). Finally, the outline for a new exhibition will be presented. It is due to take place in Dusseldorf, Germany, probably in 2013, and it will explore the interdependencies of Art and Alchemy beyond the realm of glassmaking.

Mikhail Lomonosov and Erik Laxman and the Dawn of Glass Technology

Kaj H. Karlsson

Åbo Akademi University, Department of Inorganic Chemistry, Biskopsgatan 8, Turku 20500, Finland

Mikhail Lomonosov and Erik Laxman and the Dawn of Glass Technology On the 18th century two remarkable persons, Mikhail Lomonosov and Erik Laxman followed each other on the chair of chemistry at the Academy of Science in St. Petersburg, Russia. Both were children of the enlightenment, i.e. nothing reached outside their interest. They were, however, two completely different personalities. Lomonosov was a theoretician and always asking ‘why’, while Laxman was a practical engineer asking ‘how’. Lomonosov was mainly stationed in St. Petersburg, Laxman traveled around whole Siberia. But both were keenly interested in all aspects of the natural world. Pushkin said about Lomonosov “The thirst for science was the strongest passion of his being which was full of passions. An historian, rhetorician, mechanic, chemist, mineralogist, artist and poet, he tried everything and penetrating everything”. Laxman’s interest covered botany, cartography, chemistry, ecology, entomology, geography, geology, meteorology, mineralogy and zoology and P. S. Pallas called him “acutissimus observator”, the most acute observer. Lomonosov begun the study of silicates around 1749-50 when he got a laboratory with high temperature facilities. Preparation of coloured glasses “both for studying the theory of colour and for various uses of these in enameling” occupied him for the rest of his life. Best known are his huge glass mosaic pictures. However, his studies on refractivity resulted also in a different line, development of optical glasses based on lead oxide. As most glasses at that time also Lomonosov’s glasses were based on potassium as alkali. To the very tips of his fingers Lomonosov was a scientist. Laxman had learnt basics of theology in Finland and got in 1762 a job as priest in the Lutheran parish St. Petersburg. From there he was sent to Barnaul a town in SW Siberia close to the Minor Altai mountain ridge to minister the hard drinking miners in the Kolyvan area. His parish was large, some 400 km across and traveling between the places he reported his findings to Linné in Sweden as well as to the Academy in St. Petersburg. In Barnaul he got acquainted to the owner of a local glass works. He became concerned, however, about the vast amount timber needed to produce the potash needed for the process. Thus he began experiments to convert sodium sulphate from Siberian lakes to sodium carbonate. His method was quite ingenious, resembling the Leblanc process invented some 20 years later. He reduced the sulphate to sulphide, mixed it with sand and melted the batch. But the process was poisonous and offensive smelling and Laxman abandoned the process when he in Eastern Siberia found a salt lake that could supply sodium carbonate. In 1784 he started a glass works near Irkutsk that supplied house hold glass for whole the district between lake Baikal and Pacific ocean. Although his glasses were in the

soda-lime-alumina system, he was the first to use soda ash for large scale production of glass. The year 1784 could therefore be regarded as the year in which modern glass making began. Even though Laxman succeeded Lomonosov at the St. Petersburg char in chemistry, it is doubtful they knew about each other. But together they can be regarded as founders of modern glass science and technology.

The 18th century arcana of William Stephens

Carlos Queiroz, Filipa Lopes, António Pires de Matos
*VICARTE, Research Unit "Glass and Ceramics for the Arts", Universidade Nova de Lisboa,
2829-516 Caparica, Portugal*

The Coima Royal Glass Factory worked from 1719 to 1747 before being transferred to Marinha Grande on the initiative of John Beare. A detailed historical study on this glass factory was published by Jorge Custódio,⁽¹⁾ who was also responsible for the archaeological excavation on its grounds. In 1769 the Portuguese King D. José I and his prime-minister Marquis of Pombal greatly supported William Stephens, allowing him to re-establish a previous ruined glass production centre that bankrupted under John Beare administration in 1767. The production at the new Royal Glass Manufacture in Marinha Grande started ca. 1770 and was administrated by William Stephens. In this work, we report some highlights of the four arcana found in Marinha Grande which consist in truly experimental notebooks where different formulations are carefully essayed and discussed⁽²⁾ while providing a unique insight into the technology available at the early years of this manufacture. The study of this four arcana was completed and in this communication we will discuss the recipes used for coloured glass while interpreting the chemical nomenclature used.

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Experimental reproduction of Iron Age Scottish glass beads: linking analytical techniques to the production of replica artefacts

Martina Bertini

*University of Aberdeen, Department of Chemistry, Meston Building, Meston Walk,
Aberdeen, AB24 3UE, UK*

Class 13 spiral decorated Iron Age Scottish glass beads (Guido, 1978) have been the subject of a detailed study of their chemical characteristics in order to unravel part of the mystery that surrounds their origin and the provenance of the glasses used in their manufacture. The technology involved in their production, however, remains uncertain, and the complexity of the patterns in the glass beads have eluded the latest attempt of exact reproduction. The literature proposed two methods that could have been used in their manufacture: the production of a grooved body by lost-wax casting in which a decoration was then enamelled, as described by Henderson in a few of his publications (1981, 1987, 1989), and the simple winding method with manual inlay as proposed by Lierke (1995). In this work the production of replica artefacts was attempted with each method described in the literature and with the aid of various techniques used in modern lampworking. Prior to the experiments, the technological features that characterize the beads were studied. The morphological description of the artefacts was followed by the study of a few specimens via LA-ICP-MS (Laser Ablation Inductively-Coupled Plasma Mass Spectrometry) and 3D Computer Tomography via Synchrotron Light for the study of the internal structure. This information was used both in the technological study and as a comparison between the original specimens and the replicas. The characteristics observed on the available pool of about 50 class 13 beads show that these specimens were not produced according to a standardized process, but much difference is observable between specimens in terms of technique, skill of the bead maker and results obtained with different raw materials. The results of the experimental manufacture of the artefacts show that the beads were probably produced with both methods, depending on the workshop. This paper will present the results of the LA-ICP-MS and 3D tomography studies, and the features linking the replicas and the originals will be illustrated and discussed, in order to shed light on the technological ingenuity that gave birth to these complex artefacts. References: 1. Guido, M. (1978) The Glass Beads of the Prehistoric and Roman Periods in Britain and Ireland. Society of Antiquaries of London, Distributed by Thames and Hudson, London. 2. Henderson, J. (1981) A report on the glass excavated from Meare Village West 1979. Somerset Levels Papers VII, pp. 55-60. 3. Henderson, J. (1987) The Iron Age of 'Loughrey' and Meare: some inference from glass analysis. Antiquaries Journal, vol. 67, pp. 24-42. 4. Henderson, J. (1989) The evidence for regional production of Iron Age glass in Britain. In 'La verre préromain en Europe Occidentale'

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“They went to larn ‘em”: British Glassmakers Help to Establish Japan’s First Western-style Glassworks, 1873-1884

Sally Haden

In the later Victorian period four British glassmakers were invited to Japan to assist in the establishment of that country’s first Western-style glassworks. Constructed in 1873 using British designs and guided initially by Manchester flint glass manufacturer Thomas Walton, the glassworks at Shinagawa near Tokyo set the seed for Japan’s modern glass industry.

Glass in 1860s Japan was a tiny craft industry; windows and domestic glass were almost unknown. Japan had only just begun to open its doors to the rest of the world after centuries of feudal society. Rapid industrialization was underway with Western technological assistance. Shinagawa was conceived for sheet glass production but there were so many difficulties that in fact sheet glass failed. Indeed Japan had no success with sheet glass until early into the 20th century.

In 1879 attention at Shinagawa turned to introducing a wider variety of Western techniques and common domestic ware was made. Skilled flint glassmaker James Speed replaced Walton, and specialized materials and equipment, a pot-maker and an engraver came from Britain. But without enough sheet glass sales to balance the books, Shinagawa had to be sold off in 1884; the British glassmakers returned home. However, the many trainees took their skills out across Japan and gave birth to the country’s modern glass industry.

Discussion is invited on the possible reasons for Shinagawa’s sheet glass problems. Faulty furnace building, design or materials? The choice of Walton, a manufacturer of *flint* not *window* glass? Japan’s rush to success?

In Sally Haden’s family it was always said of her great grandfather James Speed that he went to Japan “to larn ‘em”. As it was unclear exactly what he had gone to “larn ‘em”, she set about some research in 2005. Roger Dodsworth of Broadfield House Glass Museum provided her with a most fortunate link, for in 2003 he had met Japanese glass historian Akiko Osumi at the London AIHV conference when she had been presenting a paper about the Shinagawa glassworks. She had been hoping to learn more about the four British glassmakers.

Ms Osumi is chairperson of the Association for Glass Art Studies, Japan and a lecturer in art history at three Tokyo universities.

Extensive collaboration has followed their introduction. Sally has now studied all four of the

British glassmakers together with their families, going back as far as possible in time so as to identify their exact background and experience in the industry. As she knew nothing about glass in 2005 it was a steep learning curve, not only in glass technology but also in genealogy and industrial history. She was delighted to find that of her four great grandfathers, three had worked in the British Victorian glass industry.

After some joint research done by Sally and Akiko in the Jardine Matheson archive at Cambridge University in 2008 looking at Shinagawa trading accounts, Akiko returned home to examine more Japanese archives. By 2009 she was able to publish a second paper including both of their findings, this time taking a close look at the initial phase of the glassworks, its ownership, construction and operation. It is yet to be translated into English. The research continues.

Developements of Siemens regenerative and tank furnaces in Saint-Gobain in the XIXth century

Marie-Hélène Chopinet

*Saint Gobain, UMR 125 CNRS / Saint-Gobain, Saint-Gobain Recherche, 39 quai Lucien
Lefranc, BP135, Aubervilliers 93303, France*

In 2001, in the ICG conference in Edinburgh, M. Cable⁽¹⁾ examined glass making progresses during the industrialization of the 19th century. He observed that engineering and transport rapidly growing had a major influence on the scale of glass manufacture, increasing the ability to obtain fuel and raw materials and distributing products to the customers. Those factors largely contributed to the expansion of the glass industry but could not take place without improvements in technology. Among those new technologies, the Siemens regenerative furnace was a crucial development in glass making because it raised maximum achievable temperatures and greatly improved thermal efficiency. In 1954, F.W. Hodkin made a controversial communication to the Yorkshire Section of the Society of Glass Technology about the Siemens-Tank Story⁽²⁾ which shows that there was some misinterpretation of information from W.E.S. Turner. Following this, the latter clarified his views to Hodkin who was stimulated to “enquire further into the points he has raised.” The Siemens “principle”, the use of gas producers coupled with a “regenerative furnace” dates back to the end of the 1850’s (British patent No.1320 in 1861). It was applied first to metallurgical and very soon to glass furnaces.⁽²⁾ The “tank furnace” was patented only in 1872 (British patent No.3478). In his letter reported by Hodkin, Turner said that “there is no doubt that the ideas of the Siemens brothers were worked out to a practical stage in England before being applied elsewhere [...] From about 1865 onwards Siemens’s gas furnaces, which until then had only acquired a solid footing in England, began to appear on the continent”. M. Cable⁽¹⁾ says that “in 1861 William having obtained a British patent was negotiating with Chance Brothers, who at first wanted an exclusive licence, which William would not grant, and dithered, even after accepting that decision.” Looking at a well documented internal report written by H. de Coqueréaumont around the end of the first World War about the development of the plate glass technology in the Compagnie de Saint Gobain, it appears that, while William Siemens was discussing with Chance Brothers, or very shortly afterwards, in 1862, he was also in contact with the Glacerie de Montluçon, not yet part of the Compagnie de Saint-Gobain, with the same aim, selling his invention, recently patented (May 1861 No 49068). During the same year in November 1862, contacts between W.Siemens and Saint-Gobain resulted in an agreement and in May 1863, the first Siemens regenerative furnace was alighted in the Saint Gobain glass factory. Besides dealing with the Siemens furnaces (regenerator and later, continuous tank furnace) developments in the Compagnie de Saint-Gobain, by analysis of the technical data contained in this unpublished report, the present paper relates a few aspects of the story of the relationship of Saint-Gobain

and W. Siemens extracted from the correspondence between the two parties during those critical years, which is kept in the Archives of Saint-Gobain.

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Glasses in the $\text{MoO}_3\text{-La}_2\text{O}_3\text{-MgO-B}_2\text{O}_3$ system

L. Aleksandrov^a, R. Iordanova^a, Y. Dimitriev^b

^a Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, blvd. Akad. G. Bonchev bl.11, Sofia 1756, Bulgaria

^b Department of Silicate Technology, University of Chemical Technology and Metallurgy, 8, Kl. Ohridski Blvd, Sofia 1756, Bulgaria

Fedorov *et al*⁽¹⁾ synthesized glasses with a high MoO_3 content (75-90 mol%) at low cooling rates ($10^2\text{-}10^3$ K/s) in the $\text{MoO}_3\text{-La}_2\text{O}_3\text{-MgO}$ systems. In our previous study we expanded the glass formation region to 50 mol. % MoO_3 applying high cooling rates ($10^4\text{-}10^5$ K/s).⁽²⁾ Participation of B_2O_3 in the $\text{MoO}_3\text{-La}_2\text{O}_3\text{-B}_2\text{O}_3$ system improves the glass formation tendency.^(3,4) These results provoke us to synthesize new generation of molybdate glasses with different B_2O_3 content. It was established by DTA analysis that thermal stability of the glasses increases with incorporation of B_2O_3 . By heat treatment of the glasses, glass ceramic and ceramic materials were obtained. For example after heat treatment of a glass with nominal composition $75\text{MoO}_3\text{-}12.5\text{La}_2\text{O}_3\text{-}12.5\text{MgO}$ (mol. %) at 500°C for 3 h $\text{La}_2\text{Mo}_4\text{O}_{15}$ crystal phase was obtained. 10 mol. % B_2O_3 added into the basic composition leads to formation of $\text{La}_2\text{Mo}_4\text{O}_{15}$ and LaMoBO_6 crystal phase. The main building units of the amorphous network are determined by IR spectroscopy. The glass formation tendency depends on the ratio between the different types of polyhedra ($\text{MoO}_6/\text{MoO}_4$). Molybdenum oxide does not stimulate the formation of BO_4 units, and there is no linkage between molybdate and borate units.

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Dissolution of sand particles and bubble removal in the model melting channel

Petra Cincibusová, Lubomír Němec

Laboratory of Inorganic Materials, Joint Workplace of the Institute of Inorganic Chemistry of the ASCR, v.v.i.

and The Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6

The new relative quantity u - utilisation of the glass-melting space for sand particle dissolution and bubble removal ($u \in [0;1]$) - was included to the formulation of the specific energy consumption and the performance of the melting space. This relative quantity was derived with the intention of evaluating the impact of glass-flow character on the processes of sand dissolution and bubble removal in a continual melting space. The simple horizontal channel was used for computation as a model space. The different glass-flow patterns in the model channel were implemented by linear temperature gradients applied on the glass level.

Some spaces with laminar melt-flow patterns without circulation were examined and the analytical solutions for melting performance in critical conditions were derived. The isothermal regime showed a relatively high space utilisation and melting performance for both examined processes owing to the absence of circulation dead spaces. In comparison with the isothermal regime, the application of a small longitudinal temperature gradient with a higher temperature on the channel output in the horizontal channel showed an increase of the space utilisation and dissolution performance by about 12%, whereas both quantities increased by more than 30% when a proper vertical temperature gradient with a higher temperature on the glass level was applied. The similar regimes did not in essence influence the utilisation of the space for bubble removal or the fining performance of the channel. The results form a knowledge base for comparison with melting spaces characterized by melt circulation.

The spaces with melt circulation were examined by mathematical modelling. The combination of a transversal and small longitudinal temperature gradients with a higher temperature on the end of the space (the transversal one should be significantly higher), which resulted in the spiral melt and bubble trajectories, showed the best value of the space utilisation for both processes. This value was in some cases even higher than in the case with laminar melt flow. The dependence of the utilization of the space on the ratio of the transversal and longitudinal temperature gradient showed maximum value. This maximum appeared in the interval of the temperature gradients ratio about 5 – 10 in the optimal cases. The utilization of the space showed increase by about 20% for sand particles dissolution process and 10% for bubble removal process.

Viscosity and viscous flow activation energy of PbO–WO₃–P₂O₅ glasses

Mária Chromčíková, Magdaléna Lissová, Petr Mošner, Kateřina Vosejpková, Marek Liška

Vitrum Laugaricio – Joint Glass Center of IIC SAS, TnU AD, FChPT STU, and RONA, j.s.c., Študentská, Trenčín, Slovakia,

Temperature dependence of viscosity of three compositional series of PbO–WO₃–P₂O₅ glasses with composition (0.5–x/2)PbO.xWO₃.(0.5–x/2)P₂O₅, x = 0, 0.1, 0.2, 0.3, 0.4, 0.5; 0.5PbO.xWO₃.(0.5–x)P₂O₅, x = 0, 0.1, 0.2, 0.3; and (0.5–x)PbO.xWO₃.0.5P₂O₅, x = 0, 0.1, 0.2, 0.3, 0.4, 0.5 measured by thermomechanical analysis is reported. The Andrade viscosity equation was successfully used for description of viscosity temperature dependence and for evaluation of temperature independent viscous flow activation energy. Obtained results are discussed in frame of the glass structure by considering the network-forming/modifying function of individual oxides. (Abstract for poster.)

Optical and structural characterization of Eu³⁺, Dy³⁺, Ho³⁺ and Tm³⁺ - doped phosphate glasses

M. Elisa^{*1}, B.A. Sava², I. C. Vasiliu¹, G. Pavelescu¹, I. Feraru¹

¹National Institute of R & D for Optoelectronics INOE 2000, Magurele, Bucharest, Romania

²National Institute for Laser, Plasma and Radiation Physics, Magurele, Bucharest, Romania

Aluminophosphate glasses belonging to the oxide system Li₂O–BaO–Al₂O₃–La₂O₃–P₂O₅, doped with rare-earth metal ions (Eu³⁺, Dy³⁺, Ho³⁺ and Tm³⁺) were obtained by a non-conventional wet route. The influence of the doping ions on the optical properties of the phosphate glasses has been investigated in relation with structural characteristics of the vitreous matrix. The optical behavior has been studied by ultra-violet–visible (UV–Vis) spectroscopy, revealing electronic transitions specific for rare-earth ions. Eu³⁺ and Dy³⁺ - doped glasses present optical absorption peaks in the UV domain whereas Ho³⁺ and Tm³⁺ - doped glasses revealed important absorption bands both in UV and Vis range. Structural information via optical phonons was provided by Fourier Transform Infrared (FTIR) absorption spectra in the 400–4000 cm^{–1} range. Optical phonons specific for the vitreous phosphate matrix were put in evidence as P–O–P symmetrical and asymmetrical stretching vibration modes, P–O–P bend, PO₂[–] symmetrical and asymmetrical stretching vibration modes, P=O stretching vibration mode as well as P–O–H water absorbance. Raman spectra acquired in the 100–4000 cm^{–1} range by 514.5 nm laser excitation source disclosed peaks also specific for the phosphate matrix, proving the role of phosphorous as a vitreous network former. Fluorescence spectroscopy measurements have been performed by excitation in the UV domain in the case of Eu³⁺ and Dy³⁺ - doped glasses, which resulted in significant fluorescence peaks in the Vis domain. The excitation of Ho³⁺ and Tm³⁺ - doped glasses in the UV–Vis range provided fluorescence bands in the Vis domain.

Raman spectra, structure and thermodynamic model of As_2S_3 - Sb_2S_3 glasses

Jana Holubová^{*A}, Marek Liška^B, Mária Chromčíková^B, Eva Černošková^C, Zuzana Jakubíková^B and Zdeněk Černošek^A

^A Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, Pardubice, CZ-532 10, Czech Republic,

^B Vitrum Laugaricio (VILA) – Joint Glass Center of Institute of Inorganic Chemistry SAS, A. Dubček University of Trenčín and RONA, Lednické Rovne, Študentská 2, Trenčín, SK-911 50, Slovak Republic,

^C Joint Laboratory of Solid State Chemistry of Institute of Macromolecular Chemistry of Czech Academy of Sciences and University of Pardubice, Studentská 84, Pardubice, CZ-532 10, Czech Republic

The structure of chalcogenide glasses of the pseudo-binary system As_2S_3 - Sb_2S_3 was investigated by comparison of the results of the thermodynamic model of Shakhmatkin and Vedishcheva with the results obtained by the analysis of Raman spectra of $x\text{As}_2\text{S}_3 \cdot (1-x)\text{Sb}_2\text{S}_3$ ($x = 1.00; 0.95; 0.90; 0.80; 0.70; 0.60; 0.50; 0.40$) glasses performed by the Principal Component Analysis (PCA) method and spectral decomposition by the method of Zakaznova-Herzog and Malfait. The PCA method identified three independent components in the studied spectral series. On the other hand, the thermodynamic modeling resulted in four components with significant abundance in the studied glasses, i.e. S, As_2S_2 , As_2S_3 and Sb_2S_3 . Finally, the correlation analysis proved the strong (correlation coefficient of 0.9999) linear dependence between the concentrations of S and As_2S_2 . Due to very low equilibrium concentrations of S and As_2S_2 only the partial Raman spectra As_2S_3 and Sb_2S_3 were calculated by the method of Malfait. The obtained results confirmed the structural information acquired from the thermodynamic model.

Bubble removal from glass melts with slow vertical circulations

M. Jebavá, P. Cincibusová & L. Němec

Laboratory of Inorganic Materials, Joint workplace of the Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6, and the Institute of Inorganic Chemistry AS CR, v.v.i., 250 68 Husinec-Rez, Czech Republic

Bubble removal from a small discontinuous melting space was investigated. A pot furnace for the hand-making of glass represents such a case. According to the way of heating of the space, two main cases of a glass flow arise. At heating from above, the molten glass circulates with the upward flow in the space centre; at heating through the wall, the upward flow occurs next to the pot wall.

The behavior of critical bubbles ($a_0=5 \times 10^{-5} \text{m}$) in the circulating field of the glass melt was studied using two approaches – a simple 2D model of the circulating space and the complete Glass Furnace Model (GFM). The simple 2D model describes the bubble behavior in the circulating field of the molten glass where temperature gradients are substituted for a corresponding angular velocity of the glass melt. In the case of heating through the wall the angular velocity is taken as constant with the radius of a rotation, and in the case of heating from above the angular velocity decreases parabolically with the radius (see Fig. 1). The latter case was then compared with the results calculated using by the complete mathematical model – GFM.

The bubble behavior was characterized by their bubble growth rate at constant temperature (or at mean temperature in the space).

The results of refining times of critical bubbles (starting from the least favorable position and thus having the longest fining times) calculated by the simple 2D model prove to be strongly dependent on the bubble growth rate. At very low values of the bubble growth rate and at sufficiently high angular velocity the critical bubble should be kept in the glass for a very long time. However, very good results were acquired in the real space using the GFM even in the case when the temperature gradient (and consequently the value of the angular velocity ω) was sufficiently high and the bubble growth rate was pretty low. The values of the fining times were even lower than the reference fining time in a quiescent liquid. A certain asymmetry of the rotating melt probably explains this result. This effect could be utilized when refining of special glasses without refining agents is required.

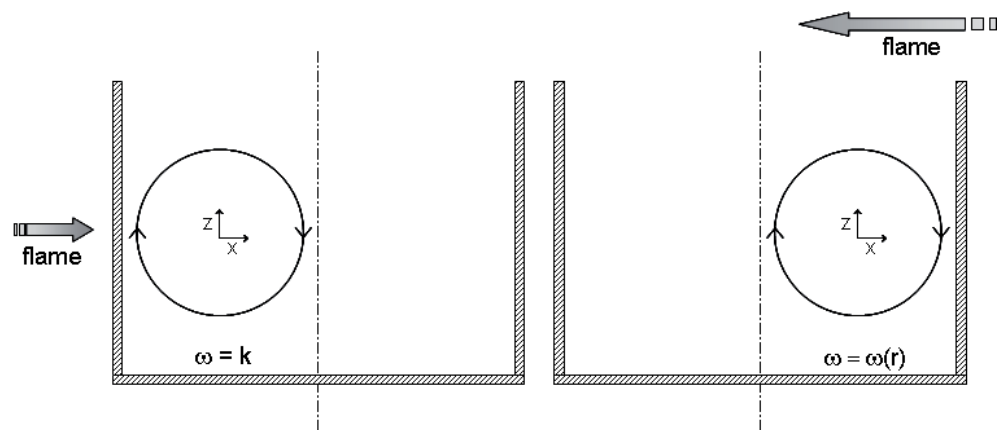


Figure 1. Two cases of the melt circulation in the pot furnace for the glass melting. The left part: the heating through the wall approximately characterized by the constant angular velocity of the melt. The right part: the heating from above approximately characterized by the angular velocity of the melt decreasing towards the pot wall. The downward part of melt circulation is important for bubble rise.

Structure and properties of TeO₂ containing lead phosphate glasses

P. Mošner^{a,*}, S. Köhler^b, K. Vosejpková^a, L. Koudelka^a and D. Stachel^b

^aFaculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

^bOtto-Schott-Institut, Friedrich-Schiller-Universität, Fraunhoferstr. 6, D-07743 Jena, Germany

Tellurium oxide containing glasses were extensively studied in recent years due to their interesting properties as low melting temperature, high dielectric constant, good infrared transmissions etc, resulting in a wide range of applications, such as acoustic materials, optical materials used in laser technology or as photochromic materials. TeO₂ is only a conditional glass former and melts containing only TeO₂ as a network-forming oxide require special fast-quenching methods to vitrify. Nevertheless, in combination with other network formers like P₂O₅, glasses with a high TeO₂ content can be prepared. This work deals with the study of the effect of TeO₂ on the structure and properties of lead phosphate glasses. Lead phospho-tellurite glasses were prepared in compositional series 50PbO-(50-x)P₂O₅-xTeO₂ (X-series) and (100-y)[0.5ZnO-0.5P₂O₅]-yTeO₂ (Y-series) with x = 0-30 mol% and y = 0-80 mol% TeO₂. Glasses were characterized by the measurements of density, molar volume and chemical durability. Thermal properties were investigated by DTA and TD methods. Their structure was studied by Raman spectroscopy. All glasses exhibit good chemical durability against water corrosion. With increasing TeO₂ content chemical durability remains nearly constant. The addition of TeO₂ to the starting 50PbO-50P₂O₅ glass composition leads only to a small changes of thermal expansion coefficient. Glass transition temperature and dilatometric softening temperature reveals a maximum in both compositional series of glasses. DTA measurements showed that all prepared glasses crystallize under heating. The lowest tendency towards crystallization was observed for the glasses with nominal TeO₂ contents between 20 and 70 mol% TeO₂ in compositional series Y. Raman spectra indicated that the replacement of PO₄ structural units by tellurate units is accompanied by the gradual depolymerization of phosphate chains and transformation of phosphate units Q²→Q¹→Q⁰. The evolution of tellurate structural units is different in both compositional series. In the structure of glass series X tellurium atoms form predominantly TeO₃ trigonal pyramids, whereas in the Y glass series TeO₄ trigonal bipyramids prevail in the glass structure.

Temperature and compositional dependence of Na₂O activity in Soda-Lime-Silicate melts

Masahiro Seto*, Toru Sugawara, Mitsuo Kato, Satoshi Yoshida, Jun Matsuoka and Yoshinari Miura.
The University of Shiga Prefecture, Hikone, Shiga, Japan

Various chemical properties of glass melts depend on Gibbs energy of mixing (G_{mix}). In spite of its considerable importance, experimental data of the G_{mix} is very limited because of difficulty in direct calorimetry at high temperature. We have measured Na₂O activity for $x\text{Na}_2\text{O}-y\text{CaO}-(100-x-y)\text{SiO}_2$ ($x=12, 16, 30$; $y=0, 5, 10, 16, 22$; mol %) melts by EMF measurements. Temperature and compositional dependence of the G_{mix} was investigated based on the analysis of measured activities.

Sample melt and alumina tamman tube with Na₂O–Al₂O₃–SiO₂ reference melt were placed in Pt crucible. Small slits were made in the tube in order to conduct an electric current by contact with both melts. The EMF between sample and reference melts are recorded by a potentiostat between 1273K - 1573K.

The Na₂O activity increases with increasing Na₂O and CaO content in the melts. CaO dependence of the Na₂O activity is more remarkable when the melt has higher Na₂O. These are caused by an increase of enthalpy of mixing by adding less basic CaO in basic Na₂O - SiO₂ melt. The partial molar Gibbs energy of mixing of Na₂O decreases with increasing temperature in almost melts, while it increases in 30Na₂O - 70SiO₂ and 30Na₂O - 5CaO - 65SiO₂ melts. This can be rationalized by a shift of the melt composition which has maximum entropy of mixing toward more depolymerised composition by adding CaO in the melts.

Corrosion of Bourre glass fibres in borate water solution

Vojtech Soltész^{1*}, Ivan Vicena¹, Marek Liška², Dagmar Galusková²,
Jean-Marie Mattei³

¹VUEZ, Hviezdoslavova 35, P.O. Box 153, 934 39 Levice, Slovakia

²Vitrum Laugaricio – Joint Glass Centre of the Institute of Inorganic Chemistry, Slovak Academy of Sciences, Alexander Dubček University of Trenčín and RONA, a.s., Študentská 2, Trenčín, SK- 911 50, Slovak Republic,

³IRSN, BO 17, 92262 Fontenay-Aux-Roses, France

BOURRE™ Glass fibers are commonly used as thermal insulation in nuclear power plant. In case of LOCA (Loss of Coolant Accident) these fibers can be strongly corroded by particular cooling solution. The pH value of coolant solution is stabilized by H₃BO₃/NaOH buffering systems. Therefore the chemical durability of BOURRE fiber and glass grains with the same chemical composition as BOURRE fibers was tested in present work. The flow-trough leaching tests were realized in isothermal conditions. The glass dissolution was followed by OES ICP and the corroded surface of glass fiber was studied by SEM/EDS.

The behaviour of the bubbles in the glass melts in the centrifugal field

Vladislava Tonarová, Lubomír Němec, Jaroslav Kloužek

Laboratory of Inorganic Materials,

Joint workplace of the Institute of Inorganic Chemistry AS CR, v.v.i

and the Institute of Chemical Technology in Prague,

Technická 5, 166 28 Prague

Fining of glass is energy-intensive process. It is necessary to search for new ways of glass fining employing new approach. The mathematical model describing the bubble behaviour under effect of the centrifugal force was derived and the parametrical study of bubble behaviour in the rotating cylinder was carried out.

Applying the centrifugal force, the bubble moves to the centre of rotation. The bubble history depends on the centrifugal force, on the pressure inside the bubble and on diffusion of gasses into/out of the bubble. All mentioned factors act simultaneously in the melt and cause a competition of the two possible mechanisms of the bubble-removal: the separation of the bubble on the curved glass level in the rotating cylinder and the complete dissolution of the bubble in the melt.

From the modelling arose the general dependence between the bubble-removal time and the cylinder angular velocity $\tau = f(\omega)$. The dependence defines the regions of both bubble removal mechanisms and provides the optimal angular velocity of the rotating cylinder, at which the bubble-removal time of the critical bubble shows the minimum. The impact of important process parameters was explained with respect to the minimum removal times of the critical bubbles at the appropriate optimal cylinder rotation velocity.

The laboratory equipment was designed and test experiments of the bubble removal in the rotating crucible were carried out.