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## Abstracts



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Ref: 1

## **Effect of substituting alkaline earth metals for SiO<sub>2</sub> on the mechanical properties and connectivity of soda-lime-silica glasses**

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Two different glass series have been produced by altering the CaO:SiO<sub>2</sub> or MgO:SiO<sub>2</sub> ratios in a base soda-lime-silica glass composition 72SiO<sub>2</sub>.13.5Na<sub>2</sub>O.10CaO.3MgO.1.5Al<sub>2</sub>O<sub>3</sub>. The mechanical properties of these series of glasses were measured and it is found that increasing CaO as SiO<sub>2</sub> is lowered reduces the indentation fracture toughness of the glasses. Meanwhile increasing MgO up to 4 mol% increases indentation fracture toughness but further MgO additions lower fracture toughness. Additions of either MgO or CaO increase Vickers hardness and density of the glasses. The connectivity of these series of glasses has been investigated using Raman and Fourier transform infra-red (FTIR) spectroscopy. In Raman studies, degree of connectivity was measured in terms of the polymerization index given by the ratio of the areas of the peaks at 500 cm<sup>-1</sup> and 1000 cm<sup>-1</sup>. Substitution of SiO<sub>2</sub> by CaO or MgO reduced polymerization index indicating that both MgO and CaO were acting as network modifiers. This was also shown by the broadening of the band at ~1050 cm<sup>-1</sup> band. Overall Vickers hardness and density tend to decrease as connectivity of the glasses increases, however the link between indentation fracture toughness and connectivity is less clear cut.

Ref: 2

## **Li<sub>2</sub>O-TeO<sub>2</sub> glasses and tellurite glass story**

Faizami Mohd Noor

Ref: 3

### **Production of luminescent glass enamels for artistic applications**

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Artists have been exploring, for a long time, light effects and using materials with particular optical properties in their artistic conceptions.

The main objective of our research was the development of low melting temperature luminescent enamels, for glass paint. The base enamel composition was doped with different rare earth oxides which glow with different colours under UV-light. It is very important to prepare enamels that fire at a low temperature (below 565°C) to avoid deformation of the original glass shape and to be possible to apply them as a painting on the glass surface. The application can be done with a brush, screen painting and spraying and it can be used in art pieces with float glass and also blow glass and sculptural pieces.

The introduction of 3d metallic oxides was also explored together with the rare earths to obtain coloured enamels under daylight light, instead of colourless ones, in order to attain new colours for the artist palette.

Spectroscopy measurements were performed in order to characterize the enamels luminescence. The T<sub>g</sub> of the synthesized enamels were also determined, showing that it was obtained low melting temperature luminescent enamels.

## **Fluorescing defect centres induced by indentation in sodium- borosilicate glasses probed by micro-Raman and EPR spectroscopy**

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Glasses from the ternary Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> borosilicate system were characterized for indentation-induced structural changes by micro-Raman spectroscopy. The selected series vary in network former ratio (B<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>) and modifier mole fraction, resulting in different structural units of trigonal and tetrahedral borate entities, and in differing numbers of bridging and non-bridging oxygen atoms. Besides structural changes and crystallization phenomena at the indentation area, fluorescing defects were also observed, due to excitation by the laser line employed for Raman scattering. Depending on the glass matrix, different rates of defect recovery were observed during successive laser irradiation of the same spot. The spatial distribution of the defects was studied by micro-Raman spectroscopy. An attempt was made to characterize the indentation-induced defects by the position and form of the emission bands as well as by their EPR signal. It is expected that indentation results in similar paramagnetic defects as those found after irradiation or thermal poling of borosilicate glasses.

## Fingerprinting first millennium B.C. glass artefacts by Sr and Nd isotopic analysis

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Since the late Bronze Age glass has seen a considerable evolution in technology, composition, physico-chemical properties and potential use in different societies. The early first millennium B.C. was probably one of the key periods in the development of early glassmaking. This project examines this important point in history by performing geochemical and isotopic research on glass artefacts from the eastern Mediterranean and the Black Sea. In particular, we examine the nature of the raw materials used and the geographical location of the glass manufacture. The use of geochemical and isotopic analysis allows us to differentiate and characterize different raw materials and attempt to provenance glass to primary production sites. The applicability of Sr and Nd isotopes on the provenancing of late Bronze Age samples has already been demonstrated by Degryse et al. (2010) and Henderson et al. (2010), who have shown a distinction in Sr and Nd isotopic ratios between Egyptian and Mesopotamian glasses. The key question of this project is to define whether similar evidence can be supplied for the provenance of first millennium B.C. glass artefacts. The Sr and Nd isotopic composition for glass artefacts from Pichvnari (Georgia) and Shechem (Israel) suggests an eastern Mediterranean origin but the precise location of the primary production centres for these glasses is still unknown. It is possible that the core-formed vessels from Pichvnari were made in a workshop on the island Rhodes, as suggested previously (Shortland & Schroeder, 2009), but more isotopic research is needed. The Sr and Nd isotopic data may also point to local glass production in Carthage. Degryse, P., Boyce, A., Erb-Satullo, N., Eremin, K., Kirk, S., Scott, R., Shortland, A.J., Schneider, J. & Walton, M. 2010. *Archaeometry* **52**, 380-388. / Henderson, J., Evans, J. & Nikita, K.. 2010. *Mediterranean archaeology and archaeometry* **10**, 1-24. / Shortland, A.J. & Schroeder, H. 2009. *Archaeometry* **51**, 947-965.

## Contrasted iron-speciation in natural glasses: a spectroscopic study

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Glasses can be formed through geological phenomena such as natural, obsidians and tektites. Obsidians are iron bearing aluminosilicate glasses formed during volcanic events, mainly in the American Cordilleras ranges and in the Mediterranean basin. Tektites differ by the absence of OH/H<sub>2</sub>O and contain different alkaline and alkaline earth contents. Their formation is associated with giant extraterrestrial impacts on Earth followed by fast cooling during ejection of melts in strewn fields over thousands of kilometres (e.g., Central Europe, North America, South-East Asia and West Africa). Many fields of science are concerned by natural glasses. Earth scientists have long been fascinated by these materials. Obsidians are unique evidence of eruption processes because they represent a frozen picture of magmatic melts. Therefore, obsidian oxidation state and thermal history have been widely studied, e.g. [1], [2]. Tektites are the memory of catastrophic asteroid impacts and the Fe environment has been studied in these glasses to better understand their formation process [3]. In material science, the longevity of natural glasses such as obsidians and tektites, which can be million years old, demonstrates that glasses can survive geologic environments and can be considered as good nuclear waste glasses analogous [4]. Because iron plays an important role in determining the physical properties of glasses, Fe speciation in obsidians and tektites compared to synthetic glasses, using optical absorption spectroscopy (OAS) and electron paramagnetic resonance (EPR) is discussed. In obsidians, OAS reveals a major contribution of Fe<sub>2+</sub> in a regular octahedral site, an unusual environment in synthetic glasses where this cation is mostly 4- and 5-coordinated [5], [6]. The presence of Fe-oxide nano-clusters, suspected since a long time from previous EPR studies [7], is confirmed by variable-temperature OAS in all the obsidians that were analysed. By contrast, tektites do not show such contribution. Specific absorption bands, assigned to Fe-Fe and Fe-Ti intervalence charge transfers (IVCT), are characterized by a spectacular intensity dependence as a function of temperature over 1000K (1000K-10K). This thermally-activated behaviour shows an activation energy similar to that observed for IVCT in various minerals. The evidence of specific Fe<sub>2+</sub> sites and of IVCT processes show the presence of Fe-oxide clusters. These clusters, showing a local re-arrangement around Fe, are related to the cooling history of the glass, as they are not found in the medium range structure of synthetic glasses [8]. The existence of these clusters and their nature seem to be related to the conditions of formation of the obsidians that were studied.

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## Local ordering around divalent cobalt in silicate glasses

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Glass composition influences the speciation of the transition metal (TM) ions and thus the glass properties as a result of the structural evolution of silicate glasses upon addition of alkali or alkaline earth. Among the best known properties of glasses, glass coloration, originates from crystal field transitions of minor TM. It provides a direct illustration of the chemical dependence of the TM ion surrounding and may help in determining TM speciation. Blue silicate glasses colored by  $\text{Co}^{2+}$  are famously used since Antiquity. However the structure-property relationship is still not fully understood. We present a XANES and EXAFS study compared with optical absorption spectroscopy of alkali lime silicate glasses containing 5mol% of  $\text{CoO}$ . Our results reveal the presence of tetrahedral  $\text{Co}^{2+}$  and its connection with the glass network. Changing from  $\text{K}^+$  to  $\text{Na}^+$  induces an increase of the local disorder around  $\text{Co}^{2+}$  in correlation with the presence of optically less absorbing species. The decrease of the contribution from the second shell atoms in the EXAFS signal agrees with the presence of higher coordinated optically silent species. Our results provide a structural basis for rationalizing the optical properties of  $\text{Co}^{2+}$  species in glasses.

## Effect of Boron addition on the thermal properties, processing window and durability of phosphate-based glasses

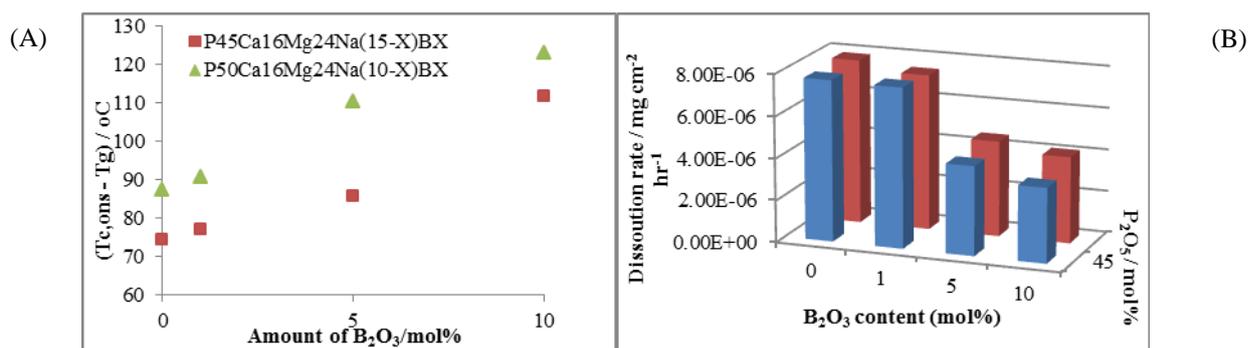
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**Introduction:** There is a growing interest in the use of phosphate based glasses (PBGs) for varying biomedical applications, since these glasses resorb completely in aqueous media and their resorption rates can be altered easily via the addition of different modifier oxides [1,2]. The aim of this study was to investigate the effect of B<sub>2</sub>O<sub>3</sub> addition on the thermal properties, processing window and durability of glasses in the system P<sub>2</sub>O<sub>5</sub>-CaO-MgO-Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> with phosphate contents fixed at 45 and 50 mol%. The effect of boron incorporation on continuous fibre drawing via the melt drawn process was also investigated.

**Experimental Methods:** In this study, PBGs in the systems (P<sub>2</sub>O<sub>5</sub>)<sub>45</sub>-(CaO)<sub>16</sub>-(Na<sub>2</sub>O)<sub>15-x</sub>-(MgO)<sub>24</sub>-(B<sub>2</sub>O<sub>3</sub>)<sub>x</sub> and (P<sub>2</sub>O<sub>5</sub>)<sub>50</sub>-(CaO)<sub>16</sub>-(Na<sub>2</sub>O)<sub>10-x</sub>-(MgO)<sub>24</sub>-(B<sub>2</sub>O<sub>3</sub>)<sub>x</sub> (where x = 0, 1, 5 and 10) were characterised for their thermal properties using differential scanning calorimetry. An assessment of the thermal stability of the glasses was made in terms of their extrusion processing window (i.e. onset of crystallisation temperature T<sub>c,ons</sub> minus glass transition temperature T<sub>g</sub>). Durability of the glasses was investigated in phosphate buffer solution (PBS) at 37°C for 60 days. Fibres were produced via melt-spinning using a dedicated in-house fibre manufacturing facility.

**Results and Discussion:** For glasses containing 45 mol% P<sub>2</sub>O<sub>5</sub> (P45) the T<sub>g</sub> values increased from 440 to 500 °C as Na<sub>2</sub>O was replaced by B<sub>2</sub>O<sub>3</sub>. Whereas, an increase from 452 to 552 °C was observed for glasses with fixed 50 mol% P<sub>2</sub>O<sub>5</sub> (P50). The processing window improved by 112 °C and 123 °C with 10 mol% B<sub>2</sub>O<sub>3</sub> addition (Figure 1A) for P45 and P50 glasses respectively, as compared to the glass with 0 mol% B<sub>2</sub>O<sub>3</sub>. This was suggested to be due to an increase in the cross-linking density and the chain length, which in turn improve the thermal properties and processing window of the glass system.



**Figure:** Processing window (A) and dissolution rate (B) values for the glasses.

After 60 days immersion in PBS, the dissolution rate for P45 and P50 glasses without B<sub>2</sub>O<sub>3</sub> was 7.7 × 10<sup>-6</sup> and 7.8 × 10<sup>-6</sup> g cm<sup>-1</sup> hr<sup>-1</sup> respectively, whilst the dissolution rate decreased to 3.5 × 10<sup>-6</sup> and 4.1 × 10<sup>-6</sup> g cm<sup>-1</sup> hr<sup>-1</sup> for the 10 mol% B<sub>2</sub>O<sub>3</sub> containing glasses, respectively (Figure 1B). Continuous fibres of between 18-20 microns were successfully drawn from glasses containing 5 and 10 mol% B<sub>2</sub>O<sub>3</sub>, whilst a non-continuous fibre drawing process occurred for the glass composition without B<sub>2</sub>O<sub>3</sub>. **Conclusion:** An increase in T<sub>g</sub>, T<sub>c,ons</sub>, processing window and durability of the glasses was observed with increasing B<sub>2</sub>O<sub>3</sub> content. The enhanced processing windows obtained were suggested to be due to B<sub>2</sub>O<sub>3</sub> incorporation within the glass backbone which facilitated the ease of fibre fabrication from these formulations as compared to the non-boron containing glasses.

**References** 1. Knowles J.C., J. Mater. Chem. (2003).13:2395-2401 2. Ahmed I. *et al.*, Biomaterials (2004),25:491-499

## Structure investigation of metaphosphate glasses using $^{67}\text{Zn}$ and $^{43}\text{Ca}$ NMR and neutron diffraction.

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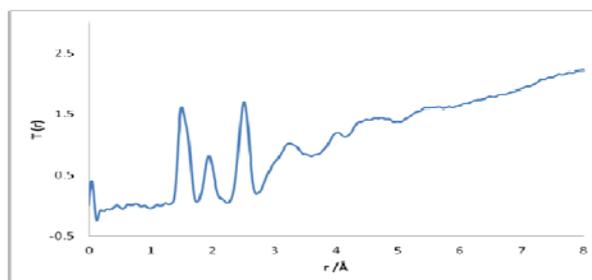
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Phosphate glasses are considered to be potential resorbable biomaterials due to their solubility and bioactive behaviour. In addition their close resemblance to natural bone makes them particularly attractive. One of the advantages of using glass based biomaterials is that the composition can be tailored to suit specific requirements, such as tailoring of solubility or incorporation of beneficial ions. Divalent zinc aids osteoblast differentiation and therefore its incorporation into a phosphate based biomaterial is desirable. In phosphate based glasses ZnO is considered to be a network intermediate, i.e. acting as both a network former and/or a network modifier. Zinc phosphate cements have long been used for dental applications, with zinc responsible for the initial setting of these cements by working as a chelating agent. In this work, the structure of a series of glasses of general formula  $\text{NaZn}_{1-x}\text{M}_x(\text{PO}_3)_3$  ( $\text{M} = \text{Ca}, \text{Sr}; x = 0 \text{ and } 0.5$ ), has been investigated using a combination of solid state NMR and neutron diffraction.

Fig. 1 shows the Fourier transformed neutron diffraction data presented as  $T(r)$ . Analysis of the data reveal two Zn-O contact distances characteristic of tetrahedral and octahedrally coordinated zinc. These compare favourably with the corresponding distances in  $\alpha\text{-Zn}(\text{PO}_3)_2$  and  $\beta\text{-Zn}(\text{PO}_3)_2$  which exhibit octahedral and tetrahedral Zn coordinations, respectively. Reverse Monte Carlo techniques have been used to analyse the neutron diffraction data to reveal detail of the structure of these glasses.  $^{67}\text{Zn}$  and  $^{43}\text{Ca}$  NMR results will also be discussed.

Fig. 1. Correlation function for glass composition  $\text{NaZn}(\text{PO}_3)_3$



Ref: 10

## **A study of the dissolution behavior of nuclear waste glasses in highly-alkaline conditions**

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High-Level Waste (HLW) and some Intermediate-Level Waste (ILW) are to be immobilised within alkali borosilicate and potentially other (boro) silicate matrices. In the long-term, these wastefoms will be emplaced within a Geological Disposal Facility (GDF). Currently, co-location of HLW and ILW in the repository is being considered. As most ILW is immobilised in cement, the plan is for the ILW section of the GDF to be back-filled with high-pH cement, in order to prevent leaching of soluble radionuclides to the environment. In general, glass dissolution occurs at an increased rate in high-pH, although some work suggests that the presence of calcium can moderate the rate of attack. The dissolution behaviour of four model nuclear waste glass compositions in high-pH conditions is being investigated, using both static (PCT and MCC-1) and dynamic (SPFT) dissolution tests with a saturated calcium hydroxide solution as the leachant. Particular attention is being paid to the roles of Ca, Mg and B, on the dissolution behaviour.

Ref: 11

## **Synthesis of Silicon Oxycarbide Glasses for Vitrification of Graphitic Nuclear Waste**

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This presentation reports early stage research into the synthesis of silicon oxycarbide glasses for the vitrification of irradiated graphite. Taking a sol-gel approach, methyltrimethoxysilane (MTMOS) and triethoxysilane (TEOS) were hydrolysed in acidic and neutral environments, then condensed in either a basic or neutral environment to form gel precursors. These were characterised by FT-IR spectroscopy. The gels were then pyrolysed at 900 °C in an argon atmosphere to yield silicon oxycarbide glasses. Changes in chemical structure were monitored by FT-IR spectroscopy and the glasses characterised by XRD and DTA. The reagents were chosen in order to minimise the formation of a free carbon phase with the aim of maximising possible graphite incorporation. A range of precursor gels were synthesised, pyrolysed and analysed in order to find the most efficient route to produce a low-free-carbon silicon oxycarbide glass as a base glass for irradiated graphite immobilisation.

Ref: 12

## **Corrosion study of a simulated Magnox glass using MCC-1 type test**

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A simulated Magnox glass which is Mg- and Al- rich was subjected to static aqueous corrosion in deionised water at 90 °C for 7 to 28 days and assessed using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy X-Ray Dispersive Spectroscopy (EDS) and Inductively Coupled Plasma - Optical Electron Spectroscopy (ICP-OES). XRD revealed both amorphous phase and crystals in the glass structure. The crystals were spinels whose compositions were shown to be Ni and Cr rich by EDS in the SEM and ruthenium oxides inside the glass. After two weeks in deionised water, glass surfaces were covered by a ~11 µm thick high Si layer from which mobile elements and transition metals like Na, B, and Fe were strongly depleted consistent with OES-derived traces of leached ions. The likely corrosion mechanism and, in particular, the role of Mg and Al in the glass structure are discussed. Keywords: high level waste glass, durability, corrosion mechanism

Ref: 13

## **Preparation and structure of alkali-alkaline earth borosilicate glasses**

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A series of  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-R}_2\text{O-R}'\text{O}$  glasses (R=Li, Na and R' = Mg, Ca, Sr, Ba) was successfully prepared using conventional heating and microwave heating. Selected structural and physical properties have been analysed using XRD, XRF, Mössbauer and FT-IR/Raman spectroscopies as functions of base glass composition and heating technology. In this paper we will present the results of our investigations and demonstrate the feasibility of unassisted microwave heating from room temperature for the preparation of silicate glasses using batch materials.

## Molecular dynamics study of K and Ba iron phosphate glasses in relation to chemical durability

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Iron phosphate glass has very high chemical durability around the composition  $40\text{Fe}_2\text{O}_3\text{-}60\text{P}_2\text{O}_5$  and hence related glasses are being studied for application in nuclear waste vitrification. A key study by Bingham et al [1] demonstrated the different effects of adding glass modifier cations. Chemical durability was reduced as expected with addition of alkali modifiers such as K, but was increased surprisingly with addition of alkaline earth modifiers such as Ba. Following this, a detailed diffraction study of K and Ba iron phosphate glasses was carried out by Bingham and Barney [2] to probe the details of local environment of modifier cations. A previous molecular dynamics (MD) study of iron phosphate glasses [3] provided insights into the key role of Fe-O-P bonds for chemical durability. Recently we have carried out new classical MD modelling of K and Ba iron phosphate glasses, with comparison to the diffraction data. This has provided a further source of information about structural details of K and Ba as modifiers in iron phosphate glasses. The results will be discussed in relation to the effects of K and Ba on chemical durability.

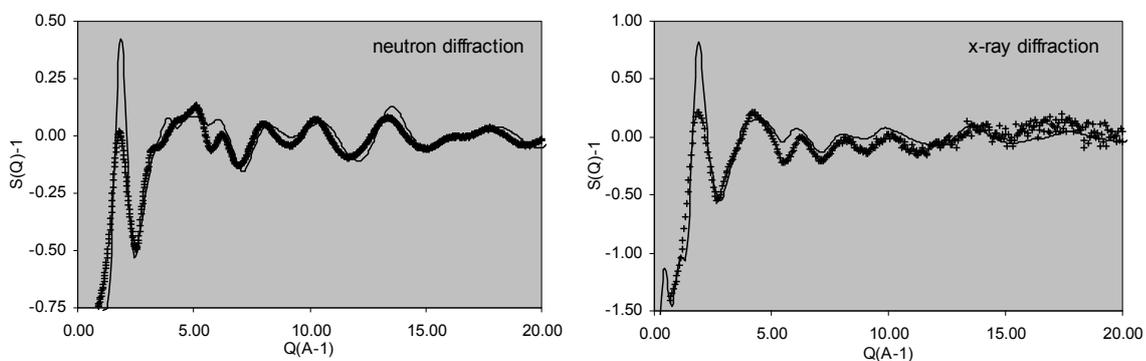


Figure 1: diffraction structure factors from MD modelling (and experiment [2]) for iron phosphate glass with addition of 20mol% BaO.

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## **Bioactive glass scaffolds and their ability to stimulate bone regeneration**

Julian R Jones

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Bioglass® has now been used in more than 1 million patients as a synthetic bone graft (NovaBone®, NovaBone Products LLC, FL) and is the active ingredient in Sensodyne Repair and Protect® Toothpaste. However its potential for bone regeneration is limited because it is only available as a particulate. One reason for this is that the original Bioglass composition crystallises during sintering. We have developed new compositions that can be sintered without crystallising and a new gel-cast foaming process that can produce porous scaffolds with interconnected pores. In vivo studies in an ovine model show 99% of the glass covered in new bone, including the internal pore structure. Using the sol-gel foaming process also avoids the crystallisation issue and allows the use of more simple compositions, e.g. 70S30C; 70% SiO<sub>2</sub> and 30% CaO. In vitro data showed bone matrix production and active remodelling in osteoblast/ osteoclast co-culture. They stimulate bone regeneration in a rat tibial defect model, but only when preconditioned. Bone ingrowth was quantified through histology and novel micro-CT image analysis. The percentage bone ingrowth preconditioned 70S30C scaffolds was similar to commercial Bioglass® (NovaBone®) and Si-HA (Actifuse®). Unlike the commercial products, pre-conditioned 70S30C scaffolds degraded and were replaced with new bone. However when the scaffolds were implanted without preconditioning, bone did not grow into the pore structure. This was attributed to a high pH inside the pore network due to burst release of calcium ions. The results suggest bioactive glass compositions and/ or pore network structures should be redesigned if sol-gel scaffolds are to be used without preconditioning to avoid excess calcium release. New compositions and pore morphologies will be proposed for improved bone ingrowth without preconditioning.

Ref: 16

## **Role of cations in binding of fluoride in alkaline silicate glasses**

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Structural role of fluoride in alkaline silicate glasses with various components have been investigated using solid state NMR spectroscopy. It is known that adding fluoride in concentrations above the solubility limit causes rigorous crystallisation of silicate glasses. However, solubility limit is dependent upon nature and quantity of other components present in silicate glasses as well as nature of the alkaline cation. Multinuclear <sup>27</sup>Al, <sup>19</sup>F, <sup>29</sup>Si, and <sup>23</sup>Na MAS-NMR spectroscopy was used to understand the structural changes introduced by the addition of alkali fluorides in the alkaline glasses containing aluminium, calcium or lanthanum. Double resonance <sup>19</sup>F-<sup>29</sup>Si and <sup>19</sup>F-<sup>27</sup>Al NMR experiments were performed to provide a further insight into binding of fluoride to components of the alkaline silicate glasses. The structural role of alkaline fluorides and how it can be affected by the high polymerisation degree of the silicate component is discussed.

Ref: 17

## **The SGT**

*Brian McMillan*

Ref: 18

## **Glass-ceramics - living materials for dental application**

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Glass-ceramics are living materials. We are able to develop different types of base glasses for glass-ceramics and use the methods of controlled nucleation and crystallization of these glasses. These processes represent the living nature of crystal growth. We cool down the materials to room temperature and special microstructures are frozen in. The authors show different, very attractive examples of base glasses and demonstrate the living processes of controlled crystallization.

Using this method, it is possible to develop high strength and high toughness glass-ceramics. The key is to develop the chemical compositions, derived from the  $\text{SiO}_2$  -  $\text{Al}_2\text{O}_3$  -  $\text{Li}_2\text{O}$  -  $\text{K}_2\text{O}$  -  $\text{P}_2\text{O}_5$  system and to control the microstructure.

Special attention is drawn to a method of twofold nucleation and crystallization in fluoroapatite - leucite glass-ceramics and oxyapatite-leucite glass-ceramics. The authors demonstrate important applications for dental restorative materials to improve the quality of life of human beings.

Ref: 19

## **The Glass Academy**

Alistair Wallace

Ref: 20

## **A history of the theories of glass structure: Can we really believe what is written in text books?**

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According to most textbooks, the theoretical approach to the structure of glass has been dominated by two opposing schools, the Russian (**crystallite theory**) and the Western (**random network theory**). The former theory is usually attributed to Lebedev and the latter to Zachariasen. However, the crystallite theory was first proposed in 1835, long before Lebedev's paper (1921), and Zachariasen neither introduced the concept of a disordered array of atoms linked by directional bonding (*i.e.* a disordered network), nor was responsible for the term **random network**! In addition, Lebedev had already abandoned the idea of fine (small) quartz crystallites in glass by 1924, but still believed that all glasses with more than one component are nanoheterogeneous, whereas the Zachariasen-Warren version of the random network theory erroneously maintained that such glasses are statistically homogeneous. The present paper will attempt to dispel some of the myths, and to present an accurate and balanced history of the theories of glass structure, up to the end of the 20<sup>th</sup> Century.

## Use of Phosphate-Based Glasses for Biomedical Applications

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### Introduction:

Current bone repair implants for use within the body are made from metals, with associated disadvantages such as ion leaching, stress shielding and can remain in the body permanently. Fully resorbable polymers have also been explored to manufacture new bone fixation devices with advantages over their metal counterparts including avoiding secondary removal operations and alleviation of disuse atrophy due to stress shielding. However, biodegradable polymers alone possess insufficient mechanical properties to serve in load bearing applications [1]. To overcome these limitations, recently a move towards degradable composite materials for bone repair applications (to replace metal plate equivalents) has been viewed as extremely favourable.

Phosphate glasses and fibres are fully resorbable materials and their degradation rates can be varied easily over several orders of magnitude [2+3]. The most common and prevalent components in these glasses are calcium and phosphate ions, which make them ideal for bone repair applications. In addition, these ions are common constituents of the body, as such no adverse inflammatory responses are expected.

In this study, fully resorbable composite bone repair plates comprising a polylactic acid (PLA) matrix reinforced with phosphate glass fibres (PGF) with increasing fibre volume fraction ( $V_f$ ) and alternate fibre geometries (random and unidirectional) were manufactured and their mechanical properties were ascertained.

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## The role of strontium in bioglass

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The changes in the structure of 45S5 Bioglass and its heat-treated versions upon SrO substitution were investigated by solid-state multinuclear magic angle spinning nuclear magnetic resonance (MAS-NMR), X-ray diffraction and differential scanning calorimetry. A series of the melt-derived glasses with SrO were substituted for calcium (0, 25, 50, 75 and 100%) on a molar basis. The effect of Sr on the structure of the glass and the influence that it has upon crystallisation will be discussed.

## Dissolution of simple phosphate glasses

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Phosphate glasses in the system  $P_2O_5$ -CaO-Na<sub>2</sub>O dissolve in aqueous solutions, and their solubility can be varied by changing the glass composition. This makes them of interest for use as controlled release materials, e.g. as degradable implants, release of trace elements or as fertilizers. However, our understanding of their dissolution mechanism is still limited and requires further investigation.  $x P_2O_5-(100-x)/2 CaO-(100-x)/2 Na_2O$  ( $x = 35 - 55\text{mol}\%$ ) glasses were prepared by a melt-quench route. <sup>31</sup>P magic angle spinning nuclear magnetic resonance spectroscopy confirmed that the glass structure changed from a network (55 mol%  $P_2O_5$ ) to short chains (35 mol%  $P_2O_5$ ) with decreasing phosphate content. Simultaneously the glass transition temperature increased but the crystallisation temperature stayed relatively constant, resulting in a smaller processing window with decreasing phosphate content. Solubility and pH in Tris buffer solution (pH 7.4) over 7 days showed significant differences with phosphate content. Glasses with high phosphate content lowered the pH of the solution, while glasses with low phosphate contents did not. Solubility varied between 90% (50mol%) and 15% (35mol%) at one day. Glasses with 45 and 50mol%  $P_2O_5$  showed a decrease in P and Ca (but not Na) concentrations in solution from day 3, suggesting precipitation of a calcium phosphate. Solution <sup>31</sup>P MAS NMR on the dissolved glass with 50mol%  $P_2O_5$  showed presence of Q<sup>1</sup> and several Q<sup>2</sup> species, i.e. phosphate chains, but also small amounts of orthophosphate. The findings suggest that the glasses dissolve by hydration of entire chains, while cleavage of P-O-P bonds occurs to some extent, and that longer chains are more easily hydrated than shorter ones.

## **Effect of orthophosphate on bioactivity of phosphosilicate glasses at different pH**

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A series of highly degradable phosphosilicate  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-CaO-Na}_2\text{O}$  glasses with only about 5 mol% of  $\text{Na}_2\text{O}$  and variable amount of phosphate up to 7 mol% of  $\text{P}_2\text{O}_5$  has been synthesised via melt-quench route and studied. The appropriate amount of  $\text{CaO}$  and  $\text{Na}_2\text{O}$  has been added to the glasses on increase in  $\text{P}_2\text{O}_5$  content in order to maintain orthophosphate speciation of phosphorus in the glasses. Degradation of glasses in Tris buffer at pH 7.3 and 9 and in acetate buffer at pH 5 on immersion for up to 3 days has been investigated. The residual solid was collected after the immersion experiments and characterised by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction and  $^{31}\text{P}$  solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR). Concentrations of calcium, sodium, silicon and phosphorus in the solutions after the immersion have been measured by inductively coupled plasma - optical emission spectroscopy (ICP-OES). The evidences for glass degradation and apatite formation have been evaluated. The results of the experiments showed that the higher the content of orthophosphate in the initial glass the faster is the formation of apatite on immersion in solution. The pH 9 is considered an optimal for the apatite precipitation in solution. However, at pH 9 no apatite formation has been found due to the low rate of glass degradation. On the contrary, the highest rate of apatite formation has been found at pH 5 due to rapid glass degradation accelerated at this acidic pH. This effect of pH in bioactivity studies and role of glass composition will be discussed and generalised for other bioactive glasses.

## **The comparison between novel fluoride and chloride bioactive glasses**

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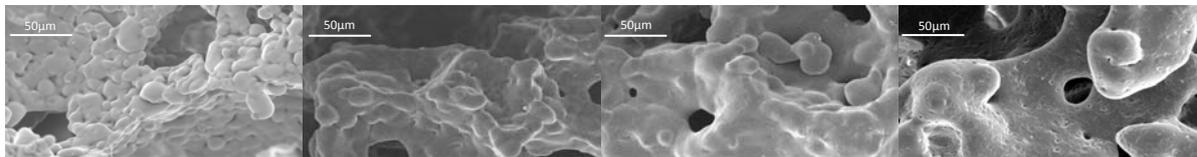
Both fluoride and chloride additives were used in glass technology typically to improve technical characteristics of glass melts. Fluoride is known typically to reduce the melting and glass transition temperature, whereas chloride is also often used as a refining agent. In highly degradable bioactive glasses fluoride is added to a composition to ensure formation of the fluoride substituted apatite in physiological conditions when the glass degrades. Fluoride substituted apatite is more resistant in acid conditions than hydroxyapatite. In addition, fluoride decreases glass transition temperature and melting temperature of the glasses. In this paper we compare addition of chloride and fluoride to a bioactive glass in order to evaluate the differences in properties and structure of the glasses. Chloride containing bioactive glasses have never been reported in the literature before. Two glass series with varying amounts of fluoride or chloride were prepared using a melt and quench route. The glass frits were dried and ground into powder. Differential scanning calorimetry (DSC), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) were used to characterize the glasses and crystallization event. Nuclear magnetic resonance was used to analyse the structure and chemical environment of the molecules. Dissolution study was performed in Tris buffer solution for the bioactivity evaluation. Both glass series show similar effects on reducing the glass transition temperature ( $T_g$ ) with increasing the halide contents. Fast apatite formation was noticed within 3 hours immersion in Tris buffer solution for all the glasses. Thus, the chloride containing bio-glasses would compete with fluoride containing bio-glasses in dental application, especially for remineralizing toothpaste.

## Maintaining amorphous glass structure in porous bioactive scaffolds

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**INTRODUCTION** Larry Henchs original Bioglass® 45S5 composition [1] cannot be made into porous scaffolds for bone ingrowth while maintaining an amorphous glass structure due to its susceptibility to crystallise during sintering, which can reduce its bioactivity. Various glass compositions have recently been developed which avoid crystallization during sintering, enabling bioactive glasses to be manufactured into porous constructs. Here, the aim was to adapt the gel casting foaming technique [2] to create porous glass scaffolds using ICIE16 (49.46% SiO<sub>2</sub>, 36.27% CaO, 6.6% Na<sub>2</sub>O, 1.07% P<sub>2</sub>O<sub>5</sub> and 6.6% K<sub>2</sub>O, in mol%) composition. ICIE16 was chosen because it has similar network connectivity similar to that of Henchs 45S5 composition [1] suggesting that the glass should have similar bioactivity. The effect of sintering temperature, and dwell time on sintering efficiency, pore network and mechanical properties was investigated. **EXPERIMENTAL METHODS** ICIE16 glass was manufactured via melt quenching. Frit was formed and ground into particle size less than 32 µm. The gel-cast foaming technique with a polymeric gelling agent was used to produce porous glass scaffolds, which were freeze dried and sintered. Sintering was assessed between 680-710 °C for dwell times of 1-5h. Scaffolds were characterised for crystallinity using XRD and mechanical and simulated body fluid testing. Pore size variation was analysed by mercury intrusion porosimetry.



**RESULTS AND DISCUSSION** Fig.1: SEM images of scaffolds sintered at 680°C at 1, 1.5, 2 and 5 h. Scale bar is 50 µm

Interconnected porous structures were successfully made by optimising the gel-casting process. XRD shows sintering at 680 °C for more than 2h induced significant crystallisation. SEM images (Fig. 1) show that the scaffolds made possess an open interconnected pore structure, after 1.5 hours at 680°C pitting formed on the surface shown to be a crystalline phase. Samples sintered for 1.5 hat 680°C showed optimal sintering efficiency (individual particles were no longer visible under SEM) and displayed good mechanical properties. **CONCLUSION** ICIE16 was successfully foamed using the gel-cast process. The optimal sintering regime was determined to be 680 °C with a dwell time of 90 minutes, in a compromise between mechanical properties and prevention of crystallisation. **ACKNOWLEDGMENTS** The authors wish to thank the EPSRC (EP/I020861) and Department of Materials, Imperial College London for financial support

## The germanate anomaly in alkaline earth germanate glasses

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For the first time, the structures of a series of alkaline earth (AE) germanate glasses have been quantitatively determined. Pulsed neutron and high-energy x-ray diffraction measurements on samples covering the full homogeneous glass-forming range in the CaO-GeO<sub>2</sub> system (21 to 41 mol% CaO using rapid twin-roller quenching) reveal broad maxima in average Ge-O coordination number,  $n_{\text{GeO}} = 4.30(3)$ , and also average bond-length,  $r_{\text{GeO}} = 1.7846(70)$  Å, at  $\square 28$  mol% CaO. These coincide with the position of maxima in the measured mass and number densities and glass transition temperatures. The positions of the maxima are at higher modifier oxide content than in alkali (A) germanate glass systems, and this is attributed to the higher bond strengths within Ae-O polyhedra compared to A-O polyhedra. Consequently, the stabilisation of [GeO<sub>6</sub>] octahedra and/or vertex sharing [GeO<sub>*m*</sub>],  $m > 4$ , are a feature of the AeO-GeO<sub>2</sub> glasses, *in contrast* to the existence of only [GeO<sub>4</sub>] tetrahedra and [GeO<sub>5</sub>] units proposed in alkali germanate glasses. The behaviour at high CaO content is therefore like that of thallium germanate glasses due to the very similar bond strengths within [CaO<sub>7</sub>] and [CaO<sub>6</sub>] polyhedra compared to [TiO<sub>3</sub>] units with stereochemically active electron lone-pairs. Atomic number densities and molar volumes demonstrate common behaviour at low modifier content in Ca, Sr, Ba and alkali germanate glass series, which is explained on the basis of germanate network cage filling by modifier cations, with concomitant accommodation of the added oxygen into the germanate network by formation of [GeO<sub>*m*</sub>],  $m > 4$ , as well as non-bridging oxygen atoms in the Ca germanate case. Analysis of atomic packing fractions reveals an average germanate network cage larger than a Ca<sup>2+</sup> ion, and similar in size to a Sr<sup>2+</sup> ion, explaining in part the propensity for NBOs in the case of Ca<sup>2+</sup> modifiers, and the very broad distributions of Ca-O bond lengths observed. Large differences in  $n_{\text{GeO}}$  between ambient pressure crystal phases and glasses are used to infer a negative correlation between  $n_{\text{GeO}}$  and liquid temperature, and possibly, between  $n_{\text{GeO}}$  and glass fictive temperature.

## The Structure of Lead Phosphomolybdate and Lead Phosphotungstate Glasses

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Glasses containing molybdenum have many potential applications. However, there is little information available on the structural role of molybdenum in glasses, and the limited information is contradictory. We have used neutron diffraction and high energy X-ray diffraction to perform structural investigations of glasses covering a wide composition range in both the lead phosphomolybdate (PbO-P<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>) and lead phosphotungstate (PbO-P<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>) systems. Although ternary glasses can often be difficult to study by diffraction, due to the large number of overlapping contributions to the correlation function, for these glasses there is a relatively good separation of the different bond lengths. Molybdenum is found to have a very unusual coordination shell. The results are interpreted together with results from complementary NMR measurements.

## Application of Raman spectroscopy to multicomponent silicate glasses

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Raman spectroscopy is a versatile, non-destructive technique that can be used to characterize the structural properties of crystalline and amorphous materials with a minimum of sample preparation, and on relatively short acquisition time-scales. As such, this technique is used in various scientific and engineering fields including the study of amorphous silicates. In this case, Raman spectroscopy has the potential to provide information on the local structure of the glass network, including the relative importance of bridging and non-bridging oxygens, and the distribution of non-bridging oxygens around network-forming cations such as Si and/or Al. Treatment of raw Raman spectra of amorphous silicates typically involves correction for various temperature and frequency dependent backgrounds, then deconvolution by a number of Gaussian peaks, each of which is associated with a particular local structural entity. However, there is significant controversy surrounding all of these aspects, in particular how to treat backgrounds, which line-shapes are appropriate for deconvolution and how to assign observed peaks to well-defined structural entities. *Ab-initio* calculations provide a promising avenue for a better understanding of Raman spectra, but such calculations are not yet available for multi-component compositions of the complexity encountered in the glass-making industry or in the Earth sciences. An alternative approach is based on Principal Component Analysis (PCA), a statistical method that makes no assumptions about the shape and the position of the bands, but that considers a given spectrum as a weighted linear combination of spectral components. Application of PCA thus requires a large number of spectra obtained over a wide but systematic compositional range. With this in mind, we are currently performing experiments in which pairs of glasses of different composition in the system  $\text{SiO}_2\text{-Na}_2\text{O-CaO}\pm\text{Al}_2\text{O}_3$  are put in contact and heat-treated to produce diffusion profiles. Compositional profiles are measured by electron microprobe and Raman spectra are collected with a comparable spatial resolution. In this way we hope to extract the relative abundance of the independent spectral components from the PCA analysis of the normalized set of spectra and discuss their interpretation in terms of structural entities. Furthermore, we will explore the use of Raman spectroscopy as a quantitative tool to measure composition in this chemical system.

## Thermodynamic model and selected physical properties of Na<sub>2</sub>O - MgO - CaO - SiO<sub>2</sub> glasses

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Molar volume, thermal expansion, glass transition temperature, and molar refractivity, 15Na<sub>2</sub>OxMgO(10-x)CaO75SiO<sub>2</sub> glasses (x = 0, 2, 4, 6, 8, 10) were measured. The structure of studied glasses was described by the thermodynamic model of Shakhmatkin and Vedishcheva. From the 27 components with the stoichiometry given by the composition of stable crystalline phases only five were found in significant abundance in the studied glasses - namely: SiO<sub>2</sub>, MgOSiO<sub>2</sub>, Na<sub>2</sub>OSiO<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>SiO<sub>2</sub>, and Na<sub>2</sub>O<sub>3</sub>CaO<sub>6</sub>SiO<sub>2</sub>. The compositional dependence of the measured physical properties was described by multilinear dependences where the equilibrium molar amounts of components with significant abundance were taken as independent variables. Based on the statistical analysis, only the statistically significant components were retained in all obtained relationships. It was proved, that the thermodynamic model describes the compositional dependence of studied physical properties with better accuracy than the model based on the glass compositions expressed by molar fractions of (unreacted) oxides. Acknowledgement This work was supported by the grant VEGA 1/0006/12, by the Slovak Research and Development Agency Project ID: APVV-0487-11, and by the project ZDESJE, ITMS code 26220220084, of the Operational Program Research and Development funded by European Fund of Regional Development.

## ***Lomonosov' color glass factory from the historical drawings***

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The celebration tercentenary of the Mikhail Lomonosov (1711-1765), the scientist, technologist, poet, artist, the first native Russian academician gave new materials about his activity.

The Archive of RAS' St. Petersburg Branch presented the exposition 'The Ust-Ruditsa Letter of Grant to Mikhail Lomonosov on the spot of land in the Koporye Uesd for construction of a glass factory'. The Letter was decorated by artists of Heraldic Department of the Senate according to recommendations of Mikhail Lomonosov is of great value. It present the activity of the scientist on the making glass and his technological innovations in that production in illustrations. The Letter consists from four pages, each of them contains drawings of allegorical images of the miniatures, the majority of them represents the equipment of the factory and the process of manufacture of color glasses at the Ust-Ruditca Color Glass factory.

All drawings can unit into nine thematic groups. The first of them shows views of the Ust-Ruditsa Factory with around buildings; the second shows the equipment of the factory and the process of tool making; the third - the preparation of components for glass melting; the forth - different modes of work with melted glass; the fifth - ways of processing of solid glass; the sixth - composing of mosaic pictures; the seventh - factory made-goods; the eight - the scientific experiments with lenses; the ninth - scenes from Lomonosov' biography after organization of glass factory.

The Lomonosov' color glass factory does not preserve, it had been closed soon after the death of the scientist. The Letter is very interesting as a source of information about history of the first Russian color glass factory and history of science and technology in Russia in the 18 century.

## **Sm-Doped Fluorophosphate and Fluoroaluminate Glasses for use in High-Resolution, High-Dose Detector Applications in Microbeam Radiation Therapy: The Role of Structural Defects**

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Microbeam Radiation Therapy (MRT) is an experimental form of radiation treatment which has the potential to improve the treatment of many types of cancer compared to customary broad-beam radiation treatment. During the treatment, parallel x-ray beams of microfine structure (20 - 100  $\mu\text{m}$  wide separated by 100 - 400  $\mu\text{m}$ ), called microbeam, carrying very large levels of dose (>1000 Gy) are delivered onto a tumor. At the present time, there are no detectors that satisfy both the dynamic range and sufficient spatial resolution requirements together to accurately measure the dose distribution across the microbeam. In order to accelerate the MRT research and proceed into a human trial stage, these detector limitations need to be overcome. Sm-doped glasses that involve the reduction of Sm-valency ( $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$ ) upon x-ray irradiation is one of the potential dosimetric detectors for this particular, but not least, application [1]. In this paper, we present new results on the current status of research on using Sm-doped glasses as a means to measure the microbeam dose profile. The basic idea involves measuring the photoluminescence signal before and after exposure to x-rays. The PL contributions from  $\text{Sm}^{3+}$  and  $\text{Sm}^{2+}$  have to be separated and suitably weighted to define a suitable and sensible response (R) function for the detector; we use the ratio of weighting constants to define the response. We report the dose-response of two basic Sm-doped glass systems: Sm-doped fluorophosphate and fluoroaluminate glasses. The samples have been exposed to a high-dose microbeam radiation at the BMIT beamline at the Canadian Light Source. The results demonstrate that the Sm-valency reduction can be used to monitor the incident surface dose in air up to  $\sim 1000$  Gy. The  $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$  conversion is accompanied by increases in the optical absorbance of the glass. The induced absorbance in fluoroaluminate glasses, however, occurs in the short wavelength region below 600 nm and does not significantly impair the measurement of the PL signal from  $\text{Sm}^{2+}$ , which is a distinct advantage of this glass system. We present results on both glass systems in terms of the dynamic range of the sensor; dependence of the dynamic range on the composition;  $\text{Sm}^{+3}$  doping; techniques to erase the recorded conversion and induced absorbance by thermal annealing and UV bleaching; and reusability. We also demonstrate that we can obtain the dose profile with high resolution by confocal fluoroscopic imaging. We show that Sm-doped fluoroaluminate glasses exhibit a number of distinct advantages, which makes this material system highly suitable for use in high-dose, high-resolution dosimetry in MRT. We discuss the results in terms of known and potential hole and electron capture defect centers in these glass systems, and their creation and annihilation; and also report recent ESR measurements to support some of the arguments. [1] G. Okada, B. Morrell, C. Koughia, A. Edgar, C.R. Varoy, G. Belev, T. Wysokinski, D. Chapman, and S. Kasap, Applied Physics Letters 99, 121105 (2011).

## Synthesis, structures and optical properties of samarium doped zinc borophosphate glasses

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Samarium doped borophosphate glasses are promising advanced materials which exhibit good mechanical stability and ease of processing, combined with interesting functional properties such as transparency, UV and x-ray fluorescence. In this study, the system ZnO-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>5</sub> was investigated by varying the glass composition, doping with different amounts of samarium, and examination of the obtained materials using a combination of techniques such as thermal analysis, UV fluorescence, x-ray fluorescence, x-ray powder diffraction and scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDAX). The results demonstrate that single phase glass material is obtained at specific synthetic conditions whereas glass-ceramic samples are formed in other conditions. The single phase glasses obtained in this way are fully transparent. It is found that both UV fluorescence and x-ray fluorescence properties of the obtained glasses depend on the excitation wavelength. Strongest UV fluorescence is found at 395nm, with emission spectra attributable to the presence of Sm<sup>3+</sup> ions. Interestingly, Sm<sup>3+</sup> → Sm<sup>2+</sup> conversion is observed on x-ray irradiation with green (535nm) laser, whereas no conversion is found on excitation with purple (400nm) laser. The observed properties can be related to the structure and morphology of the glassy materials as evidenced by the SEM-EDAX investigation and powder x-ray diffraction data. From this study, it can be concluded that samarium doped zinc borophosphate glasses are promising candidates for medical x-ray imaging and data storage applications, in addition to potential use as down-shifting materials in photo-voltaic, optoelectronic, and sensor devices.

## **Thermophotovoltaic opportunities within the glass industry**

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The generation of electricity by thermophotovoltaic (TPV) cells is a technique offering a wide range of opportunities for energy recovery in high temperature industries such as glass manufacturing. This paper will introduce the fundamentals of TPV technology where radiant heat is directly converted to electricity and will describe current applications. The main components of a practical TPV system will be introduced including the use of optical control to improve overall system efficiency. The results of a laboratory trial will be employed to discuss electricity generation opportunities within a glass plant and also outline the main considerations which need to be addressed during an industrial feasibility pilot.

## **Overview of microfabrication techniques for lab-on-a-chip devices using glass substrates**

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ASCUS Art-Science Collaborative*

Lab-on-a-chip is a term applied to the scaling down of single or multiple laboratory processes to a chip-based format for the handling of low volumes of fluids.

The Analytical Chemistry Workgroup at the University of Hull is involved in Research and Development for lab-on-a-chip applications with an emphasis in the biomedical and clinical realm. While a number of materials such as plastics, silicon, and metal, can be used for the fabrication of these "microfluidic" lab-on-a-chip devices, glass is often a favourable option due to its optical transparency, chemical resistance, thermal stability, and its rigidity. At the University of Hull, for example, glass is the material of choice for the majority of applications.

Here, we demonstrate the manufacturing capabilities and processes available at the University for the production of such lab-on-a-chip devices and illustrate the multiple steps required for their fabrication from glass substrates.

The main uses, advantages and disadvantages of microfluidic lab-on-a-chip-devices versus conventional analytical chemistry methods are introduced, and current trends in microfluidic chip design and layout are shown.

The photolithographic and wet etching processes employed to produce glass micro chips will be illustrated and explained, together with information on substrate selection and preparation, micro drilling methods, and thermal bonding methods

Ref: 36

## **Oldfield Award Winner 1<sup>st</sup> prize presentation**

Ref: 37

### **The thallium (I) environment in oxide glasses**

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Thallium (I) is a highly unusual species. Superficially, it is a large, univalent cation which might be expected, on the basis of cation potential, to behave like K<sup>+</sup> or Rb<sup>+</sup>, having a first coordination sphere with a symmetric distribution of ~ 7-8 oxygen ions. However, at moderately high concentrations of Tl<sub>2</sub>O in a binary oxide glass, the Tl<sup>+</sup> coordination changes dramatically with the formation of a lone-pair of electrons on the Tl<sup>+</sup> ion and the adoption of a highly asymmetric, low coordination to oxygen. Instances of this change in coordination are here reported for borate and germanate glasses and it is shown how Tl coordination also affect the coordination of the network former cations. Thus the borate and germanate anomalies are both perturbed by the presence of the lone-pairs.

Ref: 38

### **High temperature indentation of float glass**

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The high temperature response of float glass to mechanical contact is being investigated, so as to develop our understanding of the mechanical damage caused to glass during both initial and secondary production processes. A series of instrumented micro-indentation experiments using a Vickers indenter have been undertaken at temperatures between 500 and 600°C using an adapted universal tester. The system was first calibrated at high temperatures by carrying out indentations on pure silica. The use of instrumented indentation means that, as well as characterizing the resultant damage via optical measurements, hardness and elastic modulus can, in principle, be extracted from the load displacement data. However this is complicated by the transition to visco-elastic behaviour as the temperature increases. The challenges associated with the interpretation of the high temperature data along with their implications for glass processing will be discussed.

## Title: **Effect of compactness on properties of oxynitride glasses.**

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Oxynitride glasses are well known for their remarkable mechanical and thermal properties. It has been widely established that the incorporation of a relatively small amount of nitrogen leads to a significant change of the glass network, and therefore to a strong change of the properties. Oxynitride glasses with significantly higher concentrations of nitrogen up to 60 e/o as well as modifier additives up to 45 e/o have been prepared by novel synthesis method, in which the modifier is introduced as a pure metal or metal hydride. Addition of nitrogen leads to an increase compactness (C) for the silicon oxynitride glasses, which can be attributed to formation of a significant fraction of three-coordinated N in the glass networks, while the addition of modifier reduce the compactness. Increase in compactness leads to increases the glass transition temperature ( $T_g$ ), microhardness values ( $H_v$ ) and elastic properties ( $E$ ), and reduce the molar volume ( $MV$ ). Variation in refractive index ( $n$ ) and density ( $\rho$ ) can be attributed to the glass compactness.

**Keywords:** Oxynitride glass; glass compactness; high nitrogen content; glass transition temperature; hardness; refractive index.

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## The Role of Rare Earth Ions in Chalcogenide Glasses.

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Rare earth (RE) ions are doped into a wide range of glasses to act as fluorescent centres in the production of fibre lasers. However, while this process is reasonably well established for visible and near-infrared (IR) wavelength technologies, the development of mid-IR fibre lasers has been hampered by a poor understanding of the RE environment when doped into chalcogenide glasses - the glass host of choice for mid-IR light generation due to their transparency to wavelengths in excess of 12  $\mu\text{m}$  [1].

Two key factors are thought to combine to create difficulties in producing mid-IR fibre lasers. The first is the purity of the glass. Purifying chalcogenide glasses is difficult and oxide/hydride impurities often present absorption bands at frequencies matching those of RE fluorescence (e.g. Se-H bonds absorb at  $\sim 4.5 \mu\text{m}$ , an emission frequency of  $\text{Dy}^{3+}$ ). Further, it is thought that any oxygen anions (more electronegative than S or Se anions) present in the glass will preferentially bond to RE ions, creating a local high phonon energy environment for the RE ion and resulting in paths for non-radiative phonon decay that prevent lasing [2]. The second factor is due to RE solubility and clustering. RE ions have a low solubility in chalcogenides ( $\sim 6\text{-}9 \text{ mol.}\%$   $\text{Re}_2\text{S}_3$  in a Ge-Ga-S glass [3], when compared to  $\sim 25 \text{ mol.}\%$   $\text{RE}_2\text{O}_3$  in phosphates [4]). As the amount of RE in the glass increases, clustering occurs, resulting in phase separation and crystallisation. The presence of Ga is thought to reduce these problems by forming complexes with the RE, and changes in fluorescence intensity on adding gallium to a  $\text{Pr}^{3+}$  doped GeAsS glass have been reported by Aitken *et al.* [5].

This paper will present structural results obtained by neutron and X-ray diffraction, EXAFS and Ga NMR for sulfide and selenide glasses doped with  $\text{Nd}^{3+}$  and  $\text{Dy}^{3+}$  respectively. These results will be considered in light of the current understanding of chalcogenide glass structure and a number of conclusions will be drawn which focus on the RE local environment, the proximity to gallium, and the effect of RE additive on bulk glass crystallisation.

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Ref: 41

## **Behaviour of indium oxide in zinc phosphate and borophosphate glasses**

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The effect of indium oxide on structure and properties of zinc phosphate and zinc borophosphate glasses was investigated. Zinc phosphate glasses doped with  $\text{In}_2\text{O}_3$  were investigated in the series  $(50-x)\text{ZnO}-x\text{In}_2\text{O}_3-50\text{P}_2\text{O}_5$  (A-series) and zinc borophosphate glasses were investigated in the series  $30\text{ZnO}-(20-x)\text{B}_2\text{O}_3-x\text{In}_2\text{O}_3-50\text{P}_2\text{O}_5$  (B-series). Glasses were obtained in both series within the compositional region of  $x = 0-20$  mol%  $\text{In}_2\text{O}_3$ . The obtained glasses were characterized by the measurements of density, molar volume, glass transition temperature and thermal expansion coefficient. Their structure was studied by Raman and NMR spectroscopy.

The observed changes in the  $^{31}\text{P}$  MAS NMR spectra of the phosphate glass series with increasing  $\text{In}_2\text{O}_3$  content reveal the depolymerization of phosphate chains due to the incorporation of  $\text{In}_2\text{O}_3$  into the glass structure. Similar characters possess also  $^{31}\text{P}$  MAS NMR spectra of the borophosphate glass series. Raman spectra show also on the depolymerization of the phosphate network.  $^{11}\text{B}$  MAS NMR spectra reveal a dominant role of  $\text{BO}_4$  units in the glass structure, only a few percent of  $\text{BO}_4$  units is transformed to  $\text{BO}_3$  units; these spectra give no evidence for the formation of B-O-In bonds. We assume that indium atoms have octahedral coordination ( $\text{InO}_6$ ) in these glasses in comparison with tetrahedral coordination of boron ( $\text{BO}_4$ ). The values of the molar volume do not change when  $\text{B}_2\text{O}_3$  is replaced by  $\text{In}_2\text{O}_3$ , which can be ascribed to higher reticulation of the structure network containing  $\text{In}_2\text{O}_3$ .

Ref: 42

## **Residual entropy and structural disorder in glass**

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As a contribution to the residual entropy debate for glasses, we have made simulations to compare the configurational entropies on simple system as calculated from either classical or statistical thermodynamics under equilibrium and non-equilibrium conditions. We have also introduced new viewpoints named 'spatial sampling' and 'phase factor of entropy' in order to fulfill a compromise between the conventional thermodynamic and kinetic views. The new viewpoints are applied to the real glass systems.

Ref: 43

## **Oldfield Award Winner 2<sup>nd</sup> Prize presentation**

## Structure of As<sub>20</sub>-Sb<sub>20</sub>-S(60-x)-Se(x) Glasses studied by Combined Raman Spectroscopy and Thermodynamic Modelling Approach

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The structure of chalcogenide glasses of the system As-Sb-(S, Se)<sub>3</sub> 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 As<sub>20</sub>-Sb<sub>20</sub>-S(60-x)-Se(x) (x = 0, 10, 20, 30, 40, 50, 60) glasses performed by the PCA (Principal Component Analysis) method and spectral decomposition by the method of Zakaznova-Herzog and Malfait. Three independent components were identified in the studied spectral series by the PCA. On the other hand, the thermodynamic model resulted in seven components with significant abundance in the studied glasses, i.e. Se, As<sub>2</sub>S<sub>2</sub>, AsSe, As<sub>2</sub>S<sub>3</sub>, As<sub>2</sub>Se<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub>, and Sb<sub>2</sub>Se<sub>3</sub>. Finally, the correlation analysis proved the strong linear dependence between the molar abundances of seven following pairs of system components: (AsSe - As<sub>2</sub>Se<sub>3</sub>), (Sb<sub>2</sub>Se<sub>3</sub> - As<sub>2</sub>Se<sub>3</sub>), (Sb<sub>2</sub>S<sub>3</sub> - As<sub>2</sub>Se<sub>3</sub>), (Sb<sub>2</sub>S<sub>3</sub> - Sb<sub>2</sub>Se<sub>3</sub>), (AsSe - Sb<sub>2</sub>Se<sub>3</sub>), (Se - As<sub>2</sub>S<sub>2</sub>), and (As<sub>2</sub>S<sub>3</sub> - Sb<sub>2</sub>S<sub>3</sub>). Using the method of Malfait, following linear combinations of Raman spectra of pure system components were obtained: (1.125 Se + As<sub>2</sub>S<sub>2</sub>); (0.573 As<sub>2</sub>S<sub>3</sub> + Sb<sub>2</sub>S<sub>3</sub>); (0.288 AsSe + 0.681 As<sub>2</sub>Se<sub>3</sub> + Sb<sub>2</sub>Se<sub>3</sub>). The experimental spectra were reproduced with excellent accuracy. The obtained results confirmed the structural information acquired from the thermodynamic model. Acknowledgement This work was supported by the grant VEGA 1/0006/12, by the Slovak Research and Development Agency Project ID: APVV-0487-11, and by the project ZDESJE, ITMS code 26220220084, of the Operational Program Research and Development funded by European Fund of Regional Development.

## Towards a universal description of local structure in model glassforming liquids

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The glass transition is a key outstanding problem of condensed matter. Among the challenges lies in understanding how solidification can occur without apparent change in structure. Among the first to suggest that glass formation is promoted by fivefold symmetric structural motifs, whose geometry is abhorrent to crystallization, was Sir Charles Frank [1]. It has taken many years to obtain convincing evidence of such motifs in computer simulation [2] and experiment [3]. Recently a consensus has begun to emerge that for a number of model glassformers, the development of such structural motifs may serve as an order parameter for the glass transition [4]. The idea that such structures are indeed causal to glass formation has been strengthened by the observation of high-temperature structure-induced vitrification [5].

Until now however, each glassforming system has been thought to exhibit a unique structural motif. Using experiments with colloids and molecular dynamics simulation, here we show that the structural motifs of three model glassformers may be decomposed into five-membered rings. These systems are polydisperse hard spheres, and the Wahnstrom and Kob-Anderson binary Lennard-Jones models, whose motifs we identify as 10-membered clusters with a degree of fivefold symmetry, 13-membered icosahedra [3] and bicapped square antiprisms [5] respectively.

While almost every particle in these systems is part of a five-membered ring, those in the structural motifs are part of up to 7 five-membered rings. We introduce the concept of identifying local structure through the number of five-membered rings a given particle is part of. In this way, all three models can be treated with the same order parameter, namely the number of five-membered rings a particle is incorporated in. Based on this analysis, we show that by biasing the number of five membered rings in a system, glass-forming ability is much enhanced. Thus Frank's original conjecture, that five-fold symmetry leads to glass formation is directly verified.

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## **Lead Crystal, the beginning and the end?**

*Barry Clark, Sarah Cable*

George Ravenscroft is credited with inventing lead crystal in the early 1670s; it became the material of choice for decorative glass manufacturers in Britain for the next three hundred years. The glass was very clear with a high refractive index and was also softer than earlier soda-lime glasses, meaning that it was easy to cut and polish and the surfaces would sparkle brilliantly. Glass making in Britain before this innovation was classified as Facon de Venise, in the Venetian style, applied decoration took the form of embellishment applied while the piece was still hot or light scraffitto engraving to the finished piece. It is difficult to blow lead crystal thinly in comparison to the low-lead cristallo of Venice. As lead crystal was adopted, the British glassmaking style began to diverge from the rest of Europe, giving our glassware a characteristic solidity and permanence and breaking free of the Venetian influence. This was a gradual process and the earliest pieces of Ravenscroft glass are recognisably facon de Venise.

The twenty-first century has seen a precipitous decline in the use of full lead crystal, the cost of fuel and wages in this country together with constraints on the uses of lead- and other metal oxides and control of polishing acids.

Barry Clark and Sarah Cable are glassmakers trained in the crystal making tradition, who have undertaken a practical study into how glass was manipulated in this period. They have used the Ravenscroft goblet, held in the Pilkington Glass Collection, St Helens, as a key reference piece from which to evolve a body of work that re-combines facon de Venise techniques with traditional British making. This paper will detail the progression of this project, with attention to some of the style elements and techniques used by Ravenscroft and his contemporaries and how these elements have been redefined for the modern age.

### *About the Authors:*

*Barry Clark has worked in glassmaking since 1993, after gaining a degree in Design History at Manchester Metropolitan University he studied and worked in Stourbridge, he has managed the national glass centre studio; run a commercial architectural glass department and worked in research, lecturing and consultancy, culminating in the establishment of his own business in 2006.*

*Sarah Cable has a degree 3-D Design: Glass, from the University of Wolverhampton and has worked for various glassmakers around the world, she is currently an associate lecturer in hot glass at Manchester Metropolitan University and a demonstrator for the world of glass in St Helens.*

## Glass making, and myth making

*Jerome Harrington*

Jerome Harrington is an artist, with a background as a glass blower, whose work explores the inter-relation between objects and ideas. He produces short films, objects and critical writing to explore how meanings and values become interwoven with the materiality of the object.

Recent works attempt to expose a cultural perception of glass, not by working with the material itself, but by examining found material - existing evidence where glass is described or depicted. This includes novels that use the word glass in their title, magic tricks in which glass is employed as a central material, and images which depict glass or glass making processes. By using found material, he aims to de-centralize his own understanding, and move to an examination of how glass is perceived by others.

In this highly visual presentation, Harrington will discuss recent research into the myth of glass flow, which despite being categorically disproved (Zanotto 1998, Brill 2012) continues to prevail and influence contemporary understandings of glass. He will trace this myth of the metamorphosis or instability of the glass object back to the production of Crown glass in the eighteenth century, discussing en route the depiction of its making process in Diderots Encyclopedia (1751). He will subsequently explore how this myth continues to prevail in the present, examining a number of examples from popular culture where the myth becomes re-stated. A number of his recent artworks explore the interplay between the Crown glass object, the myth of glass flow and the use of glass in magic and conjuring tricks.

Within Harringtons practice, the myth of glass flow is a subject of continuing fascination because it demonstrates an interaction between a historical object and the present; between myth and knowledge, and between the physicality of material and a mental conception of it.

### Biography

Jerome Harrington is an artist based in Sheffield, and is currently undertaking a practice based PhD in Fine art at Sheffield Hallam University. Jerome studied glass at Edinburgh College of Art (1998) and the Gerrit Rietveld Academie in Amsterdam (2004). Recent exhibitions include: *A Conference for The Glass Archive*, Site Gallery, Sheffield (2007); *Making fact Making fiction*, National Glass Centre, Sunderland (2008); and, *An object described by fragments*, SIA Gallery, Sheffield (2012).

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## **What the Siemens Brothers did for the Glass Industry**

*Michael Cable*

By the middle of the nineteenth century glass makers were aware that progress would be greatly advanced if three problems could be solved. The first was to decrease the vast amounts of heat squandered by sending very hot combustion gases straight up a chimney and into the atmosphere. The second was to find more efficient ways of burning their solid fuels. The third

was to operate continuously thus avoiding waste of time and resources in warming up or standing off before good ware could be produced. The first improvement was to use regenerative furnaces for melting glass as had been suggested by R. Stirling in 1816 but he did not pursue his suggestion and it was then forgotten until Friedrich Siemens had the same idea in 1856 and brought it to success in 1860. The second was to gasify solid fuels by partial combustion in a gas producer. Several pioneers developed suitable apparatus and a simple but effective gas producer was invented by William Siemens. The third problem was solved by cooperation between Hans Siemens and his brother Friedrich who made the first effective tank furnace in Dresden in 1867.

Friedrich then continued his career in the glass industry making further notable advances in furnace design and in thermal toughening of glass.

## **Acid Etching Technique and Stained Glass: Art vs. Science**

Oksana Kondratyeva

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When technical development reaches a certain level, science and art merge together into aesthetics. Albert Einstein: The development of stained glass art was always linked to the level of scientific knowledge. Among many methods used by the stained glass artists, one particular technique stands out: hydrofluoric acid etching. The technology of the acid etching application to the flashed glass was formed over centuries and reached maturity when the hydrofluoric acid was discovered by the Swedish chemist Carl Scheele in 1771. The hydrofluoric acid decomposes the molecules of silica dioxide that allows a stained glass artist to achieve smooth colour transition by removing the layers of flashed glass by controlling the density of the acid and exposure time. The flashed glass was invented as a response to the fact that the coloured glass produced using traditional methods was often too opaque. Red glass made of copper presented particular problem. Therefore, it had to be flashed - a bubble of clear glass was blown first, and then it was dipped into a crucible of red. By removing the layer of coloured glass it is possible to have two colours (e.g., red and white) on a single piece of glass. The white section can then be partially or fully coloured yellow by applying silver staining technique. The author traces the history of acid etching technique to the early medieval time when the first abrasive methods were applied. Abrading in Middle Ages revolutionized design of stained glass windows and led to its frequent application predominately in heraldic stained glass windows. The author shows earliest examples of abrading applied onto flashed glass. Fast forward to the 20<sup>th</sup> century and we see how the leading Art Nouveau artists started to apply acid etching technique to the 3D objects: sculptures, vases, lamps whose designs followed the shapes and forms found in flora and fauna. The famous School of Nancy and Émile Gallè in particular are, probably, the brightest representatives of this art movement. In conclusion the author discusses the practical problems of the hydrofluoric acid usage that stained glass artists face nowadays and shows richly illustrated examples of contemporary applications of acid etching onto flashed glass in ecclesiastic and secular architecture.

## **Medieval glasses from north Adriatic area: local productions or Venetian importations?**

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The Middle Ages represent a period of fundamental importance in the history of glass production. Indeed, after 800 AD a series of events caused a radical change in glass manufacture both in the Islamic world and in the West. In both areas, natron, the source of alkali used from the middle of the first millennium BC, was replaced by plant ash. In the West, wood ash had become the main fluxing agent, whereas in the Middle East and southern Europe, the alkali source is generally believed to be ash from marsh plants. In Italy, and in particular in north Adriatic area, the soda ash glass is generally attributed to Venetian production, since this city was one of the most important glassmaking centre from the Middle Ages onwards. So far, many studies of Venetian archives have proven the existence of glass trade between Venice and its hinterland, but a clear distinction between Venetian production and possible local productions of the hinterland is still lacking. In order to shed more light on this issue, an extensive study on north Adriatic glasses was carried out inside the project PRIN 2009. About 70 glasses, dating Late Middle Ages and coming from different sites located in north-east Italy (Rocca di Asolo, Padova, Aquileia, S. Severo and Rontana) have been analysed. They belong to different types (nuppenbecher, flat based beakers with blue rim, anghistera and kropfflasche bottles, gambassino beaker), all well attested in the sites of interest. The bulk chemistry of the samples was determined by means of Electron Probe Microanalysis (EPMA) or X Ray Fluorescence (XRF). Major and minor element compositions allowed to distinguish different compositional groups, related to the use of different fluxing agents and/or different silica sources. These groups were then compared with literature data and, in particular, with the composition of coeval samples coming from Venice, in order to identify possible similarities or dissimilarities. Results indicate that some samples show a good correspondence with Venetian compositions, supporting the hypothesis of a common provenance. On the other hand, some other samples are clearly not comparable with Venetian productions, suggesting that Venice was not the only glass supplier for the north Adriatic area. Further scientific analysis and literature search are still in progress, with the purpose of identifying these ateliers.

## **A collection of 17th - 18th century English glass goblets found in Casa dos Bicos (Lisbon, Portugal): analytical characterization and preservation**

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During the archaeological excavations that occurred between 1981 and 1982 at Casa dos Bicos in the city of Lisbon (Portugal) several fragments of colourless glass goblets were found. From this collection a set of 48 fragmented goblets with baluster stems and different arrangements of knobs, thought to be of English origin, is now under study. The glass fragments were characterized using analytical techniques such as  $\mu$ -EDXRF (micro Energy Dispersive X-Ray Fluorescence), PIXE (Particule Induced X-ray Emission), optical microscopy and Raman microscopy. The analyzed glass was determined to have high contents of lead, between 26 and 39 wt%, and a range of silica content from 50 to 60 wt%. Regarding the glass goblets typology and the analytical results obtained it is possible to conclude that they are typical of late 17th to 18th century English production or *façon d'Anglaise*. The glass objects also exhibit several corrosion degrees where one can find practically non-corroded glass, iridescence or opaque glass with brown crusts. These corrosion products are also under analysis. The study of this collection is part of a larger project that comprehends the study and characterization of glass collections that were found in the Portuguese territory with the aim to contribute to the knowledge of the history and artistic value of the these collections in Portugal in order to improve a better preservation and appreciation of this legacy.

## **Creation of a borosilicate layer upon gilding of Mycenaean vitreous relief fragments vs. weathering-induced polymerization in Classic Hellenic vitreous samples - an experimental study**

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Ancient glass samples from Greece were studied in terms of their chemical composition and the structural variations induced by weathering or their surface modification, using infrared (IR) and Raman spectroscopy. The historic samples consisted of blue vitreous Mycenaean relief fragments from the Late Bronze Age as well as blue Classical Hellenic glass vessel fragments. The chemical composition of the samples is consistent with typical soda-lime-silica glasses, and the deep blue colour is caused by the absorbance of  $\text{Co}^{2+}$  ions in tetrahedral coordination. In most vitreous samples vibrational spectroscopy reflects the nominal glass composition, with a predominance of Q3 groups (silicate tetrahedra with 3 bridging and 1 non-bridging oxygen atoms). On corroded surface areas silicate tetrahedra with 2 or even 3 non-bridging oxygen atoms were also identified, as a result of weathering effects. This study focuses on selected samples, in which the spectroscopic measurements on the samples surface were indicative of highly polymerized glass structures, resembling the spectra of highly polymerized silica or highly polymerized low alkaline borosilicate glasses. Measurements on cuts on the sides of the fragments show that only a very thin layer (<1 to 10  $\mu\text{m}$ ) on the front and back of the samples displayed such a fully polymerized glass network. Possible chemical reaction mechanisms and conditions for the formation of a silica-type layer by a sol-gel process, or of a borosilicate layer after gilding using borax as a flux were previously discussed [1]. However, this paper includes not only the results of gilding and leaching experiments on model laboratory glasses, but also further examples from archaeological vitreous findings which represent the ensuing results of both mechanisms, i.e. weathering and gilding of glassy artefacts. [1] D. Möncke, D. Palles, N. Zacharias, M. Kaparou, E. I. Kamitsos, L. Wondraczek, Formation of an outer borosilicate glass layer on Late Bronze Age Mycenaean blue vitreous relief fragments, *Phys. Chem. Glasses: B* 54 (2013) 52-59.

