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Science I

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Self sensing using glass fibres in composite materials

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Fibre reinforced composite materials are being increasingly used in safety critical applications such as aircraft structures. Various techniques have been proposed for monitoring the long term chemical and mechanical behaviour of such structures. In this talk I will review work carried out jointly between the glass group and the composites group at Sheffield using glass fibres to monitor the behaviour of fibre reinforced composites. The review will cover two classes of sensors. The first class uses evanescent wave spectroscopy and chalcogenide based fibres, that transmit in the infra-red, to monitor the chemistry of the resin. The second class utilizes the E-glass reinforcing fibres to detect mechanical damage to the composites. Proof of concept for both types of glass sensors will be given and future research needs identified.

Ref: 4

Preparation and characterization of optical waveguides of Er³⁺ - doped tellurite glasses by field-assisted Ag⁺-Na⁺ ion-exchange.

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It is requested to enhance the speed and density of telecommunication with increasing in the demand for optical communication. As one of the solutions, the wavelength division multiplexing (WDM) method attracts attention. A wideband optical amplifier as one of optical devices is indispensable in order to amplify communication light that attenuates by transmission. An Er³⁺-doped tellurite glass is a superior material as a broadband amplifier at 1.5 μ m in WDM network. An optical waveguide forms the basis for an integrated optical device applicable to an amplifier and laser for high-speed signal processing in telecommunication. Ion-exchange method is effective and to make an optical waveguide on a substrate glass owing to its simplicity, flexibility, reliability and low cost. Especially, field-assisted ion-exchange accelerates ion-exchange and diffusion of ions deep into the substrate by electrical effect.

In this study, characterization of planar optical waveguides by field-assisted Ag⁺ - Na⁺ ion-exchange has been carried out. 12Na₂O10NbO₂.525WO₃53TeO₂ +1.0Er₂O₃ glass (in mol%) was prepared as a substrate glass. After sputter-deposition, Ag film was formed on the glass substrate, and a voltage was applied to the sample in an electric furnace. The optical properties were analyzed by using UV-Vis-NIR spectrophotometer and prism coupler, and the relationships among optical and wave-guiding properties of the waveguides and ion-exchange conditions were clarified.

Ref: 5

Preparation and characterization of Nd³⁺, Er³⁺-singly doped and Er³⁺/Yb³⁺ -codoped low silica yttrium aluminosilicate glasses

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Rare earth aluminate and aluminosilicate glasses have been of great interest due to their high elastic modulus and hardness, high refraction index, excellent optical properties, and good corrosion resistance. Moreover, rare earth aluminate glasses and rare earth aluminosilicate glasses are known for their ability to accommodate high concentration of rare earth photoluminescence active ions (e.g. Nd³⁺, Er³⁺, etc.), and low phonon energy due to the aluminate network. These properties predetermine rare earth aluminate and aluminosilicate glasses as potential candidates for various applications e.g. in solid state lasers, optical waveguides and optical amplifier hosts.

In the present work, we report the preparation and characterization of Nd³⁺ and Er³⁺ doped glasses in the system Y₂O₃-Al₂O₃-SiO₂ with silica content up to 20 mol. %. The glasses were prepared in the form of microbeads by flame-spaying technique. The prepared glass microbeads were characterised by optical microscopy, SEM, XRD, FT-IR and DTA. Optical absorption and photoluminescence properties of the prepared glasses have been studied. For the Er³⁺ doped glasses, the effect of increasing codopant concentration - Yb³⁺ ions, serving as sensitizer that will enhance the upconversion (UC) efficiency of Er³⁺ ions through energy transfer, have been investigated.

Keywords: yttrium aluminosilicate (YAS) glasses, Er³⁺ and Nd³⁺ doping, Yb³⁺ codoping, optical properties

Science II

Ref: 6

Atomic mobility in silicate glasses and melts

Corinne CLAIREAUX, Marie H el ene CHOPINET, Michael TOPLIS, Mathieu ROSKOSZ

At many stages of the glass making process and application, atomic mobility is an essential factor to understand and control. This phenomenon is particularly critical during the heating of crystalline raw materials to form a liquid and during the subsequent cooling of that liquid to form a glass. For this reason, a clear understanding of the factors affecting atomic mobility in molten silicate matrices would be of significant help both in optimizing glass composition and synthesis conditions.

Atomic mobility will be studied by juxtaposing glasses of contrasting compositions, treated for variable duration at high temperatures. These experiments will be performed using two polished presynthesized glass plates, wide enough to ignore edge effects. As the two disks will have a compositional contrast, there is a stepshaped chemical offset across the glassglass interface. With time spent at high temperature, this initial compositional profile will be modified by the action of chemical diffusion. In the liquid state, atomic mobility will condition the rate at which chemical homogeneity may be attained.

The system studied contains two contrasting network modifying cations (Na and Ca), two contrasting network forming cations (Si and Al), and the anion O. Common sodalime glass is in this chemical system, making the results directly applicable to questions of industrial interest. In detail, the compositional pairs are centred on 63% SiO₂, 13% Na₂O, 12% Al₂O₃, 11% CaO plus additions of SO₃ and C as fining agents.

Before beginning formal diffusion experiments, our first goal is to manufacture starting glasses with a high degree of chemical homogeneity. The objective is to obtain less than 1% difference in composition in a 1 kg batch melted in a laboratory crucible. Glass was melted in electric furnaces to avoid convection and to easily detect inhomogeneities caused by the density differences in the silicates formed during melting.

Once the glass was annealed, a core of glass was collected over the entire height of the crucible. The sample was analysed from top to bottom with an electron microprobe to obtain quantitative information concerning the glass composition. Raman spectroscopy was used to provide a rapid and qualitative estimate of the degree of homogeneity of the glass.

In order to optimize glass quality, the effects of: i) temperature (and associated, variations in the melt viscosity and diffusion coefficient), ii) the particle size of raw materials, and iii) the influence of variable amounts of fining agents, were all studied systematically.

First results evidenced that the influence of the melting temperature on the composition gradient in the final glass is negligible. Size of calcium oxide particles seems to control part of the segregation phenomenon.

Title: Oxynitride glasses.

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Abstract:

Oxynitride glasses are a branch of high performance glasses, obtained by incorporation of nitrogen atoms into oxide glass network. 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 have traditionally been synthesized by melting mixtures of glass modifier metal oxides, SiO₂ and Si₃N₄, yielding glasses with nitrogen content up to typically *ca.* 30 e/o. However, a novel synthesis method (developed by our group), in which the modifier is introduced as a pure metal or metal hydride has enabled the preparation of oxynitride glasses with significantly higher concentrations of nitrogen up to 60 e/o as well as modifier additives up to 45 e/o. The obtained glasses are found to be homogenous, translucent gray to opaque black. Compare with their oxide glass counterparts, oxynitride glasses show high values of glass transition temperature (1050°C), microhardness (10.50 GPa), Youngs modulus (151 GPa) and refractive index (1.93).

Keywords: Oxynitride glass; glass forming region; high nitrogen content; glass transition temperature; hardness; refractive index.

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**Structural studies of rare earth doped BaTi₂O₅ using
neutron diffraction and EXAFS**

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It has recently been shown that rare earth doped barium titanate glasses have useful material properties, such as high refractive indices and luminescence. In order to better understand and tailor the optical properties it is important to have an accurate description of the structure and coordination around the rare earth. Aerodynamic levitation and laser heating was used to produce both BaTi₂O₅ (BTO) and R_{0.3}Ba_{0.7}Ti₂O_{5.15} (R = Nd, Gd, Er, Yb) glass spheres. The complementary techniques of neutron diffraction and EXAFS were employed to allow an insight into the structural differences that occur, both with the addition of the dopants, and with the variation in rare earth ion size. Initial analysis suggests there is little difference in the coordination around the Ti atoms in all samples, implying that the titanium network retains its structure with both variations.

The Structure of Amorphous Calcium Carbonate

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Amorphous calcium carbonate (ACC) is thought to play a key role in many biomineralisation processes that occur in various sea organisms.[1] This work is part of a project aimed at understanding the structure of ACC utilising both experimental and computational techniques. Very few structural investigations have been performed on ACC, mainly due to its instability and tendency to transform to the more stable crystalline form calcite within about 1 hour after synthesis. However, a model structure for ACC has been proposed by Goodwin *et al.* in 2010.[2] Presented here will be a synthesis method used to obtain stabilised ACC with experimental results of stabilised ACC including the x-ray diffraction (XRD), x-ray absorption fine structure (XAFS) and the neutron diffraction data. Also presented alongside this data will be the initial computational modelling results fitting experimental x-ray and neutron data to a computer model of ACC using the Empirical Potential Structure Refinement (EPSR) fitting program.

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Ref: 10

A time resolved ^{31}P MAS-NMR study of a novel bioactive glass M Mneimne*, DS Brauer, RG Hill, N Karpukhina *Queen Mary University of London, Institute of Dentistry, Mile End Road, London, UK*
The aim of this study was to provide a structural and kinetic understanding of the formation of biomimetic apatite from a high phosphate and fluoride containing bioactive glass. The principle application for this glass is as a remineralising additive in toothpaste where the ability to form fluorapatite (FAp) in as short a time frame as possible is highly desirable. The dissolution and apatite formation in a physiological buffer solution with pH 7.4 has been investigated for this novel high phosphate containing glass (6mol%) and compared with a low phosphate containing glass (1mol%). The degradation of the glass phase and crystallisation of apatite with time has been followed by ^{31}P solid-state magic angle spinning - nuclear magnetic resonance spectroscopy (MAS-NMR) and X-ray diffraction (XRD). ^{19}F MAS-NMR was also used to distinguish the nature of the apatite formed. ^{31}P and ^{19}F solid-state MAS-NMR results on the novel bioactive glass immersed in a physiological buffer solution showed the gradual atomic rearrangement around phosphorus and fluorine. Direct quantification of the time resolved ^{31}P MAS-NMR spectra gave clear information on rate of glass dissolution and apatite formation. Complimentary evidence from XRD and ^{31}P MAS-NMR showed that the novel higher phosphate containing glass formed apatite in a significantly shorter time frame than the low phosphate glass used for comparison. ^{19}F MAS-NMR showed that the presence of fluoride in the glass led to formation of FAp rather than hydroxyapatite (HAp). In conclusion, fluoride and high phosphorus content in the bioactive glass promoted the rapid formation of FAp which is more stable than conventional HAp and more attractive for dental applications.

Ref: 11

Phosphate based bioactive glasses have an advantage over traditional silicate based bioactive glasses in that they are closer in composition to natural bone. Certain applications, such as coatings on long term implants, needs the solubility to be reduced without reducing the bioactivity; a common approach to achieve this is adding high valence cations such as aluminium. Small amounts of aluminium improve the bioactivity, however continuing to add aluminum will result in a decrease in the bioactivity of the glass. It is assumed that this change in bioactivity is due to a structural rearrangement in the local environment of the aluminum. Glass of composition $(\text{CaO})_{44.5}(\text{P}_2\text{O}_5)_{44.5}(\text{Na}_2\text{O})_x(\text{Al}_2\text{O}_3)_{11-x}$, where x is 3, 6, 8, 11, were made using a standard melt quench process and studied using neutron diffraction. The observed change in atomic-scale structure suggested by the data, in particular the local aluminium environment, will be linked to the measured change in bioactivity.

Symposium I

Science III

Ref: 12

The structural role of chalcogens S, Se and Te in As_2Ch_3 glasses

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Chalcogenide glass structure is more difficult to elucidate than an analogous oxide glass due to the tendency for chalcogens to form homopolar bonds. While in As_2O_3 all As atoms are bonded to three oxygen atoms, and all oxygens are bonded to two arsenic atoms, $\text{As}_x\text{Se}_{(1-x)}$ (for example) will have varying ratios of As-As and Se-Se bonds (sometimes forming Se chains), depending on composition. Nonetheless, to understand these structures is of great importance when developing them as materials for optical applications and, although relatively simple, Arsenic chalcogenide glasses, As_2Ch_3 , are of great scientific interest.

As_2Se_3 has a NLO response ~1000 times larger than that of SiO_2 in the near infrared region, and both As_2S_3 [1] and As_2Se_3 [2] have been used as the core material in SCG fibres operating between 2 and 4 μm . The increase in NLO response when replacing S for Se in this system, and others (eg GeCh_2), is well documented [3-6]. However, while there are a number of diffraction studies on this system in the literature [7-9], none are comprehensive or attempt to relate the structure to optical properties. Reports of the presence of homopolar bonds in GeSe_2 [10], and the absence in GeS_2 [11] suggests that the formation of homopolar bonds plays a role in determining the NLO response of the glass.

This presentation is a structural study of a series of glasses $\text{AsSe}_x\text{Ch}_{(3-x)}$, where Ch is S or Te and x = 0, 1, 1.5, 2 and 3. By using neutron diffraction, with additional input from Se NMR and Raman, the changes in glass structure with composition will be determined. Ch-Ch bonds have been identified in As_2Ch_3 glasses containing both Se and Te. Therefore, identifying and quantifying the defects present, understanding how the concentration varies with composition, and relating their presence to NLO response key goal of this study.

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Thermoanalytical properties and structure of As-Sb-Ch (Ch = S, Se) glassy systems

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Chalcogenide glasses whose composition contains elements of the groups IV or V of periodic table and chalcogen elements S, Se and Te have been intensively studied materials because of their possible applications, e.g. as photoconductors and memory switching devices. Study of the structure of amorphous semiconductors is one of crucial keys for understanding their physical properties and thus for designing for application. In this work thermal properties of $As_{40-x}Sb_xCh_{60}$ (Ch = S, Se; x changes from 0 to 24 at.%) and $As_{20}Sb_{20}S_{(60-x)}Se_x$ bulk glasses (x = 0 -60 at.%) were studied by both conventional differential scanning calorimetry (DSC) and StepScan DSC, the later allows fairly good separation of reversible changes from kinetic processes (enthalpic relaxations, in our case). Thus the glass transition temperature free from the influence of thermal history could be determined from StepScan DSC data. Using conventional DSC, the crystallization ability of glass forming melts were also studied and treated by usual procedures for non-isothermal crystallization analysis. Chemometric analysis of Raman spectra by PCA (Principal Component Analysis) and spectral decomposition by the method of Zakaznova-Herzog and Malfait combined with results of thermodynamic modelling based on Shakhmatkin and Vedishcheva approach were used to obtain information about basic structural units of the studied glasses.

Evolution of the mechanical properties of the tin and air sides of float glass as a function of hydration time

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Abstract

Soda-lime-silica float glass has been exposed to accelerated weathering conditions (95% relative humidity at 40°C) for periods of time varying from 3 to 49 days. Nanoindentation data will be presented showing significant differences in the hydration behaviour of the tin side and the air side of float glass. In particular the nanohardness of the air side is initially lower than that of the tin side and this value is further reduced after only 3 days exposure to 95% r.h. at 40°C and continues to drop significantly with increasing exposure time. In marked contrast the nanohardness of the float side is relatively little affected by the exposure to 95% r.h. at 40°C. Similar results are obtained for the reduced moduli of the surfaces. The data to be presented confirm that the presence of tin significantly reduces the rate of near surface hydration of float glass as compared to the air side.

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High Lead Oxide Glass Structure

Oliver L. G. Alderman*, Diane Holland, Alex C. Hannon, Steve Feller

The structural role of Pb^{2+} in oxide glasses has been studied by diffraction methods for over three quarters of a century. With improvements in measurement and analysis techniques, over the years the intermediate role of PbO , in terms of glass formation, as distinct from both glass forming oxides, such as silica, and modifying oxides, such as soda, has become more clear. In this contribution analyses of high resolution x-ray and neutron diffraction data collected on lead silicate and germanate glasses containing up to 80mol% PbO (93.7 wt.%), which can be formed by rapid twin roller quenching, are presented. The results are unique in terms of the high PbO content of the glasses, and the high spatial resolution obtained using pulsed neutron diffraction, and are analysed both by peak fitting and empirical atomistic modelling driven by the measured pair distribution functions and bulk densities.

Symposium II

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Oxyfluoride Glass-Ceramics

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This paper will give an introduction to glass-ceramics, crystal nucleation and growth. This will then be followed by an in depth look at oxyfluoride glass-ceramics including; fluorcanasite, fluorichterite, fluormica and fluorapatite systems.

The importance of glass structure in relation to the crystal phases that form will be discussed in relation to the fluorine speciation in the glass.

The presentation will then focus on fluormica glass-ceramics that are the basis of machinable glass-ceramics. The importance of the design of the starting composition will be emphasized and the determination of appropriate nucleation and growth heat treatments.

Finally fluorapatite glass-ceramics for biomedical applications will be discussed. The importance of amorphous phase separation in achieving bulk nucleation will be outlined and its role in determining crystallite size. Real time neutron diffraction and small angle neutron scattering results will be presented. Factors of importance in obtaining nano-crystalline glass-ceramics based on oxyfluoride systems will be discussed.

Science IV

Ref: 21

Zinc-containing bioactive glasses: Dissolution and apatite formation

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Bioactive glasses degrade in the body, releasing ions and forming apatite. They are used as bone replacement and regeneration materials in orthopaedic and periodontal applications since 1985. Lately they have also been used as a remineralising additive in dentifrices. Incorporation of zinc into bioactive glasses is of interest because it is bactericidal and essential for bone growth and wound repair. As zinc is an intermediate element, studying its structural role in bioactive glasses is important for the successful design of zinc-releasing bioactive glasses. Two series of bioactive glasses ($\text{SiO}_2\text{-P}_2\text{O}_5\text{-CaO-SrO-Na}_2\text{O-CaF}_2\text{-SrF}_2\text{-ZnO}$) have been produced by a melt-quench route. In the first series it was assumed that ZnO behaves as a network modifier (i.e. maintaining a constant network connectivity if all zinc forms non-bridging oxygens), while in the second series it was assumed that ZnO enters the silicate network (i.e. maintaining a constant network connectivity if all zinc forms Si-O-Zn bonds). Zinc-free glasses were used as controls. Ion release and apatite formation were investigated in Tris buffer solution (initial pH 7.3) at 37°C over up to one week. Dissolution under acidic conditions was investigated in acetic acid solution at pH 4. Solutions were analysed by inductively coupled plasma emission spectroscopy, and glass powders before and after treatment were characterised by infrared spectroscopy and X-ray powder diffraction. While in Tris buffer about 80% of Ca, Sr and Na ions in the glass were released, the release of zinc was negligible. By contrast, under acidic conditions, nearly all of zinc was released within about 15min. Apatite formation in the zinc-containing glasses was delayed by 24h to several days compared to the zinc-free controls. These results suggest that in bioactive glasses, zinc enters the silicate network rather than behaving like a typical modifier cation. Magnesium, which is also an intermediate element, was shown in the past to partially enter the silicate network (about 15%) and partially act as a modifier. The ion release behaviour here, however, suggests that nearly all of the zinc enters the network, forming Si-O-Zn bonds, which are acid hydrolysable. This results in negligible zinc release under neutral conditions (as zinc is bound in the silicate network), but under acidic conditions these Si-O-Zn bonds are hydrolysed, resulting in the release of most of the zinc within just a few minutes. As apatite formation was inhibited in both series, i.e. independent of glass network connectivity, it suggests that even very low zinc concentrations in solution affect apatite formation. Further experiments, particularly by solid-state nuclear magnetic resonance spectroscopy, are necessary to further elucidate the role of zinc in bioactive glasses.

BOROSILICATE GLASS ALTERATION IN ACIDIC AND BASIC CONDITIONS WITH VARIOUS CALCIUM CONTENTS

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In the French geological repository concept, intermediate-level vitrified wastes could be disposed of in cement medium. Glass dissolution mechanisms and kinetics are expected to strongly depend on chemical composition as well as the pH of leaching solutions. Experiments were conducted in various cement waters corresponding to different stages of the cement aging. In order to investigate the calcium effect more precisely, the initial alteration rate of a simplified nuclear glass was studied in various calcium content solutions with a wide pH range at 50°C. The initial alteration rate was clearly dependent on both the pH and calcium in solution. The presence of calcium increased the initial alteration rate between pH 4 and pH 10.8, with a maximal factor of 5 around pH 8 compared to the reference media (same pH in HCl or KOH solution). Conversely, the initial alteration rate diminished beyond pH 10.8, with a factor of about 6 at pH 11.7. Glass surface characterizations by ToF-SIMS revealed a calcium incorporation into the alteration layer formed at pH 11.7. These findings give a first insight into the formation of a calcium silicate passivating layer that could modify the alteration kinetics through the Si-O bond hydrolysis. The calcium concentration effect (5, 50 and 150 mg.L⁻¹) on the initial alteration rate is also discussed. These results are used to improve our knowledge of nuclear glass alteration in cement waters, represented by alkali dissolution and equilibrium with Portlandite.

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Corrosion of 725QN Glass Fibers in Borate Water Solution.

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Abstract

725QN 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 725QN fiber was tested in present work. The static and 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.

Effect of divalent cations and chloride salts on the dissolution of silicate glasses

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The dissolution kinetics and morphology of silicate glasses are of interest in the glass industry (short term alteration in various conditions) and in the nuclear industry (glass wasteforms, altered on the very long term in static conditions). The dissolution of multicomponent silicate glasses involves ionic exchange and hydrolysis reactions, that are kinetically controlled by diffusion and surface respectively, giving rise to the formation of thick and porous glass-water interphases, referred to as "gels" in simple silicate glasses. The purpose of our work is to investigate the effect of divalent metal cations present in solution as chloride salts, such as Zn^{2+} , Fe^{2+} , Mg^{2+} and Ca^{2+} on the dissolution of silicate glasses. In the present study, the initial dissolution rates of a borosilicate and a soda-lime silicate glass have been measured at $T = 80^\circ C$ in solutions with increasing concentrations of salts, with or without a buffer to fix the pH (7.5). Calibrated powders are used to control the S/V ratio, as well as polished glass plates to allow for surface characterization (ToF-SIMS, AFM). For Zn^{2+} that has an important effect in diminishing the Si-O-Si hydrolysis rate (at pH 7.5, Figure 1), adsorption isotherms are measured to investigate the glass- Zn^{2+} surface reactivity. The aim of this work is to understand how the cations may modify the elementary processes (ionic exchange, hydrolysis) and what consequences this may have on the long term dissolution. In addition, the effect of chloride anions on the initials is specifically studied in alteration experiments with KCl salt.

Time (days)

Figure 1: Normalized leached fractions (NL) of left) Si and right) Na for a sodium borosilicate glass altered in three solutions, TRIS/HCl (buffer), TRIS/HCl and $ZnCl_2$ 1.10^{-4} mol.L⁻¹ named 10⁻⁴, and TRIS/HCl and $ZnCl_2$ 1.10^{-2} mol.L⁻¹ named 10⁻². The sharp increase in NL is attributed to the opening of porosity due to Na and B departure during the first stage of alteration (L. Sicard, et al., J. of Phys. Chem. C. 112 (2008) 1594-1603.)

Science V

Ref: 25

Surface Crystallization Behavior and Nonlinear Optical Property of Bismuth Zinc Borate Glasses

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Non-centrosymmetric Bi₂ZnB₂O₇ (BZB) crystal in a family of melilite [1] is attracting much attention because of its own optical nonlinearity. Glasses in bismuth zinc borate system have a good ability for glass formation and good stability against chemical attacks, and the systematic survey on the crystallization of BZB phase in the glass system will lead to a new field or application for nonlinear optical glass-ceramics.

In this study, crystallization behavior of stoichiometric 33.3Bi₂O₃-33.3ZnO-33.3B₂O₃ glass was investigated. The target BZB crystals were precipitated on the glass surface by heat-treatment at higher than 440°C. However, the glass samples changed in shape by softening at elevated temperatures. In order to fabricate BZB-crystallized glass-ceramics maintaining its original rectangular shape, ultrasonic surface treatment (UST) was confirmed to be effective, which preceded the crystallization heat-treatment, and lowered the crystallization onset considerably [2].

In the case of lower heat-treatment temperature, ~430°C, unknown phase other than BZB was also precipitated. It appeared on the glass surface only, and was found to be a metastable phase, as is reported for Ln-containing bismuth borate glasses [3]. Optical evaluations, such as transparency, refractive index and optical nonlinearity were carried out for the transparent surface crystallized glasses with BZB and/or metastable phases. According to the analysis of Maker fringe patterns, the metastable phase will be another candidate of target crystal with sufficient optical nonlinearity. The relationship between the crystallization behavior and resulting nonlinear optical property of both phases was discussed.

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Mr James Stevens, University of Sheffield

For New Researchers Forum

Title:

Understanding the effect of refractory spinel phases on HLW glass processing.

Abstract:

Refractory spinel phases are known to form during the vitrification of wastes arising from nuclear fuel reprocessing. Understanding the route of formation, quantity and distribution of these crystals in the melt and the final product will aid in predicting if any long term detriment to the stability and durability of the waste form is to be expected. The general chemical formula for spinel present in the vitrified simulated waste has been investigated and comparative data for spinel crystal identification as a function of waste loading has been investigated. The fraction of spinel crystal in the vitrified waste has been analysed. A simplified thermodynamic model of the vitrification process has been developed.

Ref: 27

GLASS COMPOSITES PREPARED BY MICROWAVE HEATING FOR THE IMMOBILISATION OF IRRADIATED GRAPHITE WASTE

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ABSTRACT

Approximately 250,000 tonnes of irradiated graphite waste is a major disposal challenge for the nuclear industries in the UK and around the world. The immobilisation of irradiated graphite waste using microwave heating offers several potential advantages over conventional heating methods including being a clean, fast and hence potentially low cost synthesis route. In this work, iron phosphate glass composites have been prepared from mixtures of $\text{NH}_4\text{H}_2\text{PO}_4$, Fe_3O_4 and simulated irradiated graphite waste. Compacted mixtures of the glass batch materials and the simulated waste were subjected to microwave sintering for various exposure times ranging from 1 to 20 minutes and cooled to produce glass composites. The resulting glass composites were then characterised by various analysis methods including assessing mass loss during processing, X-ray diffraction (XRD), scanning electron microscopy (SEM) and density measurement. The glass composites were shown to immobilise simulated irradiated graphite waste. Work is ongoing to understand more fully the effect of process variables and to improve the mechanical integrity of the simulated wasteforms.

Keywords: Glass composites; Microwave heating; Irradiated graphite waste

Ref: 28

The Development of Glass Compositions for the Vitrification of Ion Exchange Resin Wastes

Ion exchange resin waste are problematic for vitrification due to their organic nature, and due to the presence of problematic anionic species which lead to phase separation in glasses. The presence of a large inventory of radiologically contaminated ion exchange resins from civil nuclear power generation means that the development of a suitable route of vitrification is essential, in order to render the radionuclides present immobile and safe. This presentation will explore the development of three potential glass compositions intended for the purpose of ion exchange resin vitrification, covering systematic studies of composition variation and the structural and physical effects of these changes and waste-loading experiments which have explored the capacity of these glass systems to retain radionuclides and withstand high concentrations of anionic species and organic species.

Ref: 29

Distribution behavior of inorganic constituents in municipal waste slag due to phase separation of vitrified slag

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The authors research group has developed a novel recycling method of inorganic wastes such as granulated blast furnace slag [1] and municipal waste slag [2], in which phase separation of glass was used to obtain SiO₂-abundant transparent glasses. The slags consist of SiO₂, CaO, Al₂O₃, and Fe₂O₃ as major constituents, and B₂O₃ is added to the slags to promote phase separation of the slag glasses. The purpose of this study is to investigate the distribution behavior of the slag constituents.

The slag used in this study was discharged from a waste incineration plant in Okayama prefecture, Japan. The powdered slag and B₂O₃ with weight ratios of 10:0, 9:1, 8:2 were mixed and melted at 1400°C for 1 hour in a platinum crucible and then press-quenched on a steel plate, obtaining slag glasses. The slag glasses were heat-treated at the temperatures above glass transition temperature, T_g. The heat-treated slag glasses were acid-treated. After vacuum filtration, the insolubles were rinsed in water and dried, obtaining the end products. Compositions of the slag glasses and end products were determined by X-ray fluorescence (XRF) analysis, and the filtrate composition was determined by inductively-coupled plasma optical emission spectroscopic (ICP-OES) analysis.

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Ref: 30

The structure and vitrification process of arsenic chalcogenide $\text{As}_{50}\text{Se}_{50}$

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Scientists all over the world for almost 300 years are trying to discover the secret of the glass transition and understand the structure of glass -Frankenheim (1835), Mendeleev (1864), Lebedev (1921), Zachariasen (1932), Winter-Klein (1953), Porai-Koshits (1959), Goodman (1975), Lucovsky (1979), Greaves (1981), Wright (1982), Elliott (1984), Gaskell (1992), etc.

The significant contribution in understanding of a physicochemical nature of glass transition process is made by the concept of polymeric nanoheteromorphous structure of non-crystalline substance proposed by Minaev (1987). According to its particular case for the individual chemical substance (ICS) -concept of polymeric-polymorphoid structure of non-crystalline substance [1,2], glass, in particular $\text{As}_{50}\text{Se}_{50}$, is a copolymer of structural fragments (polymorphoids) of different crystal polymorphous modifications (PM).

Polymorphoids has no translation symmetry (long-range order), but characterized by strictly defined intermediate-and short-range orders inherent to one of the PMs taken part in glass formation.

This concept shows that all effects in glasses are the result of various PMs polymorphoids interconversion process. The high temperature and low temperature PM (HTPM and LTPM) are the most probably participants of this process.

Crystalline arsenic selenide $\text{As}_{50}\text{Se}_{50}$ exists in two polymorph modifications.

HTPM As_4Se_4 is isomorphic to the molecular modification of realgar ($\alpha\text{-As}_4\text{S}_4$). HTPM was not fully identified by x-ray scattering.

Cooling of $\text{As}_{50}\text{Se}_{50}$ glassforming melt in the range from the melting temperature T_m (~280-300°C) to the Tamman's glass transition temperature $T_g(T)$, transforms viscous flow liquid into a solid brittle glass.

The glass transition process is a dual process of copolymerization-depolymerization: the copolymerization of HTPM and LTPM polymorphoids in the range of $T_m-T_g(T)$ and depolymerization due to the decay of LTPM polymorphoids and turning them into HTPM polymorphoids above the generally accepted today glass transition temperature « T_g », and the decay of HTPM polymorphoids and transformation them to LTPM polymorphoids below « T_g ». « T_g » temperature unjustly replaced the Tamman's temperature T_w (indung) on the "property-temperature" dependence associated with reversible interconversion polymorphoids HTPM \leftrightarrow LTPM and therefore may be called the temperature T_{rev} (for $\text{As}_{50}\text{Se}_{50}$ $T_{rev}\sim 170^\circ\text{C}$). Thus, the concentration ratio of polymorphoids (CRP) HTPM:LTPM

increases above and decreases below T_{rev} . Glass annealing above the T_{rev} temperature leads to crystallization in HTPM and, accordingly, annealing below T_{rev} leads to crystallization to LTPM.

A CRP of different PMs, changing in dependence of the vitrification process conditions, is a most important internal parameter of the glassforming thermodynamical system that quantitatively determines the structure and properties of the ICS [2], in particular, glass $As_{50}Se_{50}$.

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Ref: 31

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Science VI

Ref: 32

Abstract title A prediction tool of the oxides melts Glass Forming Ability

A prediction tool of the oxides melts Glass Forming Ability Roula. Abdelmalek* , Boubata Nouar & Moussaoui Islam. *Jijel Univ.; PNR-ANDRU- LIME; Eng. Sci. Fac.; Jijel; 18000; Algeria; amkroula@univ-jijel.dz* Abstract. The glass forming ability (GFA) quantifies the behaviour of oxides to solidify in an amorphous state. The oxide Global Relative Glass Forming Ability (GRGFA) is a new analytic model to compute it [1]; it is based on both thermodynamical and cristallochemical considerations. This criterion takes into account the isobaric thermal capacity (C_p) and the ratio of the cell volume (V) with the ionic distance (d_{ExOy}) that were both omitted in all prior GFA models. The accuracy of this global and relative approach is comforted by its depending parameters panoply: values of the dissociation energy (E_d), the coordination number (l), the melting temperature (T_m), the cation and anion radii (r_c and r_a), the cation valence (v_c), the cell volume (V_{ExOy}) of the considered oxide combined to values of C_p and V/d_{ExOy} . Thus, the GFA of any oxides melt may be computed as following: where GFA_m is the GFA of the studied (m) oxides melt, u is the uncertainty coefficient, n (i) is the number of the melt constituting oxides ($O_1 - O_n$), O_i is the amount of the considered oxide and $GRGFA_{oi}$ is the Global Relative Glass Forming Ability of the i -th constituting oxide. The uncertainty coefficient value (u) is proposed to be the ratio where FO, IO and MO are the amounts sums of forming oxides (FO), intermediate and modifying oxides (IO and MO), respectively. The algebraic sum is then considered to be the melt GFA intrinsic value.

As application on several SiO_2 -based glasses and ceramics chemical compositions, the computing according to this quantitative model permits to determine a GFA_m frontier value sorting glasses from ceramics. Thus, this model may be used as a predicting tool of oxides melts GFA (determination of minimal content of glassforming oxides and maximal contents of intermediate and/or modifying oxides).

Keywords: Oxides, Oxides Melts, Glass Forming Ability. 3D surface plot (distance weighted least squares) of GFA_m against uncertainty coefficient (U) and melt intrinsic GFA (Intr. GFA).

Ordering and structural changes at the glass-liquid transition

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Ordering types in the disordered structure of amorphous solids and structural changes which occur at glass-liquid transition are discussed revealing ranges of sizes with medium range order and reduction of topological signature of disordered bonding lattice.

Recent direct AFM-visualisation of fractal structures near the glass-liquid transition temperatures [1] gave direct proofs that the glass transition is associated with structural changes in the disordered distribution of atoms [2]. Transformation of a liquid on cooling into a glass (i.e. glass transition) can take place at melt cooling rates rapid enough that crystallisation is kinetically avoided. Liquid-glass transition phenomena are observed universally moreover all liquids can be in practice vitrified provided that the rate of cooling is high enough to avoid crystallisation. Both glasses and liquids are isotropic, e.g. the translation-rotation symmetry of particles is unchanged at the glass-liquid transition. Nevertheless glasses have elastic properties of isotropic solids which are qualitatively different compared liquids. The difficulty to understand the glass transition is because of almost undetectable changes in the structure of amorphous materials despite of the qualitative changes in characteristics and extremely large change in the time scale of relaxation processes [3].

Although both liquid and glassy (e.g. solid) phases have a topologically disordered structure there is a significant change in the topological signature of their bonding system at glass-liquid transition. Namely, it has been recently revealed that the Hausdorff dimension of bonds changes from the 3 in the solid (glassy) state to $D_f = 2.55 \pm 0.05$ in the liquid (molten) state [2]. E.g. melted amorphous materials have a fractal geometry of bonds and because of that a liquid-like behaviour, whereas glasses (solid amorphous materials) a 3-D geometry of bonds and because of that they have a solid like behaviour. The glass-liquid transition is a percolation-type phase transition in the system of broken bonds - configurons with formation near the percolation threshold of dynamic [2] or twinkling [1] fractal structures and it is therefore associated with the reduction of the Hausdorff dimension of bonds. The average size of clusters formed at temperatures not very far from glass-liquid transition temperatures is described by the correlation length $\xi(T)$. Depending on range of sizes involved the structure of an amorphous material can be hence characterised as follows:

- i. Short Range Ordering with molecular type units such as tetrahedral structures in silicates, at atomic size range;
- ii. Medium Range Ordering with fractal structures (dynamic or twinkling which can be frozen in the glassy state) at correlation length range;
- iii. Disordered state which is homogeneous and isotropic at macroscopic sizes.

Therefore medium range order recently revealed in metallic glasses [4] can also serve as a proof that glass-liquid transition is a percolation-type phase transition. Moreover both theory and experiment reveal the same dimensionality for remnant clusters in glasses which are fractal structures with Hausdorff dimensionality ≈ 2.5 . Note that molecular dynamic simulation has also revealed percolation clusters (made up of icosahedrons [5]) at glass transition.

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Ref: 34

Glass transition temperature T_g and direction reverse temperature T_{rev} of different polymorphous modifications interconversion in glassforming substance

Minaev V.S. State Unitary Enterprise Scientific-Production Center SPURT, Moscow, Russia Tamman (1933) [1] identified the two most important temperatures of glassforming substance on property-temperature dependence - the inflection temperature T_w (windung in German) and the transformation temperature from a highly viscous liquid to fragile solid glassy state - T_g , which lies below T_w .

Lindig (1959) used the symbol T_g to indicate a temperature within the glass transition range which characterizes the intersection of the temperature dependence of the properties in the liquid and glassy state (i.e. T_w). Thus, Lindig has canceled Tamman's T_g and T_w and the last temperature designated as T_g , reducing glass transition range by about the half.

Majority of scientific community agreed with this "innovation" because Tamman, did not formulated the physicochemical essence of the inflection temperature T_w . This essence has been identified only in the late 90s -early 2000s, in the concept of polymerpolymorphoid structure of glassforming substances (Minaev [2,3]). Accordingly with this concept, glassforming liquid and the glassy state have a common physicochemical nature - they are composed of structural fragments (polymorphoids) of different crystalline polymorphous modifications (PM) without a translation symmetry (long-range order), copolymerized to a greater or lesser degree, respectively, in a glassy or a liquid state. Interconversions and changes of the concentration ratio of polymorphoids (CRP) of

1

different PM under various external influences and time -the fundamental reason of the structure and properties changes in glassforming substances during the relaxation process.

Consideration of results obtained by Winter-Klein (1953), Nemilov (1976), Artamonova (1983), Mazurin and Minko (1987), Popescu (2000), Landa et al. (2004), from the point of view of our conception conclusively proves the truth of the Tamman's glass transition temperature $T_g(T)$ and illegitimacy of replacement of Tamman's temperature of inflection T_w which lies approximately in the middle of the glass transition interval -on the « T_g ».

Data on polymorphic transformations in the glass and glassforming liquids presented by Bernal and Fowler (1933), Deeg (1957), Brückner (1970), Elliot (1984), Landa (1984), Blinov (1985), Popescu (1985), Gerber and et al. (1988), Golubkov (1992), Greaves (2008) and other authors, were analyzed and generalized by Minaev (2004-2011). Results with all certainty have shown that the Tamman's inflection temperature T_w (common today « T_g ») is nothing but the reverse temperature T_{rev} of polymorphoids' interconversion direction of high-and low-temperature polymorph modifications (HTPM and LTPM) of glassforming substances (polymorphoids of quartz and cristobalite for SiO_2). The temperature above the T_{rev} occurs the process of polymorphoids transition LTPM→HTPM and below - HTPM→LTPM. And, accordingly, there is an increase in CRP HTPM: LTPM above T_{rev} and its reduction -below T_{rev} until their eventual crystallization. The prototype of the T_{rev} temperature is a polymorphic transformation temperature T_{tr} HTPM↔LTPM in the crystalline substance.

Thus after the determination of the physico-chemical meaning of Tamman's T_w , glass

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transition temperature " T_g " which is common today becomes an artefact and should be replaced by the temperature, which can be assigned with symbol T_{w-rev} , showing the pioneering role of Tamman in establishing this inflection and physical-chemical nature of this inflection, which determines the fundamental difference in the glass transition process above and below this temperature.

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3

Overcoming of some shortcomings of the thermodynamic modeling of glass

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The well and commonly applied thermodynamic glass model of Shakhmatkin and Vedishcheva is based on the assumption of the ideal solution behavior (ideal mixing = zero mixing enthalpy plus regular mixing entropy) of different structural groupings stoichiometrically corresponding to stable crystalline phases of the particular glassforming system.

The present contribution deals with solving the problem of missing information about the stable crystalline phases (missing phase diagram) and, simultaneously, of the - at least partial - overcoming the shortage of the ideal solution behavior.

The proposed method uses the spectroscopic (e.g. solid state NMR, Raman, infrared, neutron scattering, etc.) determination of the relative abundance (concentration) of various structural units (no complete set of units is needed to be monitored) in a set of glasses of different composition. The hypothetical set of structural groupings (stable crystalline phases) is confirmed by nonlinear regression analysis of experimental concentration data. The model of simultaneous equilibria determined by the values of equilibrium constants followed from the molar Gibbs formation energies of individual structural groupings is used for evaluation of calculated concentrations. The example of using the quantum (DFT) molecular dynamics simulation data as a zero estimates of the molar Gibbs energies of the structural groupings is illustrated in the present work. The non-ideality is (at least) partially included by releasing the numerical values of individual molar Gibbs formation energies for optimization in the non linear regression analysis of experimental concentration data. The minimum of the sum of squares of deviations between the measured and calculated concentrations of different structural groupings is used as a target criterion in the above regression treatment. From the experimental point of view it is very important that not a full set of experimentally measured concentrations is needed for this procedure. Allowing the deviations of molar Gibbs formation energies of individual groupings from the correct experimentally determined values represents the simplest way of overcoming the strictly ideal behavior of the system proposed by the model of Shakhmatkin and Vedishcheva. In some respect (e.g. like a preliminary step) this method resembles the introduction of Lewis' activities for description of the thermodynamics of the non ideal solutions.

Science VII

Ref: 36

THE CHEMICAL BOND APPROACH TO GLASSY STATE

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Dedicated to Prof. S.A. Dembovsky (1932-2010)

The most of the present day theories of glass are physical in nature. This means that chemical bond, as chemists know it, is actually absent there, either completely or being represented by simplified models such as sticks or springs. Another tendency is physical modeling of glass transition by means of hard spheres or grain materials, an approach that ignores chemical bond as a real object. The term Physics and Chemistry of Glass, being also the name of leading journals (both English and Russian), implies now that physics concerns with glass theory while chemistry - with synthesis of glassy compositions with variable properties. A similar situation exists in the problem of glass structure, which is compared with crystallographic order (symmetry operations that create the atomic arrangement) but not with chemical bonds that define the atomic arrangement, both in crystals and glasses. In crystals there is characteristic translational long range order. In glasses, in addition to classical short-range order (*Zachariasens* classical model of continuous random network, CRN), there is a direct evidence for medium-range order, MRO (observed by FSDP) and indirect evidence for non-crystalline long-range order, LRO. There is no a conventional understanding of even MRO. The chemical bond approach presented here is based on the *Dembovskys* concept about hypervalent bonds (HVB) as alternative bonding states that, interacting with normal covalent bonds, provide glass formation and particular properties. I was lucky to elaborate this concept together with its author for more than 20 years [1]. As a result an original model of self-organization of HVB in CRN, the bond wave model has arisen [2-5]. The present day state of this model, including structural aspects (e.g., interpretation of MRO and specific *wavy* LRO) and synergetic aspects (e.g., information fields for bond wave), is given.

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Ref: 37

Molecular dynamics modelling of phosphate glasses

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Molecular dynamics simulations with rigid ion potentials have been used to model a range of phosphate glass structures: pure P_2O_5 , and Na, Ca, Fe and Tb phosphate glasses. The results show distinct P bonding to bridging and non-bridging oxygens as expected, and show reasonable agreement with experimental neutron and x-ray diffraction data. The models illustrate key differences of phosphate glasses compared to silicate glasses: lack of bonding to bridging oxygens, and durability increasing with modifier content. The latter culminates in the striking durability of iron phosphate glasses. It is difficult to reproduce the experimental Q_n distributions from ^{31}P NMR, which is often a limitation in models of oxide glasses. This becomes more difficult for compositions where Q_m - Q_n ordering is expected, such as ultraphosphate glasses. The models also enable a study of the distribution of modifier cations. The factors influencing the distribution of modifier cations can be understood in some cases, such as Tb phosphate glasses, but it remains a challenging topic for other phosphate glasses.

Ref: 38

Structural relaxation of PbO-WO₃-P₂O₅ glasses

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The structural relaxation of three compositional series of PbO-WO₃-P₂O₅ glasses with composition (0.5 - x / 2) PbO • x WO₃ • (0.5 - x / 2) P₂O₅, x = 0, 0.1, 0.2, 0.3, 0.4, 0.5; 0.5 PbO • x WO₃ • (0.5 - x) P₂O₅, x = 0, 0.1, 0.2, 0.3; and (0.5 - x) PbO • x WO₃ • 0.5 P₂O₅, x = 0, 0.1, 0.2, 0.3, 0.4, 0.5 was studied by thermomechanical analysis. The relaxation was described using a mathematical model based on the stretched exponential relaxation function with relaxation time proportional to actual viscosity. The viscosity dependence on thermodynamic temperature and fictive temperature was expressed by Mazurins approximation. The relaxation parameters dependence on the glass composition was studied. It was found that the modulus is increasing with increasing amount of WO₃ in all glasses. On the contrary, the width of the spectrum of relaxation times is decreasing with increasing amount of WO₃ in all studied glasses.

Ref: 39

Effect of alkaline-earth oxides on the devitrification of fluor-alumino-phosphosilicate ionomer glasses: an XRD and NMR study

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Calcium fluor-alumino-phosphosilicate glasses are widely used to form glass ionomer cements for medical and dental applications, and are able to crystallise into apatite-mullite mixed-phase glass-ceramics that can show excellent osteo-integration and osteo-conduction properties when implanted in the body.

Replacement of some or all of the calcium content by other alkaline earths can produce useful property modifications such as radio-opacity. The biocompatibility of these new materials will depend on their chemical and also phase composition. The latter can be determined to some extent using x-ray diffraction (XRD) though the large number of phases present, combined with the complexity of some of the crystal structures, makes the XRD patterns difficult to resolve and interpret. It is fortunate that the constituents of the samples contain several elements with nuclei which are relatively easy to observe using nuclear magnetic resonance (NMR) and ¹⁹F, ²⁷Al, ²⁹Si and ³¹P are used in the current study. The glass-ceramics are generally dominated by an aluminosilicate phase (mullite for Mg²⁺ and Ca²⁺; celsian for Sr²⁺ and Ba²⁺) and a

fluorophosphate phase (fluorapatite for Ca²⁺, Sr²⁺ and Ba²⁺; and wagnerite for Mg²⁺).

Ref: 40

The Role of Oxygen in the Germanate Anomaly

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As modifier oxide is added to a germanate glass, it is commonly found that there are maxima or minima in the thermophysical properties at a specific composition, and this behaviour is known as the *germanate anomaly*. There is now a body of evidence to show that there is a corresponding growth and subsequent decline in the proportion of germanium atoms which have a coordination number greater than the tetrahedral value of four. However, it has been observed that the mean Ge-O bond length also grows, but then does not decline for high modifier content. It is firstly shown that the behaviour of the bond length can be explained by considering that bridging oxygens may be coordinated by modifier cations, as well as two Ge atoms, so that in effect the modifier cations pull the bridging oxygens away from the Ge atoms. It is then shown that oxygen can be viewed as playing a role in the germanate anomaly; the way in which modifier oxide is accommodated in the network appears to depend on how many modifier cations are coordinated to the bridging oxygens.

Science VIII

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Functionalization of glass surface by nanocomposite TiO₂ films

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The properties of glass are excellent, but for some specific applications it can be useful to modify its optical, thermal and other properties. In present study the nanocomposite TiO₂ films were used for functionalization of glass surface. The TiO₂ films deposited on glass substrate have been prepared by the sol-gel method. The films were coated from sols with different size of TiO₂ nanoparticles by dip-coating technique. The sols with different particle size were prepared by aging. The prepared samples were characterized using ultraviolet-visible (UV-VIS) spectroscopy and atomic force microscopy (AFM). The influence of nanocomposite TiO₂ films with different particle size on changes of optical properties, surface morphology and topography of glass surface coated with films was studied.

Ref: 43

Study of water physisorption on TiO₂-SiO₂-Al₂O₃ thin film by impedance spectroscopy

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The influence of precursor sols composition on physisorption of water on SiO₂-TiO₂-Al₂O₃ films prepared by sol-gel method was studied by impedance spectroscopy. The composition of prepared layers, expressed by SiO₂:TiO₂:Al₂O₃ ratio, was in the range of following molar ratio: 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. Complex impedance spectra of thin film sensor at various relative humidities - in the range 0.13 -97.7 %, and in the frequency range 1 kHz to 1 MHz were measured. Measured dependences of complex impedance on frequency were processed by complex nonlinear least squares method. Serial connection with different counts of -(R/C)-, -(R/CPE)- and -R- equivalent circuits was used to analyze obtained spectra. The equivalent circuits were associated with physisorption of water, space charge polarization regions, and bulk or surface conductivity of the films. The dependencies of the relaxation processes on the value of relative humidity and determine composition influence is used to analyze the process of physisorption of water.

Effect of different conventional melt quenching technique on purity of lithium niobate (LiNbO₃) nano crystals phase formed in lithium borate glass

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Abstract:-

The glass system (45 Li₂O + 45 B₂O₃ + 10 Nb₂O₅) were fabricated by the conventional melt quenching technique poured in water, at air, between two hot plates and droplets at the cooled surface. The glass and glass ceramics were studied by differential thermal analysis (DTA) and X-ray diffraction (XRD)

The as quenched samples poured in water and between two hot plates were amorphous. The samples poured at air and on cooled surface were crystalline as established via X-ray powder diffraction (XRD) studies. Differential thermal analysis was measured. The glass transition temperature (T_g) and the crystallization temperatures were calculated.

Lithium niobate (LiNbO₃) was the main phases in glass ceramic poured at air, droplets at the cooled surface and the heat treated glass sample at 500, 540 and 580°C addition to traces from LiNb₃O₈. Crystallite size of the main phases determined from the X-ray diffraction peaks are in the range <100 nm. The fraction of crystalline (LiNbO₃) phase decreases with increase the heat treatment temperature.

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Reinterpretation of residual entropy in terms of structural disorder and calorimetry

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Germany *cInstitut de Physique du Globe, 4 Place Jussieu, 75252 Paris cedex 05, France* The residual entropy of glasses is still the subject of controversy. First, two values of residual entropy, one based on calorimetric formula and the other based on probability population, are compared by employing a theoretical model. It is shown that two values are almost equivalent. Next, the reason why the value of entropy based on probabilistic view agrees with that based on calorimetry is discussed in contrast with the other definition based on the kinetic view. Finally, the physical and chemical meanings of such residual entropy are reinterpreted in connection with structural disorder in real crystals and glasses.

Science IX

Ref: 47

Aspects of the Correlation Between Host Composition and the Optical Spectra of Transition Elements Doped Oxide Glasses

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The presence of transition element cations within the lattice of oxide glasses modifies significantly the profile of their electromagnetic radiation absorption (NUV-NIR range). Such modifications have various positive or negative consequences on the way the host behaves in some of its applications. Moreover, interpretation of the optical spectra allows, in some cases, a better understanding of the way glass structure is affected by compositional changes. Therefore additional information on the correlation between host structure and spectra is of both scientific and technological interest.

In this work a first aspect examined was the way modification of the composition - from that producing a "normal" to one generating an invert silicate glass - affects the optical spectra. It was observed that the invert host modifies the spectra in a way indicating stabilization of higher oxidation states (V, Mn, Cr, Fe) and the displacement of the $O_h \leftrightarrow T_d$ coordination states equilibrium to the right (Co and Ni).

A second aspect examined was the spectral effect of substituting alkaline with alkaline-earth cations [(RO) with R=Co, Mg, Zn] in the composition of phosphate glasses. It was determined that an increase in the amount of alkaline oxides favors, in the case of probe dopants like Cu or Mo, the higher oxidation states, like in the case of silicate glasses. However an increase of alkaline earth content in binary P_2O_5 -RO glasses has the opposite effect, suggesting a decrease in host basicity as a result of strengthening of the bonding among the atoms of the host. In the case of copper, hosts of the form P_2O_5 -RO (RO \geq 50mol%), allow obtainment of ruby-glass without the need for a "striking" stage.

It was found out that glass composition markedly influences also the interaction of transition element dopants. Only redox type interaction was observed, with the Cr-Cu and Cr-Mn couples being the most active. The interaction modifies profoundly the optical spectra, which - when both types of metal are simultaneously present in the melt - exhibit a non additive spectral profile. The interaction intensity strongly depends on the host glass basicity, taking place only for basicity exponent, pB, values in the intermediary range.

The Environment of Fe²⁺/Fe³⁺ and Dy³⁺ Ions in a Sodium Borosilicate Glass

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The neutron diffraction isotopic substitution technique is employed to investigate the environment of both Fe²⁺/Fe³⁺ and Dy³⁺ cations in a sodium borosilicate glass. In the case of the Dy³⁺ ions, a special form of the isotopic substitution method, the null technique, is used, in which the neutron scattering length for Dy³⁺ 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 Dy₂O₃, 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 data were recorded for five samples; the base glass, the base glass incorporating natural Fe₂O₃ or Dy₂O₃ and similar glasses containing ⁵⁷Fe₂O₃ or ⁰Dy₂O₃, where ⁰Dy denotes Dy³⁺ with a zero scattering length.

The data are Fourier transformed to yield the real-space total correlation function, $\gamma(r)$, and the first coordination shells of the Fe³⁺/Fe²⁺ and Dy³⁺ ions are investigated via a peak fit to the isotopic difference correlation function $\Delta\gamma(r)$. Conclusions are drawn with respect to both the structure of the base glass and the environment of the Fe³⁺/Fe²⁺ and Dy³⁺ cations.

Glass response to the electron irradiation

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Glass irradiated with an electron beam reveals both microscopic and macroscopic changes inside (and in the vicinity of) the irradiated volume. The changes include surface roughness, chemical composition, density, hardness, Young modulus, and chemical bonding (bridging and non-bridging oxygen). Generally roughness is increasing even for the very small doses; alkali ions tend to escape from the irradiated volume sooner or later, hardness and Young modulus decreases with dose, and the density changes depends both on the composition and the electron dose. The contribution reports some effects caused mostly by medium-energy electrons (50 keV). The used beam is a defocused one to eliminate the influence of the temperature on the observed phenomena. The roughness and volume changes were monitored by AFM (Atomic Force Microscopy) while the chemical changes were recorded on-line by EPMA (Electron Probe Microanalysis), mechanical properties were measured by nano-indentation.

The glass response in mixed alkali glass, binary alkali-silicate glass, and vitreous glass is reported. In mixed alkali glass low irradiation doses showed the volume compaction, extent of which was linearly dependent on alkali ion content. It is shown the compaction can be expressed as the superposition of the relaxation around alkali ions and the silica network relaxation. High irradiation doses cause alkali depletion from the surface glass layer and reveal a typical MAE response in volume changes. Volume changes of three types of commercial vitreous silica (Homosil, Herasil, Infrasil) were observed and distinguished differences in their response to irradiation were revealed. Although most of glasses show volume expansions at high doses, vitreous silica revealed only compaction.

Ref: 50

Mössbauer spectroscopy of glasses: a UK perspective

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1

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Modern society produces toxic wastes ranging from nuclear wastes with various levels of radioactivity, to incinerator ashes such as sewage sludge ash which contains heavy metals. The harmful nature of some components of these wastes means that safe immobilisation can be necessary. Therefore methods have been, and are being, developed to immobilise these wastes. Vitrification is used in the UK to immobilise high level liquid waste (HLLW) arising from nuclear fuel reprocessing. The study and development of suitable methods and materials to immobilise waste is the focus of the work reported in this paper. ⁵⁷Fe Mössbauer spectroscopy has been used during these studies to identify the valence state and coordination of the iron in glasses and ceramics.

A material designed to immobilise waste requires structural stability, compositional flexibility, thermal stability and chemical durability. Optimum properties are obtained by modifying the composition and production parameters of glasses and ceramics.

UK high level waste (HLW) borosilicate glasses have been studied to determine the effects of Fe₂O₃ addition on glass chemical durability, thermal properties, density and redox [1]. Results indicated that 5-10 wt% Fe₂O₃ addition provides

optimum improvement in chemical durability. ^{57}Fe Mössbauer spectroscopy revealed that Fe is present in these glasses as Fe_{3+} ions in tetrahedral coordination, strengthening the glass network through increased network polymerisation.

Also ^{57}Fe Mössbauer spectroscopy has been widely used to study iron-containing phosphate glasses to investigate the redox and structure [2]. The particular attraction of these glasses is their combination of low melting temperatures and high chemical durability. Extensive studies have been performed [3] on the doping of iron-phosphate glasses to improve the properties that make them suitable for waste immobilisation. We have shown that modification of these glasses by a number of components substantially improves physical properties. However, interestingly, ^{57}Fe Mössbauer spectroscopy has shown that such modifications produce only small changes in Fe coordination and in $\text{Fe}_{2+}/\text{Fe}_{3+}$ redox ratio. Therefore the iron in these glasses is relatively immune to compositionally-induced changes in these glasses [4].

Vitrification is being considered as a possible technology for safe disposal of toxic waste streams such as sewage sludge combustion ashes (SSA), since vitrification of such waste is becoming more economically viable due to higher landfill costs and stricter legislation. ^{57}Fe Mössbauer spectroscopy has been used [5] to determine the coordination of the Fe in the glass. The glass composition has been modified to improve the glass forming properties of the waste and the potential of the glass to be used in another application.

Alternative energy efficient methods of vitrifying waste such as dielectric heating have also been investigated. The effect of internal heating, choice of precursor, local atmosphere, and melt time on the iron redox in iron phosphate glasses has been investigated by ^{57}Fe Mössbauer spectroscopy. Short melt times coupled with reducing local sample environments have enabled homogeneous glasses to be formed with significantly higher $\text{Fe}_{2+}/\text{Fe}_{3+}$ redox ratio than the corresponding conventionally melted glasses.

Vitrification is also being considered for immobilising some legacy wastes that are by-products of the UK's early nuclear power programmes. These wastes are often present in relatively small volumes and may be chemically diverse and poorly characterised. They include several wastes that are rich in the problematic actinide plutonium.

Despite its myriad uses in the field of glass science and technology, highlighted in the glasses discussed here, the range of UK capabilities in Mössbauer spectroscopy has begun to dwindle in recent years. The facility at the Materials and Engineering Research Institute, Sheffield Hallam University, is one of the few remaining UK Mössbauer facilities and it is important that such facilities remain available in the future. There is a range of opportunities for research collaborations, and these issues will be discussed in the context of future UK research infrastructure relevant to the glass community.

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The short- and intermediate-range order in sodium borosilicate glasses: a thermodynamic approach.

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The structure of such practically important and widely used materials as sodium borosilicate glasses still presents an unsolved problem. At present, neither NMR nor Raman spectroscopy, even in their modern variants, can provide information on the **real** structure of glasses containing two vitreous sub-networks.

This is due to the fact that experimental studies can be performed only separately on each of the sub-networks, either the borate or silicate one. Therefore, the results available in the literature correspond to an unrealistic case of two sub-networks existing independently in the glass structure. It is clear that such data cannot be used either for understanding the specific features of the structure or establishing the structure-property relationship in borosilicate glasses. The thermodynamic approach suggested in this paper enables

the above problems to be successfully solved, since it allows the structure of these glasses to be calculated for the case of the co-existing borate and silicate sub-networks, throughout the glass-formation region, at the level of the short-range and intermediate-range order. This approach considers structural changes in terms of the Gibbs energy of a given system, due to which it contributes a strict **physical meaning** to the explanation of structural changes in glasses as their composition varies, and establishes the relationship between the two ranges of order in the glass structure.

Measurement & Technology

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A typical glass furnace hold hundreds of tonnes of molten glass in a continuous 24/7 process. Accidental use of incorrect ingredient in the initial mixture of raw materials can have severe financial consequences. XRF is used to demonstrate the capability of positively identifying raw material types using the FingerPrint application.

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Measurement & Technology

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Vitreous Materials within the High Level Waste & Spent Fuel Waste Handbook

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Over the years a large number of technical documents have been published by the International Atomic Energy Agency covering the development and deployment of various technological solutions and related issues in the area of pre-disposal management of radioactive waste. This body of work was recently reviewed by a team of experts for quality and relevance with the conclusion to consider the consolidation and revision of these multiple reports into smaller number of technical reports or handbooks including High Level Waste & Spent Fuel Waste Handbook (HLW/SFW Handbook) which is among eight technical topics for the new series of handbooks identified as sufficient to provide adequate technical support for pre-disposal activities in waste management. The basic structure of these handbooks is a relatively brief discussion of the subject matter that will provide a roadmap to the specific topic. This roadmap will be supported with an extensive body of information in the Annex that is cross-referenced to the main body of the handbook. The Appendices to the handbook will contain the relevant IAEA publications, selective technical overviews and critical reviews, and reports from member states as appropriate. The HLW/SFW Handbook overviews the requirements for pre-disposal management of HLW and SFW, gives the information on waste inventory required for HLW and SFW, overviews of NFC back-end options with details on selecting wasteforms and packages, gives an overview of processing technologies with details on processes and melters used to vitrify HLW and pre-conditioning processes, casks used to store and dispose of SFW and sealing technologies for SNF containers.

The HLW/SFW Handbook intends to give updated information on vitreous materials in the form of both relatively homogeneous glasses and glass matrices incorporating crystalline disperse phases which are currently as most reliable hosts for nuclear waste immobilisation. Glasses are typically formed on rapid

cooling of melts and so avoiding crystallisation since little time is allowed for the ordering processes. Whether a crystalline or an amorphous solid is formed on cooling depends also on the ease with which a random atomic structure in the liquid can transform to an ordered state. Most known vitreous materials are characterized by atomic or molecular structures that are relatively complex and become ordered slowly. Although, compared to crystalline materials of the same composition, glasses are metastable materials, their relaxation to crystalline structures is kinetically impeded so that practically no phase changes such as crystallisation can occur within very long times which for silicate glasses exceed the lifetime of Universe ($\approx 1.5 \cdot 10^{10}$ years). The high chemical resistance of silicate glasses allows them to remain stable in corrosive environment for many thousands and even millions of years. Several glasses are found in nature such as obsidians (volcanic glasses), fulgarites (formed by lightning strikes), tektites found on land in Australasia and associated micro-tektites from the bottom of the Indian Ocean, moldavites from central Europe, and Libyan Desert glass from western Egypt. Some of these glasses have been in the natural environment for about 300 million years with low alteration rates of less than a millimetre per million years.

The physical and chemical durability of glasses combined with their high tolerance to compositional changes (as glasses are solidified solutions) make glasses irreplaceable when highly toxic substances such as nuclear wastes need reliable immobilisation for safe long-term storage, transportation and disposal. Nuclear waste vitrification is attractive because of its flexibility, the large number of elements which can be incorporated in the glass, its high corrosion durability and the reduced volume of the resulting wasteform. Vitrification involves melting of waste materials with glass-forming additives so that the final vitreous product incorporates the waste contaminants in its macro- and micro-structure. Hazardous waste constituents are immobilised either by direct incorporation into the glass structure or by encapsulation when the final vitreous material can be in form of a glass composite material. Vitrification is a mature technology and has been used for HLW immobilisation for about five decades in France, Russia, USA, UK, Germany, Belgium and Japan [1-4]. Both borosilicate and phosphate glasses are currently used to immobilise nuclear wastes, moreover in addition to

relatively homogeneous glasses novel glass composite materials are used to immobilise problematic waste streams. The spectrum of wastes which are currently vitrified increases from high-level to low- and intermediate-level nuclear waste such as legacy wastes in Hanford, USA and nuclear power plant operational wastes in Russia and Korea. The excellent durability of vitrified radioactive waste ensures a high degree of environment protection. Waste vitrification gives high waste volume reduction along with simple and cheap disposal facilities. Although vitrification requires a high initial investment and then operational costs, when account is taken of transportation and disposal expenses, the overall cost of vitrified radioactive waste is usually lower than alternative options.

The report aims both to give to Member state experts the information available on vitreous materials used for nuclear waste immobilisation and to invite contributing comments to improve and keep most updated the contents of topical High Level Waste & Spent Fuel Waste Handbook.

1. M.I. Ojovan and W.E. Lee. *New Developments in Vitreous Nuclear Wasteforms*. Nova, New York (2007).

2. D. Caurant, P. Loiseau, O. Majérus, V. Aubin Chevaldonnet, I. Bardez and A. Quintas. *Glasses, Glass-Ceramics and Ceramics for Immobilization of Highly Radioactive Nuclear Wastes*. Nova, New York (2009).

3. C.M. Jantzen. Development of glass matrices for high level radioactive wastes. In: M I Ojovan. *Handbook of advanced radioactive waste conditioning technologies*, 230-292, Woodhead, Oxford (2011).

4. I.W. Donald. *Waste Immobilisation in Glass and Ceramic Based Hosts*. Wiley, Chippenham (2010).

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Title: Energy savings and energy production from glass furnace.

Authors : Area Impianti S.P.A.: Dr. Alessandro Monteforte, Dr. Dawid Dacko

Francesco Zatti, Paolo Piccolo

Heat recovery offers two important opportunities: „**energy saving** & „**energy production**. Both offering big advantages from the economical and also environmental point of view. Energy production is clear to everyone, but the advantages offered by energy saving in matter of operating costs and equivalent emission shall not be underestimated as well. At the same time both solutions face with two key points: availability and return of investment: **R.O.I.** is the result of the combination among the specific needs and goals of the plant (earn or save, or both), local rules and regulations, possible public economic incentives and the actual energy that can be recovered. **Availability** depends from the technical concept. Area Impianti has studied and applied solutions with a specific air/gas plate heat exchanger that enable to improve availability and reliability of the system. The air is used both for cooling down the flue gases and as a carrier fluid for the recovered energy. This solution is very flexible and suitable both for energy saving and energy producing scopes.

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History & Heritage

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Manufacturing of Mouth-Blown Glass

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Keywords: mouth-blown glass, stained glass, restoration glass, window glass.

To blow glass with a glass-maker blow pipe was the standard procedure to make sheets of glass between the 16th century and the beginning of the last century. 1905 glass was drawn from a furnace for the first time (Fourcault). Pilkington started production of industrial float glass in the 1960ies.

Glashütte Lamberts is one of three companies worldwide which produce until today glass with methods and tools of medieval glass-makers. Batch (quartz sand, sodium carbonate and limestone), cullets and metal alloys are melted in ceramic pots fired with natural gas.

The Starter gathers the molten glass onto the end of the blow pipe. He is responsible for the right amount and the perfect shape of the gather.

The Glass Master rotates the glass and inflates the glass to a balloon. The red hot balloon is developed to a cylinder which finally is placed in an annealing lehr to cool down and to remove any inherent tensions.

The Cutter scores the cylinder lengthwise. The scored glass is heated again, layed open and flattened. After the second cooling term in another annealing oven the glass sheet passes quality inspection.

The special method of production - each and every sheet of glass is unique- leaves traces of the process on the surface: fine lines from the forming steel trough and small bubbles give a distinct individuality.

Mouth-blown glass has an outstanding brilliance. More than 5,000 colors/tones are available.

Individual sheets measure approx. 60 x 90 cm and are approx. 3 mm thick. Restoration glass is available in 85 x 95 cm, 2 mm thick (or 85 x 80 cm, 3 mm thick).

Mouth-blown glass is the first choice for restoration work. Almost all colors/tones can be made on demand.

Mouth-blown glass is also an excellent choice in modern art and architecture. Laminating mouth-blown glass on bigger sheets of float glass offers new dimensions of colorful artwork.

Without mouth-blown glass restoration of historical windows can not match the historical view. The process - mouth-blown/handmade- makes the distinction.

Summary

Being a very traditional way of making clear and colored glass sheets mouth-blowing still is the best way to make unique, brilliant pieces of glass for restoration, art and architecture.

Lucien Delloye or how an mechanical engineer of the nineteenth century reigned over the whole Continental Glass Industry during thirty-four years ?

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In 1939, in the Journal of the Society of Glass Technology was published the obituary notice of an honorary fellow, Lucien Delloye, saying that it was appropriate that they should record something of the extraordinary respect, authority and affection associated with his name throughout the Continent of Europe, and, indeed, the world. Who was Lucien Delloye, why was he so well known in the glassmaking world? He entered the Company of Saint-Gobain in 1881 as a mechanical engineer in the general management of the plate glassworks. He began his activities in the grinding and polishing of mirrors, finding solutions to a problem quite typical of the changes taking place at this time, the necessity to decrease the costs and increase the yield in the glass factories. He was then entrusted with the task of building and directing the new factory that the Company had decided to set up in Pisa (Italy) in order to keep its share of the market in this part of Europe. His most difficult task was the training of a staff made of people quite unacquainted with this industry. In 1896, he was called to Paris as the assistant to the General Manager, M. Biver, and became General Manager at the death of the latter in 1908. He decided to build factories in Spain, Netherlands and Germany. Convinced that the future of the Continental glass industry would lie in union and organisation, he developed collaboration with the other glass manufacturers in all countries. In 1904, he united the effort of the main glass producers on the Continent and created the International Convention of Glass Factories. The First World War interrupted his work, but as soon as peace was declared the old contracting parties renewed their Association, which had Lucien Delloye as chairman during thirty-four years. He strengthened its relations by an agreement with the great manufacturers of Great Britain, and he had cordial relationships with America. The end of the nineteenth century and the beginning of the twentieth century saw major changes in techniques, in products and their commercialisation. Delloyes technical skills were quickly noticed and brought him very fast to the Management of Saint-Gobain at a time when another engineer, M. Hector Biver had already shown to the Company that the formerly employés supérieurs could succeed in the role of General Manager despite the fact that they did not belong to the financial partners. It is perhaps significant that the International Convention was brought about by a mechanical engineer from one of French Grande Ecole, who had lived in London for a few years because of the 1870-1871 war between Germany and France. In a time when all associations with competitors are forbidden, it is interesting to go back to a time when agreements between them were not easy, but allowed, and most probably ensured the development of the glass industry before and after the tremendous chaos that was the First World War.

Workshop of LC Tiffany

The New York workshop of LC Tiffany, towards the end of the 19th century, completely revolutionised the technique of 'stained glass' production. Traditional glass windows were made of one layer of glass, jointed together with lead strips, the glass, clear or coloured, usually 'stained' either *en grisaille* or with coloured stains.

The Tiffany workshop often used several layers of glass, some transparent and some opalescent, together with staining and even etching to give a much richer effect. This paper will discuss this work using images from the three Tiffany windows in the UK :-

St Peter's Kirk, Fyvie, Aberdeenshire

St Cuthberts Parish Church, Edinburgh

St Andrews Parish Church, Kimbolton, Cambridgeshire

John P Smith

42 Vespan Road

London

W12 9QQ

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Society of Glass Technology Conference 2012 History and Heritage

Stained Glass in Wales

Since 2009 I have been preparing a new online catalogue of stained glass at the University of Wales Centre for Advanced Welsh and Celtic Studies. Based initially on previous research, while working on the Imaging the Bible in Wales Project (2005-8), with the addition of much new additional fieldwork, the resource now contains over 5,500 images of more than 2,000 windows in Wales, and continues to grow.

The catalogue covers the period from the fourteenth century up to the present day. It is searchable by date, subject, artist or firm and location or type of site, and provides additional information on sites and artists, with links and bibliography. During the course of this research, it has been possible to attribute, date and interpret many new windows, particularly from the Victorian period, and the catalogue therefore provides a new easily accessible resource for researching stained glass.

The funding for the project ended in October 2011, However, a second phase of the project has been initiated whereby users have been able to submit comments and corrections, as well as provide additional records and photography to make the survey more comprehensive.

The paper would deal both with the fieldwork and work attributing windows, as well as addressing the functional and technical aspects of the online catalogue.

<http://stainedglass.llgc.org.uk>

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Stained Glass in Portugal: memory, tradition and new challenges for the future

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² Faculdade de Belas-Artes da Universidade de Lisboa, Largo da Academia Nacional de Belas-Artes, 1249-058 Lisboa, Portugal a ferndomus5@gmail.com <<mailto:ferndomus5@gmail.com>> **Keywords:** Stained glass; Portuguese historical heritage; architectural skin; contemporary glass art

Abstract

The history of stained glass in Portugal is a wide subject and deserves to be studied in detail: representing the economic and social power of the Church in their most important buildings reflected also the power of the state in rhetorical and propagandistic programs in the fascist period of Estado Novo. The Portuguese stained glass was a consequence of different economic, political, social and artistic factors, all contributing to make artists, technicians, architects and general public to have a complex and interesting relation with stained glass.

From Middle Ages to modernity, sharing with the rest of Europe a strong Christian heritage in art and architecture - a determinant factor of their proliferation in earlier times, the most important studios reflected the rich history of the country. From the beautiful stained glass examples in Batalha Monastery to the modernist drawings of artist Almada Negreiros, Portugal celebrated and integrated stained glass in very important religious and secular buildings. However, the singularity and aesthetic austerity of most recent Portuguese architecture doesn't leave much space for contemporary stained glass and contemporary artists do not seem to be specifically attracted to express themselves through stained glass. Art historians, scientists and conservators are, in fact, the ones that most frequently celebrate this art in Portugal, due to the rich heritage that the country possesses and the public and private collections still being studied.

But this art is slowly gaining new force, seducing artists and architects alike, integrating different materials to have a more assertive presence in Portuguese contemporary art.

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