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## **Mirrors, spectacles and looking glasses in Antwerp and the Duchy of Brabant in the 16th and 17th century. Aspects of production and use. The archaeological and historical evidence**

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In today's high-tech society glass is one of the most appreciated materials, used in a broad range of applications both for architectural and other purposes. Glass fiber, glass ware, as well as windows, are an inseparable part of our contemporary material culture. This has not always been the case. Until recently, optical glass was considered to be more or less a luxury, not only in the Middle Ages but up until the 16th and 17th centuries. However, this impression has recently been challenged by the continuously growing archaeological material, from religious, secular, noble and urban sites, and from rural environment too. The purpose of this paper is threefold: at first, to provide a brief introduction into glass trade and distribution in the Brabantine region, drawing on upon the comparative analysis of the archaeological finds, of historical literature. Secondly, to illustrate the increasing importance of Antwerp as an international glass distribution centre from the early-fifteenth century onwards. And thirdly, to assess the affordability, use and consumption of optical glass in the context of material culture during the Early Modern Period in the former Duchy of Brabant and beyond.

## **Medieval Window Glass from the Blackfriars Site in Newcastle upon Tyne - An Archaeological Assessment**

Cat Moore

*MA Dissertation, Durham University*

The site of the former Dominican Friary (Blackfriars) in Newcastle upon Tyne was excavated between 1957 and 1988, and the excavation remains unpublished. Among the small finds was a vast quantity of medieval window glass, with a date spread from the 13<sup>th</sup> to the 16<sup>th</sup> centuries. The glass was all highly fragmentary and at the start of this project was largely still encased in the mud it had been deposited in four and a half centuries earlier. The problem with assessing such an assemblage was manifold: the sheer quantity of material; the condition of the glass; and a lack of scientific analysis and budget.

The most appropriate way of making an informed assessment of the excavated glass was through an archaeological, and not an art historical study. This is largely because the art historical discipline does not commonly address quantities of white or unpainted metal, and also in response to the small size of the fragments - forming a complete understanding of painted motifs, or a window scheme is impossible. It was decided to select a single context (BF82 HA737) as a sample. This was due to the size of the context, comprising almost 1,000 fragments of glass, and also in reaction to the time and materials constraints outlined above. In order to quickly gain an idea of the total area the glass covered, a simple measuring matrix sheet was devised.

Following cleaning and some conservation work, the fragments were subjected to visual analysis. Once certain of what was in the context, *comparanda* were sought from other site and excavation reports, as well as publications focussing on glass still *in situ*, such as the work of the Corpus Vitrearum Medii Aevi (CVMA). Research into any existing archival records was undertaken for the site and the glass, including information on potential donors, and stylistic influences.

The quality of the metal, colours and paintwork was exceptional; enough to rival some of the best known medieval glass in England at that time. Unfortunately, archival research did not uncover evidence of donors or patrons, though the glass itself suggests the involvement of patrons who had an understanding of what could be achieved in the medium.

Whilst there are some visual similarities between the Blackfriars glass and those stylistic motifs commonly associated with the York school, it is too confining to place the Blackfriars glass under the influence of one particular workshop. This is, I think, a departure from the traditional art historical approach to glass studies as well, but one that seems wholly appropriate in an assemblage which is geographically distant from any major regional schools, and which has been excavated from an area with strong trading links across the entirety of North Western Europe.

Much remains to be discovered through a fuller study of the remaining Blackfriars glass; though further resources are required to take this project further, it will, upon completion, do much to dramatically expand our knowledge and understanding of medieval window glass in Newcastle upon Tyne and Northern England as a whole.

## **Unstable historic glass: Further observations**

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Chemical instability of historic glass manifests itself, among others, by a characteristic network of small cracks on the surface, frequently called crizzling. It is believed that a source of the phenomenon is innate glass chemical instability, caused first of all by an excess of alkalis and deficiency of stabilizers, such as CaO. There are, however, some other factors that might play an important role in the process, while others inhibit the corrosion process. Two of these are discussed in the paper. The first concerns the corrosion mechanism within a 'closed system', when no reaction products are removed from it, and is based on the examination of a severely crizzled seventeenth century goblet stem with encased liquid inside its hollow bulb. The second case is focused on the role of some other glass constituents, in this case Fe and Cu, which might increase glass durability and prevent or at least slow down the development of the crizzling.

## Adhesives for Glass Conservation

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Glass has always been a challenge to repair, both because of the way it breaks, and the early lack of suitable adhesives. Natural resins and the early synthetic adhesives did not bond well, were sensitive to heat and/or moisture, and often yellowed. Fortunately, newer and more stable synthetic resins have provided better options. The choices of an adhesive for glass conservation can be narrowed to very few knowing the requirements or guidelines:

- .== The material should not damage the glass during application, curing or ageing.
  - .== It should bond well.
  - .== It should be removable or reversible without risk of damage.
  - .== It should be water clear
  - .== It should be easy to use, with consistent results
- .== It should remain stable within the parameters of a Class A resin (100 years)

Two very different resins can be recommended as adhesives for repairing glass, and these are Paraloid B-72, an acrylic copolymer, and epoxy resins. B-72 is a solvent-based adhesive and the epoxies are two-part resin/hardener liquids that are thermosetting adhesives. Both adhesives have advantages and disadvantages for use on glass. The advantages of B-72 over previous adhesives are numerous and include its stability, reversibility, moderate strength and non-yellowing. Epoxies can provide almost invisible repairs, and can be chosen to match different refractive indices.

No adhesive is easy to use when repairing glass and significant experience is required. Glass repairs that involve dozens or hundreds of fragments require careful and precise alignment, usually requiring low-power magnification under a binocular microscope.

Both B-72 and epoxies are suitable for various assembly techniques, including piece-by-piece assembly (or additive assembly), and injection, or infiltration by capillary action.

## **Restoring medieval stained-glass transparency: luminescent ionic liquids for the removal of corrosion crusts**

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Medieval stained-glass often present encrustations, deposits and dirt that require important cleaning operations, rendering these artistic objects more accessible from an aesthetic point of view and for the preservation of this cultural heritage. These corrosion crusts, mainly composed by insoluble salts such as calcium carbonate ( $\text{CaCO}_3$ ), sulphate ( $\text{CaSO}_4$ ) and oxalate ( $\text{CaC}_2\text{O}_4$ ), are very difficult to remove without damaging the glass surface. The methods that present a higher efficiency - like chelant agents (e.g. EDTA solutions), weak acids and ionic resins - are the same that may induce damage or long-term risks to the glass surface. In this work, ionic liquids (ILs) designed for controlled and efficient removal of the insoluble glass corrosion crusts were synthesized. Besides removing the crusts, and in order to assure the complete removal of both impurities and solvent (IL) after the cleaning, to avoid further glass corrosion, these ILs are intrinsically fluorescent, to inform the user if the glass surface is without any trace of those compounds at the end of the process. The cleaning tests were made in artificially corroded glass samples and in archaeological stained glass fragments from a Franciscan friar in Canterbury, and the IL used -  $[\text{P}_{6,6,6,14}][\text{ANS}]$ , intrinsically luminescent - was very efficient and relatively fast removing corrosion crusts from the glass surface and may be considered as a new alternative to conventional cleaning methods.

## **Silane Hybrid Coatings for Protection of the Medieval Glass Mosaic**

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Chemical durability of medieval glass is often low and there are a number of cases when it is necessary to protect the glass surface. Glass objects exposed to the surrounding environment in exterior, such as stained glass or mosaics, can be mentioned as considerable risks examples. Among the last-mentioned objects belongs mosaic of the Last Judgement on the St. Vitus Cathedral located within Prague Castle <[http://en.wikipedia.org/wiki/Prague\\_Castle](http://en.wikipedia.org/wiki/Prague_Castle)>. This monumental work (84 square meters) completed in 1371 at the request of Charles IV is for Central Europe very unique. The project headed by The Getty Conservation Institute focused on protection of mosaic glass against environment was processed during the years 1992-2008. Important output of this project was the successful restoration of the mosaic, which was carried out in 1998-2000. The protection system of the mosaic is based on multilayered films. The lower layer is formed by organosilanes and protects the glass surface and also forms an adhesive layer for the upper double layer of coating based on fluorinated polymers.

Originally used organosilane is no longer produced therefore the aim of this work is preparation and study of new protective coatings based on multifunctional silane systems, which could be possibly used during any mosaic re-conservation.

Studied layers are prepared by dip coating technique and their stability is studied after exposure to: (a) accelerated aging tests (at high level of RH in humidity chamber and UV light in QUV Weathering Tester) and (b) long-term tests in exterior. Parameters such as adhesion, stability of optical properties (by UV-VIS), surface wettability (contact angle measurement) and any change in the composition (FTIR spectroscopy) are studied for each layer. The quality of the deposited film, respectively the rate of defects, is determined by SEM / EDS. The possibility of practical application of used products and application suitability are also investigated.

## **Mapping Papanaidupet - The Final Stage of the most Predominant Glass Bead Industry of the World**

*Alok Kumar Kanungo Humboldt Experienced Researcher, Humboldt-Universitat zu Berlin Institut fur Asien-und Afrikawissenschaften Zentralasien-Seminar Invalidenstrase 118, Unter den Linden 6, 10099 Berlin*

In the field of bead studies Indo-Pacific glass beads has become synonymous with the Papanaidupet. Production of this tiny bead which has been one of the most advanced in nature perhaps took place first in India and then spread to the rest of the Pacific and ruled the bead world for more than two thousand years starting from pre and early Christian era. They travelled both to the East and the West, following the same routes and the same destinations as the agate and carnelian beads. Till recent past Arikamedu in south India had been claimed as the earliest production site of these beads and operated for the longest period, until the work of the present author at Kopia revealed that such beads were also produced in north India before Arikamedu perhaps following the same technology. However, the only surviving traditional Indo-Pacific bead industry for at least last two hundred year is at Papanaidupet, Chittor district, Andhra Pradesh, India. The industry at Papanaidupet having retained many traditional ways has been crucial in answering many archaeological puzzles relating to glass in general and glass beads in particular. It still holds the key to many problems of glass, bead, technological development and trade contacts. It is unfortunate that that for last decades the industry is on the verge of disintegration, posing a danger of an end of a golden era in glass and glass bead history. At present only two furnaces are working that too only when they get the orders whereas just 20 years back there used to be about 20 furnaces working everyday working day and night. The present work aims at a detailed and exhaustive recording of the entire village, production cycle of this glass industry and the people involved with it. This will be useful in finding the answers about ancient glass bead technology, its continuation, and trade related questions; and piece together the history of glass bead making in the Indo-Pacific. It will also help in preserving a model for glass and glass bead researchers in future before it is too late.



Ref: 8

## **Art and Alchemy - The Mystery of Transformation**

*Dedo von Kerksenbrock-Krosigk*

*Glasmuseum Hentrich, Stiftung Museum Kunstpalast, Dusseldorf*

A retrospect on an exhibition held at the Museum Kunstpalast in Dusseldorf, Germany, from 5 April to 10 August 2014. This project featured art mainly from the 16th century until today, and glass regrettably played only a minor role.

However, the new perspective that this show offered for looking at and understanding art may have implications for the approach towards the history of glass as well. Some of these implications will be presented and discussed, hopefully with a vivid and critical response from the audience.

Ref: 9

## **Glass in Iron Age Britain Insights into the past**

*Elizabeth M. Foulds Durham University, Department of Archaeology, South Road, Durham, DH1 3LEA*

A history of British glass begins in the Bronze Age. However, only a handful of artefacts can be attributed to this period (i.e. Must Farm, Cambridgeshire), and it is really in the Iron Age (c. 800 BC - 43 AD) that glass objects become more numerous. These objects are beads, which sadly have seen little study since the 1970s and 1980s, and previous approaches have tended to focus on typological and scientific approaches, rather than to understand the social impact of these artefacts. In the past, glass was assumed to have been an intrinsic exotic medium through which British Iron Age peoples expressed their status and wealth. However, burial evidence is geographically and chronologically limited. In addition, glass beads are rarely found in caches, unlike metalwork. Thus, it becomes difficult to compare such artefacts to understand the Iron Age view of materials and their relationship to status. There is very little evidence to support the idea that glass was intrinsically a high- or low-status material. Instead, glass beads are found at a range of settlements and in a small number of localised burials, which has implication for understanding Iron Age daily practice. This paper aims on the one hand to increase the awareness of the importance of this object for understanding the history of glass in Britain, and on the other to demonstrate that beads are much more than types and dates, as they also provide valuable insight into the daily life in Iron Age Britain. Therefore, it takes a social approach to understanding a variety of aspects of glass beads. Through a regional comparison of different characteristics, such as use, colour, and motif, it becomes clear that Iron Age beads were highly regionalised and perhaps even reflect local aesthetics.

Ref: 10

**Early glass in England:  
Analysis of the Late Bronze Age Glass Beads from Stotfold, Bedfordshire**  
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Archaeological investigations by Albion Archaeology near Stotfold, Bedfordshire, in the UK discovered an un-urned cremation burial comprising cremated bone, fragments of copper alloy tubular ring, a small piece of gold sheet and a collection of glass beads. There were seventeen annular beads in translucent blue glass and one cylindrical glass bead in translucent blue and opaque white glass. Carbon dating of the cremated bone gave a Late Bronze age date, making the beads amongst the earliest to be found in the UK. This presentation provides the results of chemical analysis of a sample from one of the beads and surface analysis of two others. The glass composition is discussed in the context of other finds from the UK and continental Europe

Ref: 11

**Understanding the historic management of window glass in Scotland using portable X-ray Fluorescence**

Craig J. Kennedy\* and K. Robin Murdoch  
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Window glass is one of the most vulnerable elements of a historic building. As demands are made on glazing to improve thermal comfort, this element of historic fabric is under threat of replacement with modern equivalents. Part of the problem in undertaking a survey of historic windows is that it is not always possible by traditional visual assessments to accurately date window panes, and hence identify which panes are historic and which are modern. The use of portable X-ray fluorescence to determine the provenance and age of glass by trace element analysis has allowed for a scientific approach to historic building surveys. By using this technique, a number of buildings in Scotland have been assessed and this has provided a valuable insight not only in to which historic glass panes remain, but can also give information in to how the buildings have been managed over time. Utilising this method, it can be shown that the Abbot's House at Arbroath Abbey, an ancient monument in state care, was completely re-glazed in one event in the early 20th century. Traquair House, a private property, appears to have replaced individual panes when necessary, for instance after breakage, leaving windows with panes of glass of varying ages and types. Newhailes, in the custodianship of the National Trust for Scotland, is a large building easily accessible to the public. Its upper floor window panes are largely historic, whilst ground floor panes appear new, indicating that vandalism and breakage have altered the historic character of parts of this building.

Ref: 12

## **'Like stars in the distance'(1): interdisciplinary approaches to the glass of al-Andalus**

Chloë N. Duckworth (a)\* and David J. Govantes Edwards (b)(a) *School of Archaeology and Ancient History, University of Leicester; (b) Independent Scholar*

This paper presents the current results of an ongoing investigation into the archaeology, history and chemistry of medieval glasses in the Iberian Peninsula, with a particular focus on glass production and consumption in those areas under Islamic rule, known collectively as 'al-Andalus'. Our approach emphasises the crucial role of interdisciplinarity in the study of ancient and historical glasses, and our preliminary results on this hitherto under-represented area are tantalising. We shall present the results of quantitative chemical analysis on glasses and glazed ceramics from both production and consumption sites in Cordoba and Malaga; the nature of the historical record and the potential for future research in this area; a review of the evidence of rescue archaeology for furnaces and other remains associated with glass production; and consider the intriguing matters of technological transfer (for example, between glasses and glazed ceramics) and technological interaction (for example, between glass makers or workers of different religious affiliations). The picture that is emerging from our investigations is a dynamic one, reflecting the social and political diversity of the Iberian Peninsula in the medieval period. There is much scope for future research and collaboration in this area, and with this in mind we aim to bring our investigations into the field of view of the wider glass community. (1) Translation of a line from a poem attributed to Muhammad Ibn Abbad Al Mutamid, last ruler of the Taifa kingdom in Seville, in which he refers to glass furnaces.

Ref: 13

## **Glass from Roman Vindolanda - Style on the Frontier**

*Barbara Birley*

*Assistant Curator - Vindolanda Trust*

Vindolanda is one of the most outstanding sites not only on Hadrian's Wall but in the Roman Empire. It has produced thousands of unique and interesting artefacts including an extensive collection of Roman glass vessels and objects.

The collection includes many pieces of jewellery including beads, bracelets and rings as well as imported painted glass vessels and delicate engraved glass. Barbara will be discussing the importance of these objects not only in terms of their archaeological evidence but also looking at the style and access to imported goods on the edge of Rome's mighty frontier.

## **Chemical analysis of late medieval and early modern glasses from the archaeological excavation at Avenida Miguel Fernandes in Beja (Portugal)**

. Coutinho<sup>1\*</sup>, S. Coentro<sup>1</sup>, T. Medici <sup>1,3</sup>, A. Lima<sup>1,2</sup>, L. C. Alves<sup>4</sup>, M. Vilarigues <sup>1,2</sup>*Unidade de Investigação VICARTE - Vidro e Cerâmica para as Artes, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal* <sup>2</sup>*Dep. de Conservação e Restauro, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal* <sup>3</sup>*Dep. de História, Arqueologia e Artes - Secção de Arqueologia, Faculdade de Letras da Universidade de Coimbra, Largo da Porta Férrea, 3004-530 Coimbra, Portugal* <sup>4</sup>*CTN (Campus Tecnológico e Nuclear), IST/UL, Estrada Nacional 10, 2695-066 Bobadela, Portugal*

A group of late medieval and early modern glass fragments from an archaeological excavation that took place at Avenida Miguel Fernandes in Beja, a town located in the South of Portugal, was chemically characterised by means of PIXE, micro-EDXRF and UV-Vis absorption spectroscopy. PIXE and micro-EDXRF analysis enabled the determination of the chemical composition (major, minor and trace elements) and UV-Vis absorption spectroscopy was used as a complementary technique to identify the transition metals responsible for the different colours observed in the glass objects.

During the archaeological intervention, a set of 137 silos was discovered. They were used as storage containers for food during the 14th and the 15th centuries. After the end of this function, they served as rubbish pits. The glass objects were found inside these silos together with ceramics, faunal remains, coins, and metal and bone artefacts. They can be dated from the 14th to 17th century, thus providing an overview of the evolution of the use of glass vessels in a Portuguese town during more than three centuries.

In this work, a selection of glass fragments spanning all the represented chronological range was studied in order to clarify the technology used, their provenance and to understand the production changes that occurred over the centuries.

Preliminary results showed that the objects so far analysed are made of soda-lime silicate glass. Cobalt and copper were the colorants used to obtain the blue and turquoise glasses, respectively, as iron is responsible for the green and yellow colours.

## **Imitate: Milk Glass a medium for material imitation**

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www.jessamykellyglass.com **Keywords: Glass, Ceramics, milk glass, imitation, materiality**  
**Introduction**

In 2009, Jessamy Kelly completed her practice-led PhD at the University of Sunderland, this investigation combined glass and ceramics in a hot state in studio practice. She is currently a Lecturer in Glass at Edinburgh College of Art. She will present her current research into glass as a medium for imitating other materials and her focused material research project which references milk glass. Glass has a unique ability to imitate other materials; cross-pollinating with other disciplines to refresh and recreate itself. The creative possibilities of creating glass which imitates other materials such as ceramic, paper, metal, wood, stone, plastic and semi precious stones is vast. To create a clear overview of the field, I explored and mapped the work of contemporary glass artists that use glass to imitate a range of materials; this enabled me to understand the context of this research project. As a starting point for my research, I explored the historical precedence of milk glass and selected key glass and ceramic examples. These objects were used as key inspiration for the project. The aim of the project was to create objects that resemble ceramic, which were re-presented through form and surface in the medium of glass. The inspiration for this began with an historical investigation into milk glass. Opaque or opaline glasses can be traced back to Egyptian times and have been used throughout history in various forms. The Venetians produced a lattimo glass in the mid 15<sup>th</sup> century which featured fine threads of white glass developed by adding tin and lead lime to the glass batch. In the 17<sup>th</sup> century, European glassmakers expanded the production of milk glass or porcelain glass to imitate Chinese porcelain, as glass was a far cheaper material to produce: the Germans produced a porzellanglas or milchglas (Bray, 1995, p.177) and in 1663, Crafft introduced beinglas to northern Europe, produced with bone ash (Loibl, 2008 pp.67-68). In the 1690s, Perrot also made opaline glass based on porcelain designs in Orleans, France (Kingery, 1986 p.171). These examples draw a close technical and aesthetic link between glass and ceramics. The creation of glass objects that directly imitate porcelain is an interesting historical precedence; which inspires my practice and influenced the use of white glass in the creation of a new body of unique artworks. Glass is renowned for its ability to imitate many materials such as the opaque, lustrous qualities of semi-precious stones; which dates from ancient Mesopotamia. In the 17<sup>th</sup> century crystal and ruby glasses were made to look as if they were made from naturally occurring rock crystal and precious ruby stones; a high value material which was ranked alongside porcelain (Von Kerssenbrock-Krosigk, 2008, p.123). This demonstrates the revered luxury status of glass throughout history. This historical precedence inspired a series of material testing which led to the creation of a palette of materials that glass can imitate. From this, a new body of glass artworks were created; which imitate agate, amber, ruby, emerald, lapis lazuli and porcelain. As a viewer we may question the exact nature and composition of the material presented; as designers and artists we subvert the semiotics of objects. By changing the materials appearance the aim was to subvert the objects meaning to create a new visual language for my practice. **Summary** In summary, this paper will introduce the creative possibilities of glass and its ability to imitate other materials. It will also discuss the material testing and research that has been carried out. It will also demonstrate how material testing advances studio practice, thus improving creativity and promoting knowledge transfer within and beyond the field of glass. **References** Bray, C. (1995) Dictionary of Glass, A&C Black, London Kingery, W.D. (1986) High-technology ceramics past, present and future, The American Ceramic Society, Westerville, Ohio Loibl, W. (2008) *Itineraries of Glass Innovation: Johann Glauber and his follower* Essay in Glass of the Alchemists, Corning

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Ref: 16

### **Talk Of The Century - a 20th Century Pattern Book Revealed**

*Nick Dolan*

*National Trust*

A pattern book that had been rescued from a skip at a glass factory, and been in private hands until a decade ago, is now brought into the public domain.

It describes and illustrates patterns, details suppliers, and proves an interesting study of the range created by one post-war firm.

This illustrated talk will reveal examples of images, pattern lists, the company and its brief history, in the context of events of the era of the factory.

## Ribbed Shells and the Roman Army

Jonathan Prior *PhD Student, Durham University Department of Archaeology, Stockton Road, Durham*

This study is examining an apparent trend in Roman glass use that may indicate particular popularity of a certain form among soldiers. The ribbed shell, or pillar-moulded bowl, (Isings 1957, Form 3) often appears in sections on late Hellenistic and Republican Roman cast glass in works on the history of glass production, but the form continues and is perhaps most common in the early Roman Empire of the first century AD. This form is one of the most frequent individual forms found on many first-century Roman sites, but Norbert Hanel noted in passing, in his 1995 report on the Xanten excavations, that it enjoyed special popularity among soldiers. Taking this observation into account when examining evidence from five different sites (two civilian and three military) from a separate on-going study, numbers appear to support Hanel's claim. In the civilian centres of Herculaneum and *Oppidium Batavorum*, at modern day Nijmegen, the ribbed shell represents just three and nine *per cent* respectively of the total collected first century glass assemblages. At the Roman cavalry fort next to *Oppidium Batavorum* the percentage of ribbed shells in the assemblage jumps to 23 *per cent* of the vessel glass assemblage. The contemporary legionary fortress *Castra Vetera*, at Xanten, Germany, has a nearly identical portion (21%) of its vessel glass assemblage made up of this form of bowl, and the fortress at Usk, in south Wales also has a lower percentage of ribbed shells, falling in at 12 *per cent* of the total assemblage. Its percentage of ribbed shells is higher than that at either of the civilian sites, and it is the best-represented individual form in the assemblage. Additionally, the destruction of this fortress falls later than those of the fortresses at Xanten and Nijmegen, closer to the end of this form's lifetime, and the Usk site had a much shorter period of occupation than any other site in this study (*ca.* 20 years). In light of these results it is intriguing to follow up this topic and see if these examples illustrate an actual pattern of popularity among soldiers that can be traced across the Roman Empire, or if these sites are exceptions that only seem to support a theory because of the conditions of their preservation and excavation. One must also ask if there is a reason that this form would survive better in military settlements than civilian ones. This paper will attempt to examine questions about this apparent trend across these and other sites to see if there really is a calculable preference pattern and will begin to explore possibilities for why this may have been the case.

## **Galileo Chini and the Italian Liberty Style in glass production: Characterization of early XX century glasses by Fiber Optic Reflectance Spectroscopy (FORS)**

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Despite the large number of stained glass windows dated to the 19th or 20th centuries, the interest of curators and scientist has been mainly focused on the Roman and medieval glass production, so that the scientific publications concerning the Art Nouveau period count just few and preliminary works. Concerning the Italian context, the number of works on the characterization of the Italian Liberty style is even lower. Since the opportunities to sample or to move many works of art out of the conservation location are very limited, the application of non invasive and portable techniques appears to be the best way to perform an in-depth characterization of the chromophores and raw materials. The present study want to summarize the first part of a deep characterization of the Italian glass production during the first decades of the XX century, focusing mainly on the works of a prominent member of the Italian Liberty style, Galileo Chini. The chance to produce his own glass and the researches to reproduce and improve the ancient recipes, made Galileo Chini one of the most interesting artists not only concerning the Italian context. The study presented has been performed on some windows produced by Galileo Chini between the 1895 and the 1920 and conserved at the Manifattura Chini Museum (Borgo San Lorenzo, Florence). Portable FORS has been used as a quick, easily transportable and totally non-destructive method for the characterization of the colouring agents, while the definition of the raw materials used to obtain the base glass is not always possible. Concerning cobalt blue glasses, for example, the study of the cobalt band wavelength allows the discrimination between soda-lime, potash or mixed-alkali base glasses, while such a kind of relationship appears to be more difficult to figure out for other chromophores and the study is still in progress. The blue glasses have been mainly obtained by the addition of cobalt oxide, identified by the absorbance triplet at 535, 595 and 645 nm, while copper has been detected in few samples by the presence of an absorption maximum at 780 nm and a weaker secondary maximum centered at 450 nm. Elemental copper is instead responsible of the red colour of some glasses and it has been identified by a flex at around 680 nm. The ferric iron is responsible of the amber shades and it is recognizable by an absorbance maximum centered at 420 nm, while cadmium sulfide has been used to obtain orange and yellow glasses and it could be identified by the presence of a flex between 500 and 580 nm. The green shades have been obtained by the addition of chromium (as a mixture of trivalent and exavalent ions) identified by a maximum doublet at 650 and 695 nm, or copper, as it could be assumed by the presence of a broad band at around 650 nm.



## **Archive and Legacy: a 20th Century Lineage - glimpses into the growth, nature and development of the Edinburgh School**

*Douglas Hogg* *Ex head of stained/architectural glass course, Edinburgh College of Art*

Last year, in December, some drawings were brought to light causing ripples of interest from the archival direction at Edinburgh University. These full-scale coloured cartoons were the work of stained glass artist Alexander Strachan who headed up a new Stained Glass department when the Royal Scottish Academy teaching schools joined together with the Edinburgh School of Applied Arts in 1911, to form the Edinburgh College of Art. This ambitious project proved to be, both philosophically and practically, the start of a movement the consequences of which could never have been anticipated at the time yet reached the turn of the century and beyond. Having absorbed much material from over a long period of time, accumulated by listening to and learning from past generations of artists and ex-studio staff etc, I shall present an immersed account of a progression which starts from that early point. At various junctures these generations of artists and craftsmen have been actively significant in their contribution to the national field of play, and as a teaching and learning facility with few to parallel it, spread a typically fresh and inventive philosophy beyond its boundaries. Amongst the names which stitch themselves inventively throughout this lineage are Alex and Douglas Strachan, Margaret Chilton, Herbert Hendrie, William Wilson, Basil Spence, Sax Shaw, a young Patrick Reyntiens and a both young and a not-so-young Douglas Hogg! Paralleling the hey-day of a past British art education system and its value in the underpinning and formenting of a national structure of creative cultural engagement - always a melting-pot of fresh influence - this will be the first time that the subject has been explored as a rich sequential pathway. I hope by way of anecdote and illustration to pull together strands of activity into one cogent development. There are serendipitous events also, taken from a personal perspective, which I would like to share. My talk shall be largely personal and unapologetically circumstantial; it will be up to archivists and historians to pick over the physically tangible remains and give the events their ultimate catalogued, trapped and uninvolved documentations.

## ***Capital Letters: techniques and creative implications of raised print in pressed glass.***

Authors: Mark Hursty\* & Dr. Kevin Petrie & Dr. Jeffrey Sarmiento

Mould-pressed glass is the most ancient hot glass forming technique. Since its semi-automation in the Victorian era, pressed glass efficiency has been a significant source of technological innovation in glass machinery. However practical it has proven in Industry, over a century of full automation and questionable artistry has led to pressed glass being virtually overlooked as a creative technique by artists in the studio. This presentation will use the evolution of raised relief, particularly mould-formed text and decoration in glass, to illustrate the creative precedents and potential of pressed glass. The topic of pressed text intersects the current creative practice-led research by Mark Hursty regarding contemporary sculptural use of pressed glass.

To map creative and technical precedents in mould-pressed glass relief, examples of text-forming will be presented in ancient artifacts, Victorian era mass-produced glass and contemporary glass sculpture. Ancient examples of moulded glass text illustrate the trans-cultural significance of pressed glass on glass technology. They feature the Roman, Hebrew, Arabic and Chinese languages. Sources from Victorian era pressed glass, a long-standing industry in Northeast England, will feature English. Finally, the current research by Mark Hursty will demonstrate how pressed glass precedent can be expanded for practical sculptural use. This will provide a practice-led example of technical and creative implications for pressed glass; one that is sustained by retaining manual skills (lost in Industrial glass pressing) but still integrated with mechanization, and digital fabrication.

## **Drinking glass design around 1670**

*Colin & Sue Brain*

British glass has often been valued as much for its design as for the quality of the glass metal and the workmanship, but it wasn't always that way. In the first half of the 17th century there was no distinct British style and drinking glass production was mainly limited to out-dated copies of Venetian or Dutch designs. All this changed 350 years ago this year with the granting of a Royal Charter to the Glass Sellers Company of London. Fortunately we know a lot about one of these founding Glass Sellers, John Greene, and his innovative glass designs from the Sloane 857 manuscripts now preserved in the British Library.

This paper aims to explore how drinking glass designs evolved around 1670 by tracing one thread through Greenes designs, looking at how a style of beer glass developed to satisfy what quickly became a dynamic fashion-conscious market. This is illustrated by surviving complete glasses and excavated fragments. Of particular interest is a recently-discovered complete glass that matches a design ordered by John Greene from Venice on 10th February 1670. However, the glass metal does not appear Venetian and there are other similar Greene drawings that do not relate to any Venetian order, so the paper considers the evidence for it being English-made.

In any discussion of glass design around 1670 there is an important chicken and egg question. Which came first: lead crystal glass, or designs compatible with lead-crystal glass? The paper argues that the designs came first and that the technical developments followed in response to market demand.

The paper concludes by highlighting the importance of the Glass Sellers as designers at this critical stage in the development of the English and Irish glass industries and showing that these classic designs quickly became iconic, evoking the taverns described in Samuel Pepys diaries

## **The art of inside painting on glass**

*Jianyong Guo*

*Manny Ling*

*Kevin Petrie*

*University of Sunderland*

The Chinese snuff bottle is one example of the crystallization of Chinese and Western cultural development. During the 16th century snuff was introduced into China for medicinal purposes. The art of painting the inside of bottles used to hold snuff is believed to have begun in the early 19<sup>th</sup> century.

After hundreds of years, it can be said that the forms of inside painting are now mature and exquisite, and that the bottles represent treasures of both Chinese artistic history and in the world of glass art as a whole.

The techniques used in inside painting of Chinese snuff bottles were well developed and traditionally relied upon classical Chinese forms, inspired by the natural world and calligraphy for subject matter.

However, there is great scope for bringing together the traditional subjects with motifs from contemporary social life. The traditional artistic culture of China needs to inherit and embrace its past, but also needs to move forward. China's modern academism in glass art is just beginning (2000). So there is an urgent need to develop in order to catch up with the rest of the world.

But the most important need is to develop glass art according to China's own cultural characteristics. I propose to use traditional art forms, including those of blowing/casting glass and the techniques of inside painting of snuff bottles, to create a new art form which can carry forward the methods and styles of Chinese contemporary glass art.

This presentation will show how I will use blowing, fusing, slumping, and outside painting combined with inside painting techniques to demonstrate how inside painting can be applied into contemporary glass art.

## **Glass, an imaginative impulse for contemporary art and vice versa**

*Francesca Giubilei*

*Independent Contemporary Art Curator and Exhibition Project Manager*

The contemporary art revolution, started by Marcel Duchamp, passed through the technique, the introduction of new materials and different approaches.

From this point, the language of contemporary art changed: glass, plastic, food and the human body too became expressive tools for the new artists.

This new concept of hybridization can be used not only for the art language but also for artists training. Today the artist is more a director than an artisan, meaning that he/she uses the technical and manual skills of the technicians to develop ideas and concepts.

Glass is one of the most interesting and suitable medium for contemporary art and especially significant for the concepts mentioned above.

Thanks to its physical, aesthetic and semiotic characteristics it is particularly appropriate for the representation, description and analysis of the contemporary instances. Moreover, the production of contemporary art in glass concerns many of the issues connected to the relationship between the artist and the artisan, their roles and their contribution to the artistic creation.

## **Renaissance Venetian enameled glass. An analytical approach**

*Françoise Barbe,*

*[Louvre Museum, Paris, France]*

*Rosa Barovier Mentasti,*

*[Venetian glass historian, Venice, Italy]*

*Isabelle Biron,*

*[Laboratoire du Centre de Recherche et de Restauration des Musées de France, Paris, France]*

*Marco Verità*

*[LAMA Laboratory, Università di Architettura IUAV, Venice, Italy]*

Venetian enameled glass is a most significant subject of the art and technology of Renaissance glassmaking. These items, which are now preserved in museums and glass collections all over the world, were made in Venice from the late 15th through the 17th centuries and were imitated in other European glassmaking centres during this period (façon de Venise glass). Furthermore, copies (fakes) of the Renaissance enameled Venetian glasses were made in Murano glass factories since the second half of the 19th century. It is known that copies made in the 19th or 20th centuries entered many collections of Renaissance enameled glass.

Present knowledge on the Venetian Renaissance enameled glass objects leaves many unclear issues to art historians and curators. Many pieces in the collections are of uncertain provenance and their authenticity is still being debated.

The chemical analysis of glass and enamels can be most useful to investigate the enameling technology of the original items and to distinguish them from façon de Venise glass or 19th century fakes. Unfortunately, only a relatively small number of analyses are available up to date, due to the impossibility of even microscopic sampling of these precious artifacts.

The existence in the Laboratoire du Centre de Recherche et de Restauration des Musées de France of an AGLAE accelerator allowed ion beam non-invasive and non-destructive analysis (in PIXE and PIGE modes) to be used to determine the quantitative chemical composition of the glass and of the decorative enamels. In the frame of a collaborative project, a number of original Venetian Renaissance items and a number of objects of doubtful provenance belonging to the French collections, were selected for analysis by a major expert on Venetian glass, in agreement with the curators.

The first results of the analyses were presented and discussed in a recent paper, compared with the analyses of Renaissance Venetian glasses available in the literature and with the recipes to make enamels reported in Renaissance treatises drawn by Venetian glassmakers. The research is presently being extended by analyzing a larger number of enameled glasses from French collections (more than 30 have been analyzed up to now). Small fragments of archaeological samples prepared in polished cross section were also analyzed by SEM-EDS by the LAMA laboratory to investigate the structure and the colouring technique of the enamels.

These analyses allow:

== a first database on Venetian Renaissance enameled glass objects to be created to allow distinguishing between objects made with a technology different from the Venetian tradition and genuine Venetian products (fakes will be recognized);

== new light to be thrown on this sophisticated, controversial decorative technique;  
== any similarities between Venetian Renaissance enamels and Limoges enamels to be examined.

The present state of the art of the project is presented and discussed.

Biron I., Verità M., Analytical investigation on Renaissance Venetian enamelled glasses from the Louvre collections, *Journal of Archaeological Science* 39 (2012), pp. 2706-2713

Ref: 25

## Venetian and *façon-de-Venise* glass objects of the Glass Collection of King Ferdinand II

Alexandra Rodrigues<sup>a,\*</sup>, Anísio Francob, Bruno Martinho<sup>c</sup> & Márcia Vilarigues<sup>a</sup> *a) Departamento de Conservação e Restauro, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Portugal and Research unit, VICARTE - Glass and Ceramics for the Arts b) Museu Nacional de Arte Antiga, Lisboa, Portugal c) Parques de Sintra - Monte da Lua SA, Palácio Nacional da Pena*

The glass collection of King Ferdinand II of the House of Saxe-Coburg and Gotha is recently being identified as the most important collection of European glass hitherto seen in Portugal. It includes objects produced in Venice, or *à la façon de Venise*, in Bohemian and Germanic territories, in the Iberian Peninsula, and probably also in the Netherlands and England. A large part of the collection was gathered by Ferdinand II in a 'Glass Room' in the National Palace of Necessidades (Lisbon), the King's first residence, and a small number of objects was kept in his second residence, the National Palace of Pena (Sintra). Notwithstanding the value and appreciation of Ferdinand II, the greatness of this collection was never fully understood until very recently. While the set in Sintra remained in the Palace, the objects from the "Glass Room" were dispersed after the King's death. Most of the collection remains unknown to the general public, residing nowadays in the storage room of Museu Nacional de Arte Antiga. The purpose of this study was to increase the knowledge on this exceptional set of glass objects, and to understand how the collection has been created in the 19th century. Some outstanding glass artworks will be presented, namely 15th and 16th century Venetian productions, including the finest *Cristallo* glass objects and Netherlandish and English *façon the Venise* examples. The provenance study of these objects has been taking into consideration similar objects and collections, records and archive documents, and information on the glass composition obtained through non-destructive techniques such as energy-dispersive X-ray fluorescence (EDXRF) and UV-Vis absorption.

## **STUDY OF GLASS - METAL JOINS DEGRADATIO**

Elżbieta Greiner-WronowaAGH- Technical University of Science and Technology Ave.Mickiewicz  
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Glass made by man has been developed for ages, but gradually its application become wider.

The glass has been used for many forms, joined with another materials too. Metal was very popular to be easily connected with glass. Actually the first forms have known as a jewellery for women, made of very single beads. Due to technological situation, some objects are suffering, because of corrosion. This created process is seriously depended on as well as outside local surrounding and direct interaction between glass and metal. Weaker material, firsts attacks and induces degradation process. Moreover the stage of each object element is important for developing corrosion. Generally, this is very complexity and must be analysed every single element separately, and later mutual activity must be considered too. The following analysed objects were presented in this paper: excavated rings, enamels on the copper base, amalgam mirrors, beaker on the bronze support. Corrosion reasons are very different and depending on various types of long-term factors acting on objects surface, such as temperature, relative humidity, light intensity, local air pollution on macro and micro-scale. Material testings have been realized by the following methods: RS, SEM, EDS, SIMS, ICP-MS, FTIR and glass-sensors as a complementary experimental materials.



## Digital-Glass Interface

*Colin Rennie*

*Senior Lecturer, Glass and Ceramics, Institute for International Research in Glass, University of Sunderland, Liberty Way, SR6 0GL.*

The current theme of Colin's work centres around the translation of scientific ideas from abstract esoteric constructs into solid and real world models or agents of understanding. It comments on the perception of scientific explanation in an increasingly secular society.

The work often involves models of organic subjects or theoretical objects contained in vessels or cubes and optically obscured or distorted. Glass is used as both a modelling material and as a controlled window through which to observe; glass has the faculty to modulate light and transparency it is a metaphor for the visible and the invisible, or the grey areas between science and myth and idea and perception.

Paying homage to the age of enlightenment, Rennie's latest work is experimental. It explores the singular pursuit of an idea or dream, whilst considering the relationship between our understanding of the digital world and the physical object. Rennie's work blends 3 dimensional modelling and analysis with traditional glassblowing skills and techniques, creating work, which is both modern and nostalgic. This presentation will describe the circular creative process through teaching informed research and research informed teaching.





<[http://www.tripadvisor.co.uk/LocationPhotoDirectLink-g227059-d635290-i38244957-National\\_Glass\\_Centre-Sunderland\\_Tyne\\_and\\_Wear\\_England.html](http://www.tripadvisor.co.uk/LocationPhotoDirectLink-g227059-d635290-i38244957-National_Glass_Centre-Sunderland_Tyne_and_Wear_England.html)>

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## The Presidents Address

## **Characterization and replication of the 19th century yellow and blue mirrored glass of the Temple of Emerald buddha, Bangkok, Thailand**

*Wantana Klysubun, Prapong Klysubun*

*Weeraya Deenan, Panidtha Sombunchoo and Suchaya Chamangpon*

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Kriab mirror is a unique Thai ancient glass mirror. It is a thin casted glass (less than 1 mm thick), with lead coated on the back side to yield mirror-like reflection. The Kriab mirror has been used in Thailand since ancient times. It was commonly cut into small pieces for decorating Buddhist temples and palaces, especially on tympanum, external walls, pillars, statues of mythical creatures, etc. Knowledge of Kriab mirror production has disappeared since the late 19th century.

In the case of contemporary Thai temples, modern glass mirrors, much thicker and more reflective, are used. Our research objective is to replicate the Kriab mirrors obtained from the Temple of the Emerald Buddha in the compound of the Grand Palace, Bangkok, Thailand.

Employing the exact replicas of the Kriab mirrors for restorative work instead of resorting to modern mirrors will return the temple to its original splendor.

Glass layers of yellow and blue mirrors were analyzed using an energy-dispersive X-ray spectrometer and a laser ablation mass spectrometer for chemical compositions. The yellow glass was found to contain 60% SiO<sub>2</sub>, 10% Na<sub>2</sub>O and 10% CaO and 10% PbO, along with other minor and trace elements that will be presented herewith. We used X-ray absorption spectroscopy (XAS) to identify iron cations (Fe<sup>3+</sup>) and manganese cations (Mn<sup>2+</sup>), both of which effectively control the color of the yellow ancient glass. XAS spectra of Fe<sup>3+</sup> and Mn<sup>2+</sup> will be shown to demonstrate the power of the XAS technique in investigating glass coloration. The blue glass was found to contain 50% SiO<sub>2</sub>, 7% Na<sub>2</sub>O, 6% CaO and 25% PbO. The XAS reveals cobalt cations (Co<sup>2+</sup>) and other coloring elements (iron, copper and manganese), thus reproducing the ancient blue color is more complicated.

Based on the analyzed compositions, glass batches were prepared accordingly. Each batch was contained in a ceramic crucible to be melted in an electric box furnace. A firing temperature was set at 1300 oC. The glass melt was poured on a stainless steel plate and pressed to form a flat sheet. We then fine-adjusted concentrations of the coloring elements until the exact-match color to the ancient glass was achieved. Details of this work as well as chemical and optical analysis of the glass replicas will be presented.

Thin casting for a target thickness of 0.5 mm has not yet been succeeded, although several methods have been tried including hot casting and fusing from frits. Hot blowing may be a possibility, but it requires considerable amount of practice. Therefore, our research seeks collaboration with experienced glassmakers.

## **Recent developments in creative glass research - case studies from art and design**

*Kevin Petrie*

*Institute for International Research in Glass (IIRG), Faculty of Arts, Design, & Media, University of Sunderland, National Glass Centre, Liberty Way, Sunderland SR6 OGL, UK*

This presentation offers case studies of creative glass research from a community of MPhil and PhD researchers who are advancing art and design practice in glass. This presentation provides an up date on this research group, which was previously discussed at the European Society of Glass Technology conference 2010. The University of Sunderland is one of the UK pioneers of creative research and is also well known for its glass department - one of the biggest and best equipped in Europe. Previous projects have blended the haptic and tacit skills of designer makers with approaches from other fields such as; science, engineering, industry, and computing as well as Fine Art and Design. This presentation focuses on research, which combines the development of new making methods for glass sculpture and design with sources of inspiration such as ethnography, calligraphy, and Chinese philosophies.

The driver for this kind of research is to provide models useful for artists and designers using glass. For the artist or designer, glass offers a myriad of creative potential. Glass as a material forms a significant strand of the canon of art and design practice, with uses ranging from large-scale architectural projects to plinth based gallery works. Glass artists and designers are traditionally trained in the UK through university programmes in art and design faculties. Here they learn how to control and manipulate glass in order to express their creative concerns. A growing trend in this sector is the development of research degrees (Master of Philosophy and Doctor of Philosophy), which allow a focused investigation of technical or conceptual aspects of creative practice. This approach is distinct from what might be termed the scientific model - although it does borrow from this at times.

It is hoped that this presentation might lead to new collaborative research strategies that utilise communities with overlapping interests like glass technology and glass art.

## **Developing artworks using Chinese philosophical notion of non-action through pâte de verre glass**

*Qu Jin*

*Manny Ling*

*Kevin Petrie*

*Jeffrey Sarmiento*

*University of Sunderland*

This presentation will frame and record creative and technical processes behind a body of original pâte de verre glass artworks inspired by Chinese philosophical idea. Pâte de verre, means paste of glass and re-emerged in the Art Nouveau period in French. The term now describes techniques employing heat-resistant moulds charged with glass powder or frit and fired. Motivated by my own position as both a glass artist using Western techniques and an educator of art with a Chinese traditional upbringing, the content of my work is rooted in expressions of my own cultural contexts. This practice-led research aims to identify, develop and demonstrate how the pâte de verre might be used to express aspects of Chinese Philosophy such as Taoism and non-action. This is an emerging discourse within the field of glass art. Glass powder offers potential for using unique qualities of the material to express this content in creation. This presentation will consist of subject findings through personal experiences, interpretation of cultural contexts, and their visualization through developing techniques to fabricate artworks in glass. It is hoped that novel concise and simple approaches will be developed for pâte de verre glass art. As a model of meaningful making throughout the research, this developing system will add to conceptual discourse and technical innovation in the field of glass art.

## **Turning the spotlight on Turner**

*Sophie Hylands*

*Department of History, the University of Sheffield*

*John Parker*

*Department of Materials Science and Engineering, the University of Sheffield*

This presentation has developed from a research project based at the University of Sheffield's Turner Museum of Glass. This project aims to find out more about W. E. S. Turner, whose collection forms the core of the museum, as well as uncovering the stories behind individual pieces within the collection.

Both the journals of the Society of Glass Technology and the University of Sheffield's archives have proved fruitful sources of information on Turner and this paper will examine his life and career, and in particular his interest in art glass and support for glass artists.

The project has also involved researching the social history of several of the pieces held by the museum and within this paper I plan to also reflect on what the Turner collection can reveal about the lives of those making and using the pieces on display, as well as the man who collected them.

## **Making light work**

*John Parker*

*University of Sheffield*

*Department of Materials Science and Engineering, Sir Robert Hadfield Building, Mappin Street,  
Sheffield, S1 3JD*

Both artists and scientists have learned over millennia how to control the interplay between glass and light using a multitude of effects based on colour, reflection, scattering and more recently fluorescence. Examples of the craftsmans art will be illustrated using pieces from the Turner Museum of Glass in Sheffield. Over the centuries some of the techniques used have appeared and then disappeared again as the recipes for producing specific effects have been lost and the processes have had to be re-invented.

My main aim in this presentation will be to put on a scientific footing those phenomena that involve precipitation colours i.e. nano or microcrystals suspended in the glass. We will talk about the nucleation and growth processes needed to create the particles, how quickly they happen, the temperature ranges at which they occur and the possible consequences of re-working the material.

We will see how redox phenomena have a vital role to play in the precipitation of metal particles. We will learn how, for many of these optical effects, size matters, whether the dopants are transparent or strongly coloured.

Finally some recent applications of these phenomena will be shown.

## Enamels in stained glass windows: a quest for blue

Andreia Machado\* a), b) & Márcia Vilarigues a), b) a) *Research Unit VICARTE - Vidro e Cerâmica para as Artes - FCT/UNL, Caparica, Portugal* b) *Department of Conservation and Restoration - FCT/UNL, Caparica, Portugal*

The production of manuscripts concerning both glass and glass paint reached a crucial point during the 17th and 18th centuries. Antonio Neri with his treatise *L'Arte Vetraria* (1612) and André Felibien with *Des principes de l'Architecture, de la Sculpture, de la Peinture et des Autres Arts qui en dependant* (1676) opened the way to several translations, annotations and experiments throughout Europe, preserving the knowledge of ancient glass painters and combining them with the technologies available. With the evolution of the production techniques, coloured glasses were slowly superseded by clear glass in which the paint was applied, giving to this form of art a colourful palette. One example is the application of enamels, a tendency that began in the 15th century, which consists of a vitreous paint that melts at a lower temperature than the glass on which is applied. It is composed by a mixture of a flux, a colouring agent and a binder. The study and reproduction of blue enamels was accessed based on the information given by the recipes and recent contributions to their study. Recipes of Antonio Neri, André Felibien, Robert Dossie and Johann Kunckel were produced, using pure chemical reagents. Parallel to this work, raw materials such as plant ashes, quartz pebbles from the river Ticino, wine lees and a cobalt ore (skutterudite) from Schneeberg, Saxony, were collected, in order to reproduce a blue enamel as similar as possible to the ones described in the recipes by Antonio Neri. With these reproductions, chemical and morphological analysis by means of optical microscopy and X-ray micro fluorescence will be achieved, and also corrosion studies are intended. With this project, we hope to achieve a better knowledge of the materials used by the artists and to place their works in context, as well as to establish the most adequate conservation procedures. King Ferdinand's private collection placed at the National Palace of Pena is the focus of this study.

## Mediaeval Blue Stained Glasses: from spectroscopy to history

Myrtille Hunault<sup>1</sup>\*, Georges Calas<sup>1</sup>, Laurence Galois<sup>1</sup>, Claudine Loisel<sup>2</sup>, Fanny Bauchau<sup>2</sup>, Michel Hérold<sup>3</sup>

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The color of stained glass windows is an essential aspect of these artworks. However, technical limits have restrained so far the extensive analysis of glass color in entire window panels. Optical absorption spectroscopy is a non-destructive technique, which enables to investigate the chemical cause of the color and to quantify it (colorimetry). We present a transportable set-up developed to measure the full range (350-2500nm) optical spectrum on full window panels. We applied this approach to the analysis of the blue glasses from the Holly Chapel of Paris (XIII<sup>th</sup> century) during the last restoration campaign. This major building of the gothic period presents exceptionally high quality stained glasses. In that time, glass composition and coloring agents underwent important modifications. Medieval glassmakers were able to obtain a large range of color hues using transition metal oxides. Blue glasses are colored with cobalt, iron, copper, and manganese. This study investigates the interdependence between Fe/Cu/Mn redox equilibriums and the influence of the manufacturing parameters. Optical spectra of the blue glasses from the Holly Chapel are compared with reference glass samples previously characterized with optical and x-ray spectroscopies. These results provide very first insights into both glass manufacturing techniques and stylistic study of the colors used in stained glass windows during XIII<sup>th</sup> century.



## **The analysis of historic glass painting technology based on the conservation of coat of arms of the Great Guild head Johan Christopher Husen (1753) in St. Olaf's Church in Tallinn**

Eve Koha\* & Liisi Junolainen *Estonian Academy of Arts, Estonia Av. 7, 10147 Tallinn, Estonia;*  
*evekoha@gmail.com* **Keywords:** Estonian historical glass painting, grisaille, painting technology analysis, conservation, copy

This paper examines the coat of arms painting of the Great Guild head Johan Christopher Husen (1753) located in the St. Olaf's Church in Tallinn, which is generally characterized by a total of ten paintings and painted details belonging to the church.

Two years ago the St. Olaf's Church administration together with Tallinn Cultural and Heritage Department coordinated the protection of historical glass paintings of the church and made decision to remove them from the windows in order to conserve them and find a safer way of display. The goal was to make these rare glass paintings more visible to people and place them after conservation in the niches in the nave of the church. As after conservation these small paintings will be placed to their original location in the windows of 15 meters height they will not be visible to people. The decision was made to order also copies for the proper exposition.

The glass painting is commonly described iconographically but the technical side of painting has very terse description. Only the grisaille technique and the list of different colours of paints were stated. It was also mentioned if the silver stain was used or if both sides were painted.

From technical view point the historical glass painting can be considered as graphical or drawn painting. This requires a very good drawing skills, excellent sense of colour and knowledge of modelling shapes in terms of light and shadow.

In the historical paintings light is of very high significance giving the painting sensitivity and verve. It is very important that angle of incidence of the light comes almost always from the top left north-west directions.

Modelling the shapes begins already in the drawings. Exposure to light lines is thinner and more delicate, but in the shadow darker and more powerful.

The first layer is the most delicate shadow and covers the larger surfaces of the painting, where the darkness is directed from half shades towards full shades. Full shade area is the darkest and these surfaces remain close to the strong contours. (A similar approach was also described by Theophilus, in his book "Schedula Diversarum Artum" in the 12th century where he wrote that glass is transparent, from where the light comes and opaque from the shade side, gradually turning brighter, as if the three pigments seem to be side-by-side.)

Thank to variety of tools and mixtures of substances there is no need for firing in the kiln of every grisaille painted layer. This is revealed also from the examination of historical paintings, where the high-light has been refined through all layers of the painting.

The glass painting firing process in the past was arduous and risky process, and therefore the development of glass painting techniques in the direction of lessening the number of kiln firings was understandable. The glass painting conservation and especially making a genuine copy requires very careful glass painting technology analysis to understand the intentions of artists in the past.

Researching the historic background and technology in depth enables to achieve an excellent results in conservation process by capturing also the emotion of historic glass painting instead of making copies of mechanical similarity only.

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## **Looking for John Thornton in the Conservation of York Minsters Great East Window**

*Sarah Brown  
University of York; York Glaziers' Trust*

In 1405 the Dean and Chapter of York commissioned the largest stained glass window ever made in medieval England, a medieval master-piece to illuminate the new cathedral choir. Depicting the beginning and the end of everything, from Creation to Apocalypse, the window is notable for the extraordinary ambition of its design. The survival into the 17th century of the medieval contract means that the name of its author, John Thornton of Coventry, has been preserved. That he did not work alone is also clear from the contract, but the exact nature of Thorntons role continues to intrigue art historians.

As conservation of the Apocalypse cycle draws to a close, this lecture will consider what new insights into Thorntons activities and influence can be gleaned from the recent exploration and conservation of this extraordinary work of art, a project which has brought together art historians, conservators and glass scientists.

## The Stained-Glass Collection of King Ferdinand II

Mathilda Larsson<sup>a</sup>, Alexandra Rodrigues<sup>a</sup>, Andreia Machado<sup>a</sup>, Bruno Martinho<sup>b</sup>, Luís C. Alves<sup>c</sup>,  
Victoria Corregidor<sup>c</sup>, Rui C. da Silva<sup>c</sup> & Márcia Vilarigues<sup>a\*</sup>

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In the vast collection of works of art gathered by Ferdinand II of Saxe-Coburg and Gotha (1816-1885) throughout his life, glass and stained glass occupied pride of place. Ferdinand II created a unique collection of stained glass with works from as early as the 14th century until the 19th century, which was displayed in the King's Palace in Lisbon. The set was recently restored and presented to the public for the first time in the National Palace of Pena (Sintra, Portugal), where it now resides. In this study, old records, iconography and non-destructive analysis are combined to gather information on the provenance of these stained glass panels. This has been part of a project started in 2010. In this presentation, the latest results of micro-energy dispersive X-ray fluorescence ( $\mu$ -EDXRF) and UV-Vis spectroscopy performed on-site to a large set of stained-glass panels are discussed. The composition of the glass objects, grisaille and glass paintings of the analysed stained glass panels is compared. This project also aims the construction of a database in which the historical studies will be connected to the analytical data, intending also to contribute to a deeper knowledge on the European glass collections.

\* presenting author

## **Three stained glass windows from Santa Croce Basilica in Florence Materials comparison for understanding the history of production**

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The restoration of three stained glass windows from the Basilica of Santa Croce in Florence, which was done by the Studio Fenice in Bologna during the years 2010-2012 made it possible to study the original constituent materials and those derived from both alteration processes and previous restoration of the windows. The study was conducted by integrating non-invasive in-situ and micro-invasive laboratory methods. The three investigated windows belonging to the Basilica of Santa Croce were the 'Franciscan Saints and Popes' (SII\_Sup), the "Genealogy of the Virgin" (NII\_Sup) and "Saints and St. Sigismund King" (N\_VIII). The three windows were removed from their original location in the occasion of the restoration and transferred to the restoration laboratory. This study allowed a in deep analysis of the artworks that was also focused to clarify some aspects regarding the identification of the artists. From the stylistic studies the first two windows, which considered almost contemporary, were attributed to the Maestro di Figline or his pupils, and the third one, which was based on a drawing by Taddeo Gaddi, shows one inscription with the names of the master glassmakers (Fra Ubaldo "de vitro" e fra Gherardino Pillecti di Firenze). The analytical project included the use of fiber optic reflectance spectroscopy (FORS) non-invasive technique, which was carried out in three different campaigns when the panels constituting the three stained glass windows were available in the restoration workshop. Based on the results obtained by the non-invasive campaigns and following the suggestions of the restorers, several micro-samples of glass together with alteration phases and materials due to past interventions were also taken. The glass microsamples were observed under the optical microscope and images at different magnifications were acquired. Subsequently, both cross and thin sections were obtained and investigated by using SEM-EDS. Infrared spectrometry (FT-IR) and X-ray diffractometry (XRD) were also employed to analyzed samples taken from alteration layers or materials used in past interventions. The analyses made it possible to assess the conservation status in relation to the type of glass highlighting some similarities in the choice of materials that supported the hypothesis of attribution and production made through stylistic studies.

## Hidden Treasures of Ukrainian Stained Glass

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The study is devoted to the artistic history and major movements of stained glass in Ukraine. The countless, though less known, threads of Ukrainian stained glass are interwoven to form a complex and yet distinguishable picture of the Ukrainian art. The research covers three periods of development: the nineteenth and early twentieth century, Soviet time (1917-1991), and period of independent Ukraine (1991-2014).

During the nineteenth and early twentieth centuries the art of Ukrainian stained glass was profoundly influenced by Western stained glass tradition. The unique stained glass iconostasis (Kharkiv, 1905), the only known in the world, is also worthy to note in this context. Stained glass of other artists, on the contrary, rooted in Ukrainian artistic traditions that grew out of the synthesis of Byzantine iconography with folk art e.g. Petro Kholodny (1876-1930), Modest Sosenko (1875-1920), Julian Butsmanjuk (1885-1967). Their profoundly lyrical style represents Ukrainian Art Nouveau.

During Soviet time, Ukrainian stained glass artists illustrated creative approach both in stylistic and technological ways. Although social realism dominated in the Soviet art on the whole, soviet Ukrainian stained glass formed its remarkable signature based predominantly on folk art: Ivan-Valentine Zadorozhny (1921-1988), Alla Horska (1929-1970).

Delle de verre technique achieved prominence in the Ukrainian stained glass in the 1970s. Such glass panels were mainly used as the part of the wall in monolith solid constructions, for instance, Central District Hospital (B. Karas, M. Levhanjan. Kiev, 1976), Funicular entrance hall (M. Shkaraputa. Kiev, 1986), tube station Postal Square (I. Levitzka, Yu. Kislichenko. Kiev, 1976) etc.

Contemporary stained glass has been experiencing controversial period: soviet style stained glass windows have been destroying; new ones have been appearing with retrospective character favouring Tiffany technique.

To conclude, as for the study of art, Ukrainian stained glass survey opens a new page and is an important contribution to our knowledge of one of the fascinating episodes in the history of European art.

## The Ephemeral in Glass Artworks

Rachel Welford\* & Cate Watkinson

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Transparency and reflection are two fundamental properties of glass and present a wealth of creative potential to the artist and designer. This presentation outlines PhD research that explores these properties, and how they can be manipulated and combined with light to enable ephemeral elements to become an integral part of a glass artwork.

These artworks sit predominantly within the field of architectural glass - and are designed to become part of the fabric of a building or urban space. They are created for a particular space, in response to the nature of that space, with the aim of becoming an integral part of an environment, aiding the development of a sense of place for its users.

The research explores ways in which architectural glass artworks can combine permanence and physicality with the ephemeral - interacting with transient light and a dynamic environment to embody change and impermanence. Translucent glass acts as a projection screen for shadows, and the reflective glass surface, to a greater or lesser degree, allows the surroundings and people within them to become part of the complex spatial relationships within the artwork.

How embodying the ephemeral in artworks can invoke a sense of the ethereal and generate meditative qualities for the viewer also forms part of the research. It will examine the relationships between artwork, environment and the ephemeral in relation to the creation of meditative, spiritual and / or sacred spaces, and wellbeing in general.

A survey of new types of glass and coatings on glass being produced for the architectural industry, and in particular how they produce variations in reflectivity and transparency, and the ability to emit light will feed into the research. Documentation of current use of these new types of glass and their application by architects, designers and artists, will place the creation of new artworks in context.

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2014 Yorkshire Water commission to create glass panels and glass balustrading for the exterior of the Headworks pumping station on Bridlington's South Promenade

2013 City of York Council commission to create a large glass screen for the main Customer Services area and art-glass manifestation lines for the main entrance doors.

2013 York NHS Trust - glass panels within lifts and a sculptural memorial to past staff, York Hospital

2011 In a Different Light - solo exhibition at Woodend art gallery, Scarborough.

1997-2004 Director, Scarborough Festival of Youth Arts,

1992-2007 Art Gallery curatorial work and informal art education in galleries and the community

Ref: 42

## **Stained glass in nonconformist places of worship in Wales.**

*Alun Adams*

*Architectural Glass Centre Co-ordinator  
University of Wales Trinity St David, Swansea*

The Puritan description of the nonconformist place of worship as Four bare walls and a sermon may at one time have been true. However over time and for a variety of reason the buildings became architecturally bolder and stained glass, often considered more in keeping with the traditions of the established and Roman church, installed.

Research in recent years has focused on denominational influence, subject matter, artists and studios and period of installation. It seeks also to photograph and record the glass against a background of declining religious observance and the closure of chapels and churches. The outcome will hopefully supplement information contained in current publications and web based information sources.

Ref: 43

## **Out of the Darkness: discovering late Georgian glass in Leeds**

*Jonathan & Ruth Cooke  
Stained Glass Conservators  
<info@stainedglassconservation.co.uk>*

The rescue of a severely damaged panel in the organ blower chamber of a Leeds church from among rubble, rotting curtains and empty bottles of communion wine, has resulted in a fascinating conservation project and fuelled the author's long standing curiosity about late Georgian ecclesiastical glass in and around Leeds.

Ref: 44

## **Adding colour to Scottish Glass**

*Jill Turnbull  
University of Edinburgh*

Coloured glass has formed part of the repertoire of the Scottish domestic glass industry since its revival in 1777. There is a very full archive in Edinburgh showing the problems encountered in producing coloured glass, the experiments undertaken and the recipes used. It includes correspondence with other glass makers as well as actual discs of experimental glass from the Holyrood glassworks.

Colours made included uranium, gold ruby and lithyalin, but examination of annual production at Holyrood from 1860-63 shows that green was the most popular. This paper will explore the material relating to coloured glass production and show some of the results.

## **English and Irish lead crystal glass in the 1670s: a reappraisal**

*Colin\* & Sue Brain*

One of the best-known facts of English glass history is that George Ravenscroft invented lead (flint) glass in 1674. Like many popular facts, closer examination suggests it wasn't exactly like that. A recent historical document unearthed by Mike Nobel demonstrates that George Ravenscroft got his patent because he was considered the first to succeed after: divers fruitless attempts by others. Unfortunately it soon transpired that Ravenscroft's initial attempt was as fruitless as the others appeared to have been. Yet somehow a viable lead crystal glass did emerge and by around 1676 was being made by several London and at least one Dublin glasshouse. 2014 is the 340th anniversary of the granting of Ravenscroft's patent for a glass resembling rock crystal and an opportunity to reappraise the quest for fine crystal glass in England and Ireland in the 1670s. This paper brings together newer and older documentary and finds-analysis evidence to explore what these divers attempts may have been, why they might have initially proved fruitless, and how the different technical problems may have been overcome.

The paper concludes by looking at potential avenues for future research to help resolve some remaining questions.



## **Structure and properties of lead borophosphate glasses modified with molybdenum oxide**

Ladislav Koudelka\*, Ivana Rösslerová, Petr Mošner, Lionel. Montagne, & Bertrand. Revel *Faculty of Chemical Technology, University of Pardubice, Pardubice, Czech Republic Université Lille Nord de France, USTL, Villeneuve d'Ascq, France*

Borophosphate glasses belong among important classes of glassy materials because they offer better thermal stability and chemical durability than phosphate glasses. The reason for the improvements in the properties of borophosphate glasses is ascribed by the transformation of linear-chain structure of metaphosphate glasses into three-dimensional structure of borophosphate glasses due to the additions of B<sub>2</sub>O<sub>3</sub>. Doping of borophosphate glasses by heavy metal oxides like MoO<sub>3</sub> and WO<sub>3</sub> are interesting due to their semiconducting properties ascribed to the presence of transition metal ions in multivalent states. In this study we prepared glassy samples from the system PbO-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub> in two compositional series (100-x)[0.5PbO-0.4P<sub>2</sub>O<sub>5</sub>-0.1B<sub>2</sub>O<sub>3</sub>]-xMoO<sub>3</sub> and (100-y)[0.5PbO-0.3P<sub>2</sub>O<sub>5</sub>-0.2B<sub>2</sub>O<sub>3</sub>]-yMoO<sub>3</sub> with 0-70 mol% MoO<sub>3</sub>. Glasses were prepared from analytical grade PbO, MoO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> using a total batch weight of 30g. The synthesis was carried out in platinum crucibles by heating up to 1000-1200°C. Physical properties of glasses were determined as well as their thermal behaviour. For structural study the <sup>31</sup>P and <sup>11</sup>B MAS NMR spectroscopy were applied as well as Raman spectroscopy. <sup>31</sup>P MAS NMR spectra showed on the depolymerization of phosphate chains with increasing MoO<sub>3</sub> content due to the formation of Mo-O-P bonds between octahedral MoO<sub>6</sub> structural units and tetrahedral PO<sub>4</sub> units. <sup>11</sup>B MAS NMR spectroscopy is able to supply information on the boron coordination in the studied glasses because these spectra possess an ability to discriminate between tetrahedral BO<sub>4</sub> boron coordination and trigonal BO<sub>3</sub> coordination due to the different ranges of chemical shift values for BO<sub>4</sub> and BO<sub>3</sub> units. The measurement of <sup>11</sup>B MAS NMR spectra of the studied glasses with the NMR spectrometer with a high resolution (magnetic field 18.8T) revealed the formation of B(OP)<sub>4-x</sub>(OMo)<sub>x</sub> mixed structural units and the decomposition of these spectra brought relative amounts of individual mixed structural units in these glasses.

## **Application of Laser Ablation ICP-MS depth profiling methods for the study of African glass beads**

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LA-ICP-MS is an analytical technique based on direct solid sampling of an artefact by a laser beam and subsequent elemental analysis of the particles generated. This microanalytical technique can be regarded as virtually non-destructive and is often used for the study of surface and bulk elemental concentrations in archaeological glass. The information retrieved provides archaeologists, art historians, conservations scientists, etc with crucial data on ancient glass technology and provenance of raw materials (sands, fluxes, chromophores, opacifiers, etc.). The analysis of archaeological glass is often challenging because of the occurrence of physical and/or chemical damage to the surface of the artefact. In particular, chemical damage as a result of long-time exposure to adverse conditions may have led to corrosion of the artefact's surface. Although LA-ICP-MS is able to remove superficial layers by performing pre-ablation passes, severe degradation of the surface, which is often not evident even with microscopic inspection, may lead to inaccurate bulk analytical data if undegraded glass has not been reached. LA-ICP-MS in line-scanning mode usually leads to retrieval of elemental data from a depth of between 1-2  $\mu\text{m}$  and is thus not the appropriate tool to retrieve bulk elemental information from severely degraded glass. To circumvent such potential problems in this study, LA-ICP-MS was operated in the so-called drilling mode, either with a low (1 Hz) or a high (10 Hz) pulse repetition rate during 50 s. This procedure generated detailed spatial information for ca. 20 elements over a shallow depth (7.5  $\mu\text{m}$ ) or less-detailed spatial information for 50-60 elements over a greater depth (ca. 70  $\mu\text{m}$ ). In this way the correct bulk elemental concentrations can be obtained as well as elemental depth profiles related to degradation phenomena may be studied. Several glass beads from two archaeological sites in Zanzibar (Fukuchani & Unguja Ukuu), dating from the 6th to 11th century C.E. were studied with this drilling approach. Chemical analysis indicates that most of the Zanzibari beads originate from South Asia, probably Sri Lanka. These results reinforce the hypothesis that trading patterns between eastern and southern Africa in the mid-to-late first millennium CE were different and suggest that this premise merits further studies.

Ref: 48

## **Computer simulation and visualization of glass-forming systems (poster)**

Wenlin Chen\*, Edwin Flikkema *Department of Mathematics and Physics, Aberystwyth University, United Kingdom*

Large scale simulation with high performance computing is being used to study glass-forming systems as well as zeolites. These materials can be regarded as consisting of a fixed network of Silicon/Aluminum and Oxygen atoms with relatively mobile Sodium and Potassium ions. Such systems can be modeled using Molecular Dynamics simulation (DLPOLY) and ab initio methods (Gaussian). Glass-forming materials are annealed from high temperature at different cooling rates. Zeolites are simulated at high pressure to study collapse and amorphisation. These processes can be followed in detail by analyzing the Molecular Dynamics trajectory file after simulation. Data such as the radial distribution function, cell parameters, etc. is collected and compared with experimental data. Visualization software such as Avizo and VMD is used to track the motion of ions in a glass and the collapsing of the Silicon/Aluminum-Oxygen framework in zeolites. This will help towards a better understanding of glass-forming systems.

Ref: 49

## **Thermal Conductivity of Refractory Glass Fibres: A Study of Materials, Standards and Test Methods**

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In the present study, the current international standards and corresponding apparatus for measuring the thermal conductivity of refractory glass fibre products has been reviewed. Refractory glass fibres are normally produced in the form of low density needled mats. A major issue with thermal conductivity measurements using various methods is lack of reproducibility in the test results due to transformation of the test material during the test. Also needled mats are inherently inhomogeneous & this poses additional problems. To be able to compare the various methods of thermal conductivity measurement, a refractory reference material was designed which is capable of withstanding maximum test temperatures (1400°C) with minimum transformations. The thermal conductivity of this reference material was then measured using various methods according to the different standards surveyed. In order to compare different materials, samples have been acquired from major refractory glass fibre manufacturers and the results have been compared against the newly introduced reference material. Materials manufactured by melt spinning, melt blowing and sol-gel have been studied and results to date will be presented here.

## **SiO<sub>x</sub>-barrier layers preventing alkali and earth alkaline metal diffusion deposited by Combustion Chemical Vapor Deposition under atmospheric pressure**

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**Keywords:** float glass corrosion; alkali and alkaline earth metal diffusion; C-CVD process; SiO<sub>x</sub>-layer; leaching-test; surface passivation

Glass corrosion is a recurring and costly problem all float glass manufacturers in the world have to struggle. It is always associated with water. At the exit of the tin bath float glass leaves the protective gas atmosphere and its surface faces air humidity for the first time. During cooling, storing or transport (different climates, sea air) hazy and foggy films can show up on the glass surface due to diffusion of alkali and alkaline earth metals in water contact. These films are the results of the first steps of glass corrosion. If the pH value of the aqueous solution increases to nine and higher in water deficiency the solubility of the SiO<sub>2</sub>-network strongly increases, too. The SiO<sub>2</sub>-network degrades.

The idea of a project at INNOVENT e.V. Technology Development is to prevent the initial reaction of the glass surface by means of the C-CVD process by integrating this technology into a float glass line. Here, under atmospheric pressure SiO<sub>x</sub>-layers are deposited. It could be shown that this cost efficient procedure can build up powerful thin barrier layers which protect the glass surface from water contact completely.

## **Rare earth doped telluro-silica glass fabrication by femtosecond pulsed laser process**

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Optical glasses play a major role in various technological applications. Unique photoluminescence characteristic of rare earth elements triggered their integration into assorted optoelectronic glass materials. Inherent emission characteristics of erbium at the 1550 nm optical communication wavelength made its position distinct among the rare earths. Er<sup>3+</sup> doped silicates are widely being explored for the development of integrated optic amplifiers and lasers in telecommunication. They also formulate the platform for photonic sensor technologies. However the rare earths segregation caused by the non-uniform doping in silica remains a challenge to the progress of such innovations.

We have developed a novel technique, ultrafast laser plasma implantation (ULPI) that enables the simultaneous implantation of multiple, atomically dissimilar ions into a silica matrix. In this paper we report the fabrication and characteristics of Er<sup>3+</sup> and Yb<sup>3+</sup> doped silica glass using ULPI. Tellurite glass targets with percentage molar concentrations 79TeO<sub>2</sub>-10ZnO-10Na<sub>2</sub>O-1Er<sub>2</sub>O<sub>3</sub> and 79TeO<sub>2</sub>-10ZnO-10Na<sub>2</sub>O-1Er<sub>2</sub>O<sub>3</sub>-1Yb<sub>2</sub>O<sub>3</sub> were ablated sequentially using an 800 nm Ti-sapphire femtosecond pulsed laser. The process was carried out at 50 μJ of pulse energy in a commercial femtosecond laser system under an oxygen atmosphere of 80 mTorr and a temperature of 973 K. During fs-pulsed laser ablation, the post-ion plasma relaxation regime produce ejecta in particulate forms ablated from the surface of target materials and due to their large kinetic energy initiate an interfacial reaction at 973K with the silica surface. Since the bond energy of Si-O in silica is only of the order of 10 eV (230 kcal per mol Silica), the interfacial reaction on surface results into the formation of a well-defined metastable homogeneous modified layer of silica. This level of composition modification was unveiled by the Energy-dispersive X-ray spectroscopy (EDX) technique, entailing an equimolar concentration of SiO<sub>2</sub> and TeO<sub>2</sub> in the modified layer. Such an extensive modification is thermodynamically unstable via melting and other conventional means.

A homogenously mixed rare-earth tellurite silica glass was produced with this technique, offering a potential solution for the erbium segregation in silica glass. The structural, optical and photoluminescence emission characteristics will be presented in this paper. This novel technique promises the realization of compact optical amplifiers and lasers on silica glass, further their integration into silicon.

## The Rigidity of Vitreous Networks: An Alternative Viewpoint

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An alternative, and much more intuitive, approach is proposed to the rigidity of (relatively) strain-free oxide glass networks, based on effectively rigid basic structural units and the true degrees of freedom that allow the formation of such networks; viz. bond torsion angles plus the bond angle at the bridging oxygen atoms. These ideas are extended to borate networks that include rigid superstructural units with no internal degrees of freedom in the form of variable bond and torsion angles, and it is shown that, for an isostatic network, the average (super)structural unit connectivity is equal to 4. The role of network rigidity in determining glass formation is discussed, together with the effects of steric hindrance, and a comparison with conventional constraints theory is presented for vitreous  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$ . Finally, it is argued that the so-called intermediate phase is merely an extended rigidity transition range, due to the chemical nanoheterogeneity that characterises the structure of glasses having more than one component, and that, in the case of Ge-Se glasses, the bonding in the interfacial regions between the Se and  $\text{GeSe}_2$  regions exhibits significant metalloid character.

## Molecular dynamics modelling of the structure of barium silicate glasses $\text{BaO-SiO}_2$

*Maha Rai\* and Gavin Mountjoy School of Physical Science, University of Kent, Canterbury, CT2 7NH, UK.*

Barium being a heavier element, provides an interest to study  $\text{BaO-SiO}_2$  glasses for the application of x-ray and thermal shielding. Molecular dynamics modelling techniques were used to make the models of  $\text{BaO-SiO}_2$  glasses. Models made were for  $x\text{BaO-(100-x) SiO}_2$  glasses with  $x=25, 33, 40$  and  $50$ . The diffraction from the model for  $x=33$  and  $40$  were compared with experimental result shows good agreement. The comparisons were done on neutron structure factor  $S(Q)$  and x-ray pair distribution function  $T(r)$ . The Ba-O CN for the glasses ranges from 6.5 to 6.9 with the average bond length  $R= 2.75$  to  $2.79 \text{ \AA}$ . However, the crystal CN for Ba-O of crystal range from 7 to 9.5 with the average bond length from  $2.78$  to  $2.91 \text{ \AA}$ . Model glasses maintained Si-O tetrahedral structure as expected. References: [1] N. Chanthima, J. Kaewkhao, C. Kedkaew, W. Chewpraditkul, A. Pokaipisit, and P. Limsuwan 2011 Prog. Nucl. Sci. Tech. 1 106. [2] C. Lara, M.J. Pascual and A. Durán 2004 J. Non-Cryst. Solids 348 149. [3] E.D. Zanotto, P.F. James and A.F. Craievich 1986 J. Mat. Sci. 21 3050. [4] H. Hasegawa and I. Yasui 1987 J. Non-Cryst. Solids 95-96 201. [5] L. Cormier, P.H. Gaskell and L. Creux 1999 J. Non-Cryst. Solids 248 84. [6] H. Schlenz, A. Kirfel, K. Schulmeister, N. Wartner, W. Mader, W. Raberg, K. Wandelt, C. Oligschleger, S. Bender, R. Franke, J. Hormes, W. Hoffbauer, V. Lansmann, M. Jansen, N. Zotov, C. Marian, H. Putz, J. Neufeind 2002 J. Non-Cryst. Solids 297 37

## Structure and properties of Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-GeO<sub>2</sub> glasses

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GeO<sub>2</sub> containing glasses are promising materials for IR technologies, nonlinear optics and design of laser devices. Furthermore, the high ionic conductivity of GeO<sub>2</sub>, makes them interesting candidates for solid electrolyte applications. This work deals with the study of the effect of GeO<sub>2</sub> content on the structure and properties of glasses prepared in the series 40Li<sub>2</sub>O-10B<sub>2</sub>O<sub>3</sub>-(50-x)P<sub>2</sub>O<sub>5</sub>- xGeO<sub>2</sub> with x = 0, 5, 10, 15 and 20 mol% GeO<sub>2</sub>. Glasses were characterized by the measurements of density, molar volume, chemical durability and refractive index. Thermal properties were investigated by DTA and TD methods. Structure of glasses was studied by Raman spectroscopy and MAS NMR spectroscopy. The obtained Raman, <sup>31</sup>P and <sup>11</sup>B MAS NMR spectra showed that the structure of starting 40Li<sub>2</sub>O-10B<sub>2</sub>O<sub>3</sub>-50P<sub>2</sub>O<sub>5</sub> glass is formed especially by metaphosphate structural units (Q<sub>2</sub>) and tetrahedral BO<sub>4</sub> (B(OP)<sub>4</sub>) units. The replacement of tetrahedral PO<sub>4</sub> structural units by GeO<sub>n</sub> units is accompanied by the gradual transformation of Q<sub>2</sub> units into Q<sub>1</sub> diphosphate units. The incorporation of GeO<sub>n</sub> units modifies also the coordination of boron atoms, where B(OP)<sub>4</sub> units are gradually replaced by B(OP)<sub>4-n</sub>(OGe)<sub>n</sub> structural units. Increasing GeO<sub>2</sub> content leads also to the partial transformation of tetrahedral BO<sub>4</sub> into triangular BO<sub>3</sub> structural units. Replacement of P<sub>2</sub>O<sub>5</sub> by GeO<sub>2</sub> results in an increase of glass density from 2.4 to 2.8 g/cm<sup>3</sup>, whereas molar volume decreases within the range of 37.9-29.4 cm<sup>3</sup>/mol. All GeO<sub>2</sub> containing glasses reveal better durability against water corrosion than the parent lithium borophosphate glass, nevertheless with increasing GeO<sub>2</sub> content within the concentration region from 5 to 20 mol%, chemical durability of glasses slightly decreases. DTA studies showed that all of glasses crystallize on heating within the temperature region of 550-650°C. Compounds formed by crystallization were LiPO<sub>3</sub>, Li<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, LiGe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and BPO<sub>4</sub>. Glass transition temperature and dilatometric softening temperature increase with increasing GeO<sub>2</sub> content, whereas thermal expansion coefficient decreases within the range of 16.9-14.5 ppm/oC. The refractive index has been measured at room temperature at wavelengths 452.9, 532 and 637.3 nm. With the replacement of P<sub>2</sub>O<sub>5</sub> by GeO<sub>2</sub>, the values of refractive index increase and Abbe number decreases.

## **Silicon Oxycarbide Glass for the Immobilisation of Irradiated Graphite from Nuclear Power Generation**

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Globally, there are 250,000 tonnes of irradiated graphite waste with no defined disposal route. With the forthcoming Gen. IV nuclear reactor designs, there is likely to be even more graphitic waste in the form of TRISO fuel particles. A formal, long-term disposal strategy is necessary. To this end, silicon oxycarbide glasses have been synthesised and characterised for use as potential hosts of irradiated graphite. The literature reports these glasses as having high chemical and mechanical durability, exceeding that of vitreous silica. Using powdered graphite as a safer analogue of the irradiated graphite, wastefoms containing up to 30 wt.% graphite have been produced through conventional tube-furnace sintering and spark plasma sintering (SPS). SPS yielded excellent densification of the wastefoms, with them remaining mostly x-ray amorphous. The interaction between glass and graphite has been probed, with the glass appearing to encapsulate rather than incorporate the graphite. A more economic route to the glass synthesis is currently underway.



## Quantitative Ion Speciation by Optical Spectroscopy: Classifying Functional Agents in Archaeological Glass Samples

Ferdinand Drünert(a)\*, Manfred Friedrich(b)<sup>2</sup>, Winfried Plass(b)<sup>2</sup>, Lothar Wondraczek(b) & Doris Möncke(a)(a)*Otto-Schott-Institute, Friedrich-Schiller-University Jena, Germany* (b)*IAAC, Friedrich-Schiller-University Jena, Germany*

UV/Vis spectroscopy is a non-destructive, quick, and straightforward technique for the qualitative and quantitative analysis of chromophores, such as transition metal ions. UV/Vis spectroscopy can reveal information on the oxidation state and the coordination of the metal ions. In contrast, the standard tool of archaeometry, i.e. quantitative chemical analysis, only reveals information on the total ion content. For quantitative analysis by UV/Vis spectroscopy the molar extinction coefficient of the studied metal ion has to be known in order to obtain the ions concentration  $c$  from the Lambert Beers Law ( $A$  is the measured absorbance,  $d$  the sample thickness):

Literature on molar extinction coefficients in glasses is rather scarce. Often the redox ratios of the metal ions are not considered or the composition deviates significantly from the glasses of interest in archaeometric research. Therefore, different model glasses were prepared to mimic the composition of a typical Roman soda-lime-silica glass, of Early and Late Medieval plant-ash-lime, or of potash-lime glasses. A modern standard soda-lime-silica glass (74SiO<sub>2</sub>-16Na<sub>2</sub>O-10CaO in mol%) was included in this study for comparison. All glasses were doped with manganese, iron, cobalt, nickel, or copper oxide and melted under more oxidizing or more reducing conditions. LA-ICP-MS was used for the quantitative elemental analysis and electron spin resonance (ESR) for the quantitative analysis of the paramagnetic ions (Cu<sup>2+</sup>, Fe<sup>3+</sup>, and Mn<sup>2+</sup>). Co and Ni ions are only present in the divalent form in glasses. However, Ni<sup>2+</sup> and Co<sup>2+</sup> are known structure indicator ions and change their coordination from octahedral in glasses with a low optical basicity to tetrahedral in glasses with high optical basicity. The optical basicity was calculated for all model glasses and is determined from optical absorption band of the structure indicator ion Mn<sup>2+</sup>. Molar extinction coefficients were determined for Mn<sup>2+</sup>, Mn<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Co<sup>2+</sup> for all studied glass systems.

## **Forged in Fire? Craft, Industry and Society in Early Medieval Ireland, AD400-1100**

Brendan O'Neill, *Irish Research Council (IRC)-Funded Postgraduate Scholar*

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Irish Early medieval settlements provide rich evidence for a range of craft and industry activities requiring the controlled use of fire. The primary evidence from archaeological sites includes hearths, open-fires, pits and pit furnaces and forging areas. Yet these distinct features were often reused for different activities over time, complicating any interpretation of the remaining archaeological and geochemical signals.

Using the case-study of Early Medieval glass making, this paper will examine how experimental archaeology can be used to provide additional data on these activities. This project has drawn evidence from primary archaeological materials, scientific analysis and practical testing to provide new, more certain criteria for labelling sites as glass-making or working. Using this refined understanding, issues of chronology as well as geographical and social specialisation on the island of Ireland can now begin to be tackled.

During the early medieval period, craft was bound up with ideas of social rank, status and gender (O Sullivan & Nicholl 2010, 82). Correspondingly, the fundamental objective of this project is to disambiguate archaeological remains so as to highlight the specific role of industry within society while testing current prevailing hypotheses relating to these activities.

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## Aluminium-free glass ionomer bone cements

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Bone cements are used as bone fillers (e.g. in vertebro- or kyphoplasty) or for anchoring implants (e.g. hip implants) into the bone, and current materials include acrylic cements (e.g. poly(methyl methacrylate, PMMA) or calcium phosphate cements. Both have several drawbacks, however, such as exothermic setting reaction (causing damage to surrounding tissue), lack of chemical bonding to bone (adhesion by mechanical interlocking only) and absence of bioactivity (growth of fibrous tissue around the implant rather than formation of an intimate bond with bone) for PMMA, and poor mechanical properties (allowing for use in non-load bearing applications only) for calcium phosphate cements. Glass ionomer cements (GIC), which set by a neutralisation reaction between an acid-degradable glass and a polymeric acid, are routinely used in dentistry, show excellent mechanical properties and form a chemical bond with hard tissue (teeth and bone) or surgical metals. The release of aluminium ions from those cements limits their use in orthopaedics, however, and the development of Al-free alternatives is therefore of great interest for orthopaedic applications. This study investigates the formation of GIC from Al-free glasses ( $\text{SiO}_2\text{-CaO-CaF}_2\text{-MgO}$  with 0, 2.5, 10 or 50% of Ca replaced by Sr on a molar base) and two different polymeric acids, poly(acrylic acid) (PAA) and poly(vinyl phosphonic-co-acrylic acid) (PVPA). Low Sr substitution (up to 10%) did not have a marked influence on cement properties, but the 50% Sr substituted glass showed much shorter working and setting times. This can possibly be explained by a larger cation ( $\text{Sr}^{2+}$ ) replacing a smaller one ( $\text{Ca}^{2+}$ ), resulting in a less compact glass network and, subsequently, a higher solubility of the glass. The glasses formed cements with both polymers, but only PVPA cements were stable in the presence of water, while PAA cements turned rubbery. The results suggest that PVPA, owing to a larger number of functional (carboxylate) groups per monomer unit, is suitable for obtaining mechanically stable GIC using aluminium-free glasses.

## **Inclusions of metals in glass for creative use**

Goshka (Małgorzata) Białek

The focus of this research was the various combinations of the two materials metal and glass, and more specifically concentrating on the application of a variety of metals in glass with different glass techniques for creative use.

In this research an application of metals in glass as a distinctive means of giving shape and internal structure and at the same time transparency, clearness and texture to glass was discussed. To illustrate the current practice in this field through the works of a number of artists who employ glass and metal in an innovative way, we had to also investigate their personal technical procedures and their reasons for the development of these procedures. Therefore the artists were asked, wherever possible, to give a statement relating to their technical and creative practice. These investigation involved artist such as Bertil Vallien, Antoine Leperier, Keith Cummings, Petr Stanicky, Markku Salo, De La Torre Brothers and many others.

Additionally the investigation explores the application of metals with glass in industries, the scientific developments in these fields and the possibility to apply these techniques for creative use by an artist in a studio environment. Many of the above artists were chosen as they have industry ties or are interested in technology, and they apply this in their artistic practise.

It was decided that the subject of this research could be interesting as a vehicle to instigate a cooperation between scientists and artists, as well as being helpful in understanding a different approach to this subject.

## **Research into 3D Printed Glass Investment Casting Moulds**

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This paper concerns a research project undertaken at Falmouth University into the use of emerging 3D printing technology in glass investment casting. This project, which has now been on going for over 4 years, has successfully developed an entirely new method for creating glass investment casting moulds with the aid of 3D printing technology. The method enables glass casting moulds to be created directly from three-dimensional computer files without the need for a physical mould pattern. The method developed is based on Additive Layer Manufacturing (ALM) technology using a three-dimensional printer - a process commonly known as Rapid Tooling (RT). The method that has been developed presents a number of significant advantages compared with conventional glass casting techniques. Work is currently underway to explore the usability of the process in various applications. This investigation includes explorations in creative glass practise as well as commercial applications. The latter aspect has so far predominately been focused on the medical sector, in particular exploring the creation of glass moulds for growing human replacement body parts, a technique which have been developed at the Royal Free Hospital, London. A current objective of this stage of the project is to further disseminate the research, and through this process identify other research partners and potential applications for this method.

## New Materials for Optical Fibres: Using NMR to understanding the Effect of Modifier on Tellurite Glass Structure

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Tellurite glasses have a range of technologically useful properties including high refractive indices, third-order non-linear optical coefficients, near infra-red transmittance and good chemical durability, all of which make them promising candidates as materials for components in a range of optical devices. However, to fully exploit the potential of tellurites, it is vital to understand the relationship between glass composition, structure, and their physical and optical properties so that materials can be tailored to meet the requirements of specific applications.

It has been reported extensively in the literature that the environment of tellurium changes from that of a four coordinated pseudo trigonal bipyramid structure ( $[\text{TeO}_4\text{E}]$ ) in  $\text{TeO}_2$  rich glasses, to pseudo-tetrahedral  $[\text{TeO}_3\text{E}]$  units as modifier ( $\text{X}_n\text{O}_m$ ) is added to the glass network [1-4]. Our recent work investigating the potassium tellurite glass system using neutron diffraction has demonstrated that, for compositions below  $\sim 15$  mol% modifier,  $n_{\text{TeO}}$  is roughly constant and *significantly less than four* (typically 3.65), even for zero % modifier [5]. The presence of  $[\text{TeO}_3\text{E}]$  units in amorphous  $\text{TeO}_2$  necessitates a significant number of non-bridging oxygens in this material and from this information, a model for the interaction between tellurium and potassium modifier has been developed that accurately predicts the variation in coordination number with composition [5].

Work is now ongoing to extend this model to more complex glass systems where the average coordination number of not only tellurium, but also the glass modifier cation, can vary with composition. This talk will report some recent work carried out on the aluminium tellurite glass system, where the modifier is able to adopt environments that are four-, five-, or six-coordinated.  $^{27}\text{Al}$  NMR studies, carried out at 20 T, quantify that the relative concentrations of these three sites and show that they vary with composition. When this information is combined with neutron diffraction data, it is possible to determine the changes in the short range structure of these materials.  $^{27}\text{Al}$  MAS DQ NMR spectra will also be presented, providing an insight into the relative proximities of the different aluminium sites and the medium range structure of the glass.

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## Chemical Evidence for Production and Trade of Islamic glass along the Silk Road

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Scientific analysis of Islamic Middle Eastern glasses has mainly focused on major and minor elemental analysis and on isotopic analysis. These approaches have provided information about the raw materials used to make the glasses and about provenance respectively.

This paper will focus on new information that trace element analysis of glasses found on the Silk Road sites can provide. Results for glass samples selected from Silk Road sites between Egypt and Iran will be discussed. There is limited evidence for the primary production of plant ash Islamic glass. Our aims are to suggest the locations of primary production zones and/or sites and to investigate glass trade between them by using trace element analysis.

Ninety-eight glass samples were obtained from Cairo (Egypt), Khirbat al-Minya (Israel), Beirut (the Lebanon), Damascus (Syria), al-Raqqah (Syria), Samarra (Iraq), Ctesiphon (Iraq) and Nishapur (Iran) dating to between the 9th and 14th centuries.

Major and minor components were determined using a Jeol JSM 8200 Superprobe (electron probe microanalysis) housed in the microanalysis research facility in the Archaeology Department at Nottingham University. Trace elements were determined using LA-ICP-MS; a NewWave UP193FX excimer (193nm) laser coupled to an Agilent 7500 series ICP-MS at the British Geological Survey, Keyworth, Nottinghamshire.

Trace elements associated with both silica and plant ashes have provided clearer contrasts between Levantine, Syrian and Iraqi/Iranian production zones than identified by using major and minor and a restricted number of restricted elements (Kato et al. 2010, Henderson 2013, 294-297). Within these broad production zones trace element analysis has, for example, revealed the use of separate silica sources used in glass found on the relatively close Iraqi sites of Ctesiphon and Samarra. One interpretation for this is that the glasses were separate melts. The scientific results have provided clear evidence for separate production zones, trade in glass (vessels) between the Levantine coast and Iran (Nishapur) and for relationships between different types of glass vessels and chemical compositions.

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## **Colored glasses: the eye's pleasure and much more.**

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Since the discovery of glass making, the coloration caused by transition elements has always been one of the most attractive properties of glasses. Still now, transition metal ions constitute the most important source of glass coloring agents. Coloration varies, for a given transition element, as a function of chemical and physical parameters such as glass composition or melting/fining conditions. At the same time, the electronic transitions responsible for light selective absorption and glass coloration provide unique information about the local structure and chemical bonding of glasses. This presentation aims to review optical absorption data at the light of complementary information provided by a broad range of experimental and numerical structural approaches, providing a unique harvest of results: unusual coordination numbers as 5-fold coordination, distribution of site geometry, sensitivity to the chemical bond, medium-range organization, heterogeneous spatial distribution... Some of these structural characteristics are inherited from the peculiar dynamics of silicate melts and may show a significant modification as a function of temperature. As transition elements can be connected to the various structural subsets of glasses, they are useful color indicators of the complex structure of these materials. Vice versa, using a better knowledge of the structural behavior of transition elements, the variation of colors may be rationalized as a function of glass composition and melting conditions.



## **The Advancements in Solid State NMR Experimentation, Methodologies and Instrumentation Impacting Upon Glass Science and Technology**

John V. Hanna  
*Department of Physics, University of Warwick,*

The solid state NMR technique has evolved remarkably over the last 10 - 20 years. Since its initial conception in the post-war period and into the 1950's, it undertook a long period of evolutionary technical development and consolidation which allowed the scientific community to evaluate the information that it provided, and reconcile this data against other characterisation techniques such as diffraction, microscopy and the vibrational spectroscopies. However, the more recent proliferation of higher magnetic field strengths, improved console characteristics (receiver sensitivity, rf stability, pulse programming flexibility) and enhanced probe capabilities (pulse power handling, MAS spinning frequencies) has truly enabled the solid state NMR technique to tackle more difficult/demanding materials and structural chemistry problems. In addition, the inception of exciting state-of-the-art sensitivity enhancement experiments such as dynamic nuclear polarisation (DNP) has facilitated the observation of insensitive nuclei and very low concentration bulk and surface species to unprecedented levels. One field of research that has benefitted greatly from all of these developments is glass science and technology. This presentation will demonstrate aspects of how these improvements to the solid state NMR technology contribute routinely to glass and disordered material research in Millburn House. The Materials Solid State NMR Group at Warwick conducts programs of research into phosphate glass, bioglass/biocement and paramagnetically doped chalcogenide gallium sulphide systems (amongst others), with these modern solid state NMR approaches being crucial in elucidation and understanding of the structure-function relationships in these materials. To conclude, aspects of the DNP technique will be discussed and how large sensitivity enhancements derived from this experiment will impact upon glass science and technology in the future. BIO

John Hanna obtained his BSc degree (physical and inorganic chemistry) from the University of Western Australia, and subsequent BSc (Hons.) and postgraduate degrees (chemical physics) from Griffith University. He managed the Brisbane NMR centre over the period of 1987-1989, and then went on to Direct the CSIRO North Ryde Solid State NMR and ASNTO Solid State NMR Facilities over the twenty year period 1989 - 2008. Since November 2008 he has been Principal Research Fellow and leader of the Materials Solid State NMR Group in the Centre for Magnetic Resonance in Millburn House at Warwick. His research interests centre on the application of solid state NMR techniques to glass and bioglass systems, inorganic oxide-based materials used in solid oxide and proton conduction fuel cell systems, battery systems, conventional and geopolymer cements, and homogeneous/heterogeneous catalysis. He has a particular focus on incorporating and rationalising solid state NMR data with structural information derived from other characterisation methods (particularly diffraction), and he is heavily involved with the use and development of DFT computation of NMR parameters to constrain structural information and generate 'NMR crystallography' formalisms. John currently sits on the User Executive Committee within EMSL at Pacific Northwest National Laboratories.

## **Modern Techniques: Aerolevitation, Time of Flight Mass Spectrometry, and Bactericidal Glasses**

Mario Affatigato\*, Steve Feller

*Center for the Study of Glass and Physics Department Coe College, 1220 First Av. NE Cedar Rapids, Iowa 52402*

This presentation will summarize the research work carried out by Prof. Affatigato and his undergraduate students over the past eighteen years. It will focus on some highlighted projects, namely: the determination of glass structure using laser ionization time of flight mass spectrometry; studies of glass modification by laser irradiation; bactericidal glass; and, most recently, glass manufacturing by aerolevitation and glasses for particle detection. The work on mass spectrometry will cover a broad range of oxide glass systems, including the borates, borosilicates, germanate, and gallate families. It has provided novel insights into the structure of glasses at intermediate length scales, measurements that are hard to obtain by any other techniques. The studies of glass structure modification will primarily center on vanadate glasses, which also form the basis for more recent electronic conductivity work at the heart of new particle calorimeter detectors. Bactericidal glass illustrates a nice collaborative project that involved simple borate glasses and helped pioneer their use in the human body-work that has led to significant medical developments by other colleagues and researchers. Finally, the aerolevitation project gives new insight into the crystallization and property behavior of glasses and melts at very high temperatures (from 2000 °C to 3000 °C), as well as opportunities for new crystal formation. The work by Prof. Affatigato and his students has been supported, over the years, by grants from the Research Corporation, the Petroleum Research Fund, private companies and foundations, and, primarily, by the U.S. National Science Foundation through its Ceramics, RUI, MRI, REU, and International programs.

## **Manufacturing High Purity Chalcogenide Glass**

Daniel William Hewak, Kevin C C Huang, Khouler Khan, Paul Bastock,

Chris Craig and Edwin Weatherby

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Chalcogenide materials are finding increasing interest as an active material in next generation optical and electronic devices. Their wide range of properties, ranging from photosensitivity, ability to host rare earth ions, electrical conductivity, phase change, exceptional optical non-linearities to name only a few are fueling this interest. Moreover, the ability to synthesize these materials in numerous forms as diverse as 2D monolayers, microspheres, optical fibres, nanowires, thin films as well as bulk glass ingots of over a kilogram in size ensures their application space is vast.

We began preparation of chalcogenides, largely based on sulphides, in 1992 and since then have built up an extensive capability for their purification, synthesis and fabrication in various forms. A key aspect of this facility is the ability to process in a flowing atmosphere of hydrogen sulphide which provided the capability of synthesis from elemental, oxide or halide precursors, processing through various chemical vapour deposition reactions as well as post purification.

In this talk we describe the range of materials we synthesize highlighting high purity sulphide bulk glass and transition metal di-chalcogenides for electronic applications, crystalline semiconductors for solar cell applications, low power phase change memory devices, switchable metamaterial devices as well as traditional chalcogenide glass and optical fibre.

### **Biography**

**Prof Dan Hewak** leads a research group investigating novel glasses for optoelectronic devices. He obtained his PhD from the University of Waterloo, Canada, in 1989, where he studied planar optical waveguides and devices. He spent three years with the National Optics Institute in Quebec City before joining the ORC where his work on optical materials was funded by IBM and Digital Equipment Canada. Since 1991 he has been with the ORC where he has developed a broad range of experience in new optoelectronic materials, and in particular amorphous chalcogenides. In the past five years DH has worked on 10 major projects, 6 as project leader and participated in 8 EPSRC funded projects as a principle and co-investigator. Relevant past EPSRC funded work includes integrated microsphere circuits, from which the world's first chalcogenide glass microsphere and microsphere lasers emerged, optical and electronic phase change memory and work on advancing the applications of chalcogenide glass and photonic devices. He has published over 250 refereed papers and conference publications and is the holder of eleven patents for novel glasses and their applications. He has presented his work internationally as both invited and contributed talks. DH has an extensive network of UK and international collaborators, both in academia and industry and serves on the TC20 Committee of the International Congress on Glass. He is editor of IEE published textbook: Properties, Processing and Applications of Glass and Rare-Earth Doped Glasses for Optical Fibres and serves on the Editorial Board for the Journal of Materials Science: Materials in Electronics.

Ref: 67

## The President's Address

Ref: 68

### **Chemical analysis of glass and glazes found in the Swedish medieval settlement Lödöse**

Bo Jonson\*1 Anna Ihr 2 1 Linnaeus University, Växjö, Sweden; 2 University of Gothenburg, Gothenburg, Sweden

The history of glass usage and possible manufacturing in Sweden has been investigated to a small extent, especially in terms of chemical analysis of the objects. The medieval settlement of Lödöse existed mainly through the 13th to 15th centuries. The town was a centre for trade - mostly with the European continent - minting and craftsmanship as well as a priory of the black friars that was established in mid-13th century. In our investigations of glasses and glazes, XRF analysis was used to monitor the chemical composition of glass objects and glazed bricks kept in the museum of Lödöse. Samples of coloured window glass from the medieval priory church, which was partly excavated around 1920, was chemically analysed by IPS. The window glass composition were found vary, but a general composition was (in wt-%) around 1 % Na<sub>2</sub>O, 13% K<sub>2</sub>O, 5% MgO, 24% CaO, 2 % Al<sub>2</sub>O<sub>3</sub>, <1 % Fe<sub>2</sub>O<sub>3</sub>, 5% P<sub>2</sub>O<sub>5</sub> and 46 % SiO<sub>2</sub>. Recent excavations in the town of Lödöse found remnants of a brick kiln. C14 analysis dated the findings to the period of around 1260 AD. As building material in the kiln and in stratigraphic older layers below it, a crystalline material was found together with a glassy material or possibly a slag. The glassy material was found to be too low in its content of carbon to originate from the smelting of minerals to metal in a blast furnace. Chemical analysis found the excavated glass to consist of approximately (in wt-%) 3 % Na<sub>2</sub>O, 3% K<sub>2</sub>O, 4% MgO, 18% CaO, 11 % Al<sub>2</sub>O<sub>3</sub>, 4 % Fe<sub>2</sub>O<sub>3</sub>, 1% P<sub>2</sub>O<sub>5</sub> and 55 % SiO<sub>2</sub>. The fingerprints of trace elements in the recently excavated glassy materials compared with church windows differ significantly, indicating different raw material sources and thus different melting sites of the respective glasses. It will be discussed if the excavated glassy material is to be interpreted as a waste product or as intentionally made glass. The latter would mean evidence for glass melting around 300 years earlier than previously known in Scandinavia. melting around 300 years earlier than previously known in Scandinavia.

## **$\delta^{18}\text{O}$ measurements of Greek-Roman glass (1th-6th century AD )**

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Twenty-six glass samples of Roman and late Roman age from northern Greece (excavations from ancient Pydna (present day Makrygialos) and its environs (Kitros Alykes, Kitros Louloudia, Paliokatachas and Aiginion) were analysed for their oxygen isotopic and chemical composition. The aim of this study was to identify the isotopic and chemical fingerprint of Roman glassware manufactured in Greece, showing different raw materials, production technology, and/or provenance. Eighteen glasses samples belong to the compositional category of natron glasses with  $\delta^{18}\text{O}$  values in the range of 15.5-16 ‰. These values are equal or very close to the mean value of Roman glassware from Europe and the Near East, suggesting that the starting materials were sands from the Belus and/or Volturno rivers or from the Levantine coast, isotopically very close to those of Belus. Eight samples present enriched values suggesting recycled production technology for these samples. Considering the high  $\text{Na}_2\text{O}$  content of samples  $\delta^{18}\text{O}$  enrichment may be explained by re-melting of previous glass and the addition of further amounts of natron as flux, thus increasing the  $\delta^{18}\text{O}$  content of the final products.

## **Mouth blown glass with integrated UV protection**

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Since many years it is common knowledge that UV rays may damage organic materials e. g. paper, wood, pigments, textiles. Even in modern materials like high tech glues ingredients react with sunlight. Until recently measures against UV rays were either simple (window shades or curtains) or rather sophisticated (films or coating). All solutions offered a more or less good protection but had remarkable disadvantages. In the case of shades/curtains electrical light has to replace daylight. Costs are involved. UV protection films must be laminated between two sheets of glass. Higher weight and expensive processing are the result. The major disadvantage of the film/lamination solution is that the life time is limited. Films are aging and lose the ability to filter UV rays. Furthermore they shrink. They need to be replaced after a certain period of time. Glashütte Lamberts found a way (patent pending) to integrate a 100% UV protection at 400 nm in mouth blown glass. No film, no coating. In a 2-step process the full protection is built up. The colour of the glass is depending on the UV barrier between almost white (380 nm) and a light yellow tint (400nm). Tests show that the UV protection is permanent and the colour of the glass does not change over time. This UV glass can be used like all other glasses. For restoration it offers an easy long term solution for protective glazing. The major installation is executed at the East Window of York Minster, UK.

## Why are obsidians black?

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Speciation of iron in obsidians (shiny, black volcanic glasses) from various localities has been determined using X-ray Absorption spectroscopy (XANES), Optical Absorption Spectroscopy and Transmission Electron microscopy (TEM). Optical absorption spectra were measured over a wide range of temperatures (from 10K to 1073K). XANES measurements show variable  $Fe_{2+}/Fe_{3+}$  ratio depending on formation conditions and provenance of the obsidian. Optical absorption spectra show a spectacular temperature-induced evolution. This is interpreted as arising from the coexistence of distinct absorption processes due to different Fe-speciations. Isolated  $Fe_{2+}$  is located in a regular octahedral site, a local environment unknown in silicate glasses, whereas isolated  $Fe_{3+}$  is found in both tetrahedral and octahedral coordinations, in the structure of the glassy matrix. The presence of iron intervalence charge-transfers processes is evidenced through the temperature dependence of the intensity of associated bands.

The specific coordination of  $Fe_{2+}$  together with the charge-transfer bands are related to the existence of iron oxide clusters (< 5nm), in the glass evidenced using TEM. These clusters (amorphous or crystalline), show a specific arrangement around iron in the glass and may be precursors of crystalline nanophases of iron oxide (titano-magnetite, magnetite or maghemite). The existence of these clusters and their nature seem to be related to the conditions of formation of the investigated obsidians. The high temperature measurements show an evolution of the structure around iron in these glasses compatible with a re-dissolution of the Fe-clusters in the glassy matrix.

## **Effect of Zn<sup>2+</sup> and Cu<sup>2+</sup>-bearing salts on the dissolution of silicate and borosilicate glasses**

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Zn<sup>2+</sup>-bearing salts have been used for a long time to protect the glass surface against corrosion of glassware in dishwashers, as well as against corrosion of flat glass foils during their transport and storage. However, the mechanisms by which Zn<sup>2+</sup> ions added in the corroding water diminish the extent of glass corrosion are not known. To describe more precisely the effect of Zn<sup>2+</sup> ions and to get insight into the mechanisms involved, we measured the glass dissolution kinetics in solutions bearing increasing concentrations of ZnCl<sub>2</sub>, using ICP-AES for solution analysis. Two glass compositions were chosen for this study : a Na-K-lime silicate glass with an incongruent dissolution behaviour, and a sodium borosilicate glass with a congruent dissolution behaviour. When the ZnCl<sub>2</sub> concentration reaches 10<sup>-4</sup> M, a value close to the solubility of Zn<sup>2+</sup> (at pH = 6.5 and T = 80°C), the release of Si from both glasses is reduced to undetectable levels. However, the global effect is different in both cases. In the alkali-lime silicate glass, the alkalis are leached at the same rate whatever the Zn<sup>2+</sup> concentration. The Zn<sup>2+</sup> ions precipitate, so that the pH is kept at a constant neutral value. When the Zn<sup>2+</sup> ions have disappeared from the solution (ie below 10<sup>-5</sup> M), the pH increases and normal dissolution occurs. In the sodium borosilicate glass, the Na<sup>+</sup> and B<sub>3+</sub> ions are *not* released and the Zn<sup>2+</sup> concentration stays constant for the first days of experiments, where the glass is definitely protected. After this first period, Zn<sup>2+</sup> ions precipitate, then the glass dissolution occurs. At the end of the experiments, hemimorphite of composition Zn<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>.H<sub>2</sub>O, was observed in the glass powder. Dissolution experiments were also performed in solutions bearing increasing concentration of CuCl<sub>2</sub> salts. They conducted to the same results, although Cu<sup>2+</sup> ions do not form insoluble hydroxysilicate analogous to hemimorphite. XPS and TOF-SIMS analysis of corroded glass were carried out to complete the picture. We propose that Zn<sup>2+</sup> ions, close to their solubility limit, buffer the pH at the glass-water interface, and by this way protect the silicate network against dissolution. For some compositions, a thin interface layer bearing Si and Zn can build up at the interface and reinforce the protection.



## Density and Packing in Germanate Glasses

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The physical properties (such as density) of binary germanate glasses exhibit a maximum or minimum as the concentration of modifier oxide is increased. This phenomenon is known as the germanate anomaly, because, contrastingly, the physical properties of silicate glasses do not exhibit a maximum or minimum. We show that it is useful to consider the partial number densities for each element. A simple model of glass density is to consider the glass to be a packing of spherical oxygen atoms. The composition-dependence of the partial number densities of binary germanate glasses have a universal form, which is different to that for the corresponding silicate glasses. We interpret the behaviour of the partial number densities using structural results from recent neutron diffraction experiments. There are two different composition regions; a densification region for low modifier content, and a de-densification region for high modifier content. In the densification region, the Ge number density changes little, but the germanate network densifies due to the addition of extra oxygen, as the average Ge-O coordination increases. In the de-densification region, the Ge number density declines significantly, due to the breaking of bridges between structural units. In contrast, the behaviour of the modifier cation number density is the same in both composition regions, and can be interpreted in terms of the modifier cations filling the voids in the germanate network. There is no evidence that the germanate anomaly arises as a result of the packing of the modifier cations; instead it arises due to bonding effects within the germanate network.

## **Unusual Cobalt and Nickel Species in Glasses: Chemical Oxidation, Photoionization and Site Geometry Probed by ESR and UV-Vis Spectroscopy**

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Cobalt and Nickel are usually present in the divalent state in glasses. Depending on the glass matrix, the coordination changes with increasing optical basicity from octahedral to tetrahedral. In medium basicity glasses occur both ion sites together with a third transitional coordination. This third site is attributed to a fivefold coordination (EXAFS, XANES) or to a pseudo-tetrahedral eightfold coordination in studies relying on magnetic susceptibility and ligand field theory. In a low alkaline borosilicate glass, doping with  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  results in different colours, as the fictive temperature of the glass is varies. In annealed glasses both ions are octahedrally coordinated. In the quenched glasses, coming from the tetrahedral coordination of the melt, the transitional coordination is frozen in. The optical spectra of the quenched glasses obtained in-situ on a heating stage, show that  $\text{Ni}^{2+}$  relaxes from the transitional state into the octahedral coordination. However,  $\text{Co}^{2+}$  relaxes not into the normally preferred octahedral, but instead into the tetrahedral coordination. From ligand field theory and magnetic susceptibility measurements, we assume that the transitional coordination is consistent with an eightfold pseudotetrahedral site geometry. We further present data on high basicity glasses ( $\text{Cs}_2\text{O-BaO-SiO}_2$ ,  $L \sim 0.7$ ) where Cobalt and Nickel are oxidized chemically to the trivalent state. The glasses have a yellow ( $\text{Co}^{3+}$ ) and violet blue ( $\text{Ni}^{3+}$ ) colour. It is assumed that the ions are tetrahedrally coordinated, since the same optical bands occur upon irradiation of soda lime silicate glass, where  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  are tetrahedrally coordinated and photo-oxidation generates the trivalent ( $\text{Co}^{2+}$ )<sup>+</sup> and ( $\text{Ni}^{2+}$ )<sup>+</sup> species. In phosphate glasses, in which  $\text{Co}^{2+}$  are octahedrally coordinated, leads irradiation to extrinsic defects characterized by two bands at 400 and 600 nm, which are assigned to octahedral coordinated ( $\text{Co}^{2+}$ )<sup>+</sup>. This defect is very stable and annealing the sample at elevated temperatures does not cause a recombination and recovery of the irradiation induced defects, but instead the transformation of intrinsic hole centre into the photo-oxidized ( $\text{Co}^{2+}$ )<sup>+</sup> species. In contrast to  $\text{Co}^{2+}$ , upon irradiation  $\text{Ni}^{2+}$  is photo-reduced in phosphate glasses. ESR spectroscopy shows distinct signals for ( $\text{Ni}^{2+}$ )<sup>-</sup> and ( $\text{Ni}^{2+}$ )<sup>+</sup>. .

Ref: 75

## **Factors that affect yellow phase formation during vitrification of highly active wastes**

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The post operational clean out (POCO) of the highly active storage tanks (HASTs) at Sellafield site will require the removal and immobilisation of residual solids from the heel of the tanks. These solids have accumulated over a number of years of nuclear fuel reprocessing on the site and have been identified as predominantly barium-strontium nitrate, zirconium molybdate (ZM) and caesium phosphomolybdate (CPM). Molybdenum compounds are known to have limited solubility in borosilicate glasses and when present in quantities that exceed the level of solubility form a secondary phase termed 'yellow phase'. Yellow phase is known to be corrosive to some stainless steels and partially water soluble. Therefore, formation of yellow phase in glasses containing nuclear waste destined for geological disposal is undesirable. A laboratory based study has been carried out to identify factors that affect yellow phase formation in glasses containing both molybdenum solids and highly active waste from nuclear reprocessing operations. A number of compositional and operational parameters which affect yellow phase formation in nuclear glasses have been identified.

Ref: 76

## **Molecular Dynamics simulation of alkali-silicate glasses**

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In this presentation results will be shown on the modelling of alkali disilicate glasses, more specifically Sodium-Potassium-disilicate with various ratios of Sodium and Potassium. Below the glass transition temperature, Sodium-Potassium disilicate can be regarded as consisting of a fixed (modified continuous random) network of silicon and oxygen atoms, with relatively mobile Sodium and Potassium ions, making the glass conductive. The ion conductivity exhibits a minimum close to a 50/50 ratio, replicating the "mixed alkali effect". Parallel effects are found in the intermediate scattering function. Advanced visualisation and virtual reality technology is used to map the available free volume of the alkali ions and to study the cooperative motion of the ions. This will help towards a better understanding of the mechanisms behind the mixed alkali effect.

## **Femtosecond laser plasma processing of glass for biosensing**

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Here we report the implantation of multiple ions into a silica glass forming an active sensor region consisting of a fluorescent rare earth ion  $\text{Er}^{3+}$ . The implantation creates a waveguiding region with more than 10% refractive index increase and hundreds of nanometres thicknesses. By controlling the optical scattering properties of the implanted region the photoluminescence (PL) lifetime of the  $\text{Er}^{3+}$  ions in the near infrared (1530 to 1600) can be anomalously increased beyond 10 ms. The measured change in PL lifetime can be therefore represent the optical absorption and scattering properties of any solid or liquid medium in contact with the implanted silica. This new approach is a great step forward in realising non-invasive metabolite sensing through skin using the ion implanted glass photonic chip. Details of ion implantation via femtosecond laser and characterization of implanted materials using FIB/TEM, SEM, Raman spectroscopy, fluorescence spectroscopy and m-line (prism coupling) will be presented. The PL lifetime based sensor concept and results for biological media and human trials will be discussed. Figure 1 shows the cross section of femtosecond laser plasma of multiple ions implanted in silica.

Figure 1 Silica glass implanted with  $\text{Te}^{4+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{Er}^{3+}$  ions using a femtosecond laser.

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## **The isobaric thermal capacity, the crystallization driving force and the Glass forming Ability of Bulk Metallic Glasses**

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The Glass Forming Ability (GFA) of Bulk Metallic Glasses (BMGs) is discussed with a lot of simple and/or complicated criteria [1, 2] while the Crystallization Driving Force (CDF) [3] (computed from the undercooled liquid as  $(DG/R.T)$ ; where  $DG$  and  $R$  are values for Gibbs free energy change at the considered  $T$  temperature and the gas constant) is the most used criterion in thermodynamics. It is similar to the Sun-Rawson GFA criterion (intensity of the bond strength between the  $E_{(2y/x)+}$  cation and oxygen anion in the oxide  $E_xO_y$  :  $SR = E_d/l.T_m$  where  $E_d$ ,  $l$  and  $T_m$  are values of the dissociation energy, the coordination number and the melting point of the studied oxide. Authors have successfully amended this criterion with the isobaric thermal capacity  $C_p$  and obtained a relative (without measurement units) GFA criterion:  $ThRGFA = (E_d/l.T_m.C_p)$  [4, 5].

In this study, author propose the Amended Crystallization Driving Force  $ACDF = (DG/R.T).(R/C_p) = DG/T.C_p$  using the isobaric thermal capacity of the studied metallic alloy instead of the universal gas constant. Some computations on some BMGs compositions reveal that the amended criterion does not invalidate the previous criterion but gives a link with the material nature (its characteristics). Computed values confirm that the GFA of BMGs increase only when  $ACDF$  decrease.

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Ref: 79

## **Effect of transition metal ions on electrical conductivity of zinc phosphate glasses**

Anirudh Yadav

The d.c. electrical conductivity of  $50\text{ZnO} \cdot 50\text{P}_2\text{O}_5$  glasses containing ( $9 - X \text{V}_2\text{O}_5 \cdot 9\text{-X CuO}$ ) where  $X=0,3,4,5,6$  &  $9$  have been studied at different temperatures. It is found that conductivity of the glasses containing  $9 \text{ mol\% V}_2\text{O}_5$  is greater than the conductivity of the glass containing  $9 \text{ mol\%}$  of  $\text{CuO}$ . The conductivity of these glasses decreases when  $\text{V}_2\text{O}_5$  is replaced by  $\text{CuO}$ . Density of these glasses has also been measured and it is found that density of the glass decreases when  $\text{V}_2\text{O}_5$  is replaced by  $\text{CuO}$ .

Ref: 80

## **Increasing the Sodium Content of UK Vitrified High Level Waste**

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*IPG* Sodium carbonate is currently being considered as a wash-out reagent for the unagitated Highly Active Liquor (HAL) storage tanks at Sellafield. This will result in a feed to the Waste Vitrification Plant (WVP) containing high concentrations of sodium as well as the high molybdenum expected to present in any settled tank solids. In an initial study, three approaches for the vitrification of high-Na and -Mo WVP feeds were considered, i.e. the addition of extra soda to a 'Ca/Zn'-based glasses, the replacement of Li with Na in a 'Ca/Zn' base glass, and the development of new borosilicate glass compositions. In each case, the maximum sodium that could be incorporated without the formation of significant yellow phase was determined for a representative high-Mo waste composition at a range of incorporations. The compositions that were at the limits of Na and Mo content then underwent a more detailed product characterisation, with the majority of the properties measured being within the ranges expected for standard MW-based Magnox and Blend products. However, the results from this initial study showed that at high  $\text{MoO}_3$  incorporations ( $\sim 10 \text{ wt\%}$ ) in both the 'Ca/Zn' and new borosilicate glass compositions, there was very little tolerance for significantly higher concentrations of sodium. This severely limits the maximum total volume of sodium carbonate that could be used as a tank wash-out reagent. Hence, a different approach is required, e.g. reducing the waste ( $\text{MoO}_3$ ) loading in the glass, developing a radically different non-borosilicate base glass, or blending the wash-out waste with existing HAL to dilute the sodium.

## **A Study of Rhenium Volatility During Simulated Highly Active Waste Vitrification**

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Volatilisation of technetium as caesium pertechnetate during vitrification of highly active waste and subsequent deposition of the condensed solids in the off-gas system has reduced the availability of the Sellafield Waste Vitrification Plant (WVP). The Vitrification Test Rig (VTR), a full scale replica of WVP, has been used to study the behaviour of rhenium as a surrogate for technetium in its non-active simulant to better understand the mechanism and to assess operational and plant design changes intended to minimise the build up of material in the off-gas system. This paper presents a summary of the work to date.

## **Glass strengthening through plasma implantation**

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We propose the use of our novel, patented technique Ultrafast Laser Plasma Implantation (ULPI) for the delivery of ions to a glass network to rapidly strengthen glass. This is in competition with the antiquated conventional technique ion exchange. This technique involves the submersion of a silicate, such as soda-lime, into a molten salt bath. Over an extended period of time, ions, such as sodium are in the starting glass are exchanged for potassium ions. This is done to 'compact' the top layer, thus enhancing various mechanical properties. Presently there is a significant and growing demand for strengthened glass, with major companies fervently seeking solutions to the growing problem of fractured glass on mobile devices. ULPI uses the ablated plasma from a target material to directly implant into a given substrate, in this case, a standard soda-lime silicate glass. This is done at temperatures below the glass transition temperature and leads to the growth of an implanted layer into the glass. The implanted layer is found to be a homogenous mixture of the implanting ions and the original substrate material. This has been successfully demonstrated with a variety of silica and silicate substrates and holds great promise for achieving a compaction of the desired region to maximise desirable mechanical properties. This technique is not only able to delivery ions such as potassium in higher concentrations than conventional techniques, but also enables an increased interlinking within the silica network. ULPI would also allow for more complex strengthening strategies to be employed, for example, the ability to localise the strengthening to predefined regions on a glass surface. This functionality allows one to consider new ways of preventing catastrophic fracturing of a glass. This could, for example, limit crack propagation to a specific area, thus not hindering the functionality of a device. As glass technology advances, it is becoming increasingly clear that glass can and should fulfil a role as a functional material, not simply a structural one. One such way of achieving this is through the incorporation of integrated photonic circuits into the design, from simple to far more complex photonic architectures. ULPI is capable of delivering both of these material aspects to a glass surface which is highly desirable from a commercial perspective due to its applicability.



Ref: 83

## **Iron-rich oxide glasses: formation, structure and properties**

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Abstract Iron can play a pivotal role in some oxide glasses used for radioactive and toxic waste immobilisation. For example it is a major component in iron phosphate glass systems, which exhibit iron contents of up to ca. 45 mol. % Fe<sub>2</sub>O<sub>3</sub>. Further examples of high-iron glasses include many natural glasses, which are generally highly durable materials. In this study we have considered very high Fe<sub>2</sub>O<sub>3</sub> content oxide glasses, which have received little research attention in the radioactive / toxic waste arena, and which could potentially offer new alternatives to the more developed and better-understood alkali borosilicate and iron phosphate glass systems. In the present study glass formation, composition, structure, and key thermal properties have been studied using a range of techniques including Mossbauer spectroscopy, XRF and XRD. The results will be presented and discussed here.

Ref: 84

## **Increasing Mo incorporation in borosilicate glasses**

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Some of the most highly radioactive nuclear wastes from the UK civil nuclear programme are stored as highly active liquids in Highly Active Storage Tanks (HAST) prior to vitrification in borosilicate glass. Clean-out of these tanks will involve removal of the HAST heel from the tanks. This is believed to mainly contain zirconium molybdate ( $ZrMo_2O_7(OH)_2(H_2O)_2$ ) and caesium phosphomolybdate phases. The main challenges related to these wastes are low solubility of MoO<sub>3</sub> and ZrO<sub>2</sub> in borosilicate glass and yellow phase formation that is partially soluble in water and when present in the melt may corrode the refractory melting vessel. Thus methods of increasing MoO<sub>3</sub> solubility and understanding what limits MoO<sub>3</sub> solubility in borosilicate glasses are of interest to the nuclear industry. The modified MW glass composition that contains CaO and ZnO, which has been developed by the National Nuclear Laboratory (NNL) seems to be advantageous for MoO<sub>3</sub> incorporation and mitigation of yellow phase, however the presence of both Ca and Mo can lead to the formation of powellite. We have therefore concentrated on other ways of improving MoO<sub>3</sub> solubility in borosilicate glasses. From initial results it appears that further additions of small amounts of Gd<sub>2</sub>O<sub>3</sub> (~ 6 wt.%) and Mn<sub>2</sub>O<sub>3</sub> (~3 wt.%) suppress the development of crystal phases.

## **Seeing Red: Lawrence Saint and the Quest for Medieval Striated Ruby**

J. Kenneth Leap - Stained Glass Artist & Designer

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**SUMMARY:** In 1928, American artist & designer, Lawrence Saint became the first head of the glass program at the National Cathedral in Washington, DC. He secured this position through his involvement with experiments to rediscover medieval techniques of stained glass while working on the windows of Bryn Athyn Cathedral from 1917 to 1928. Bryn Athyn is a small suburban community, center of the New Church, Swedenborgian denomination located 20 miles north of Philadelphia, Pennsylvania, which started as a utopian society on land that was purchased by millionaire industrialist John Pitcairn. With several others, Pitcairn founded the Pittsburgh Plate Glass Co. in 1883. This provided the resources for the extraordinary flourishing of architecture in the Bryn Athyn community: Bryn Athyn Cathedral, Pitcairns home, Cairnwood, and the home of his son Raymond, which is now the Glencairn Museum. These three buildings form the core of a newly designated National Historic Landmark District.

Following his father's death, Raymond Pitcairn took over the building of a church home for his community. The style he chose was that of the medieval gothic cathedral. Pitcairn was obsessed with recreating, in the most authentic way possible, the techniques used in the 12<sup>th</sup> century. As the American sheet glass on the market in the teens and 20s was unacceptable for his purpose, Pitcairn funded craftsmen to recreate the colors and quality of the mouth blown glass of the middle ages. The crowning achievement of the Bryn Athyn glass factory was a striated ruby glass nearly identical in quality to the copper-based reds unique to 12<sup>th</sup> & 13<sup>th</sup> century Europe. Sadly the Bryn Athyn records are incomplete and the recipe lost. Building on the knowledge learned in Bryn Athyn, Lawrence Saint ultimately succeeded in creating his own version of this glass for his windows at the National Cathedral which were constructed between 1928 and 1936. Before his death in 1961 Saint gave all of his 1300 formulas to the Metropolitan Museum of Art where they were forgotten by time. This presentation will spin an engaging mystery; traveling from Bryn Athyn, to the Smithsonian Institution, to the Corning Museum of Glass then on to Europe unveiling lost documentation and presenting modern attempts by glass blowers to produce this elusive glass. It seeks to answer the question, Can the craftsmen of today truly reproduce the materials of the past?

