

SGT NEWS



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CRYSTALLISATION 2003

the time resolved evolution of this new Y-Fe phase has been evaluated during four isothermal anneals. They report a temperature independent Avrami exponent of 1.7 ± 0.1 . An activation energy of 2.2 ± 0.5 eV and a frequency of $\sim 10^{15}$ /s have been found for the nucleation and growth of this phase.

The crystallisation of fluorosilicate glasses was determined by M Beggiora and I M Reaney of the Department of Engineering Materials, University of Sheffield and M S Islam of the Department of Chemistry, University of Surrey using high purity SiO_2 , $\text{AlO}_{1.5}$, CdF_2 , PbF_2 , ZnF_2 and ErF_3 . Upon heat treatment, Pb rich nanocrystals form which host most of the rare earth ions. X-ray diffraction suggests that the nanocrystals have a fluorite structure but the low volume fraction of the crystals and their small size means that unambiguous identification of the crystal structure is not possible. Therefore, $(1-x)\text{PbF}_2 \cdot x\text{ErF}_3$ ceramics were fabricated in order to study this phase in more detail. In addition atomistic simulation techniques have been used to investigate the defect chemistry of $\beta\text{-PbF}_2$ in an attempt to clarify the mechanism of incorporation of Er^{3+} ions in the lattice.

The effect of changing the substituent oxide and its amount on the thermal stability towards crystallisation of glasses of formula $(2.5-x)\text{CaO}x/3\text{M}_2\text{O}_3 \cdot 2\text{SiO}_2$ ($\text{M}=\text{La}, \text{Y}, \text{In}, \text{Ga}$) was studied by F Branda, A Costantini, G Luciani and B Silvestri of Università Federico II, Napoli. The stability to crystallisation increases as M_2O_3 is substituted for CaO. Moreover, the higher the ionic field strength of

the substituting cation, the greater the effect. This can be ascribed to: (a) the decrease in density of nonbridging oxygens when a network former oxide (Al_2O_3 , Ga_2O_3) is introduced; (b) the increase of the transverse bond strength (the greater the higher the ionic field strength of the cation) when a network modifier oxide is introduced.

J Deubener of Institut für Nichtmetallische Werkstoffe, Technische Universität Clausthal looked at the changes in entropy accompanied with the glass transition of five alkali silicate melts. Rheometric data and the Adam-Gibbs theory of relaxation are utilised to calculate the configurational entropy $S_{\text{conf}}(T_g)$ at the glass transition for each melt. These results, together with calorimetrically determined data of silicate glasses from literature are used to illustrate a compositional trend of 13 silicate glasses involving glass transition temperature and configurational entropy. It is assumed that the configurational entropy, which represents the number of all sampled local potential energy minima, is reduced when the melt is cooled down in the metastable state. Accordingly, for those melts which exhibit a deep supercool limit, ordering of various topological contributions may promote nucleation events and may help to explain the increased volume nucleation tendency in glasses.

Experimental high pressure crystallisation of a natural granitic melt was carried out by F G F Gibb of the Department of Engineering

The Seventh International Symposium on Crystallisation in Glasses and Liquids was held this year at the University of Sheffield, UK. Starting in the United States in 1960 this is a major conference with a long tradition. With growing interest in glasses and glass-ceramics, this conference looks to bridge the gap between the scientific understanding of nucleation and growth in glasses, and the industrial applications of glass ceramics. This was an international event with representatives from Brazil, Argentina, Russia, Japan, Saudi Arabia, USA, and many European countries.

The papers that appear in the April issue of *Physics and Chemistry of Glasses* look at applied research for various applications.

M Al-Jawad and S H Kilcoyne of University of Leeds, School of Physics and Astronomy and P Manuel of ISIS Facility, Rutherford Appleton Laboratory investigated the kinetics of formation of a novel Y-Fe phase using *in situ*, kinetic neutron diffraction. This phase exists over a short temperature range, between the formation of elemental Y and YFe_2 , during the crystallisation of amorphous $\text{Y}_{67}\text{Fe}_{33}$. It does not appear in any published phase diagrams of the Y-Fe system. Using the Avrami-Johnson-Mehl model for crystallisation and growth kinetics,

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Materials, University of Sheffield and P G Attrill of Parexel International, Sheffield. To ascertain how rapidly granitic magma can be cooled and still crystallise completely, experiments were carried out on a natural granite at 150 MPa using three linear cooling rates (1°C/h, 0.1°C/h and 1°C/day) and with three H₂O contents (1.57, 2.6 and 5.57%). Prior to cooling, samples were held at 800°C for 624 h so that only partial melts were produced thus avoiding the need for 'seeding'. At the fastest cooling rate it was found that most of the melt was effectively quenched to glass but complete crystallisation could be achieved at cooling rates of 0.1°C/h or slower. The temperature by which crystallisation is complete is a function of both cooling rate and H₂O content such that cooling at 1°C/day with only 1.57% H₂O results in complete crystallisation just below 700°C while a melt with 5.57% H₂O cooled at 1°C/h will never fully crystallise. Crystal growth rates of the main minerals, alkali feldspar, quartz and biotite, are also functions of cooling rate so that reducing the cooling rate of a granitic melt by a factor of 10 increases the grain size of the resulting rock by about two and a half times.

Crystal nucleation rates (I), viscosities (η) and heats of crystallisation (ΔH_c) and fusion (ΔH_f) were reported by C J R González Oliver and D O Russo of Centro Atómico Bariloche, Argentina and P F James of the Department of Engineering Materials, University of Sheffield for six soda-lime-silica glasses surrounding the NC₂S₃ composition. The classical nucleation theory (CNT) was adopted for the analysis of the nucleation rates, for some of the glasses, in terms of the measured viscosity for each glass and the driving force (ΔG) calculated from ΔH_c , ΔH_f , T_m (melting or liquidus temperature) and the measured specific heat DC_p changes between the crystal and supercooled liquid. For the base glass G2 a good description of the experimental nucleation rate versus temperature T can be obtained from theory if the interfacial energy σ is allowed to increase [$(d\sigma/dT) > 0$] slightly with temperature within the nucleation range, as found previously by one of the authors. However, from closer examination of other factors, since ΔC_p decreases strongly with decreasing T in part of the nucleation range and elastic stresses

could possibly alter significantly $\Delta G(T)$, a possibility is that σ may not necessarily need to change with T to give a satisfactory theoretical fit to the nucleation data. A glass G20 having nominally higher SiO₂ content than G2 and showing increased nucleation relative to G2 at the lower T end of the nucleation curve was also analysed, following the procedure for G2. Useful information may be obtained for explaining the effect of glass composition on nucleation.

L Gránásy, T Pusztai and T Börzsönyi of Research Institute for Solid State Physics and Optics, Budapest, Hungary, J A Warren of National Institute of Standards and Technology, USA, B Kvamme of University of Bergen, and P F James of the Department of Engineering Materials, University of Sheffield presented a phase field theory for the nucleation and growth of one and two phase crystals solidifying with different crystallographic orientations in binary alloys. The accuracy of the model is tested for crystal nucleation in single component systems. It is shown that without adjustable parameters the height of the nucleation barrier is predicted with reasonable accuracy. The kinetics of primary solidification is investigated as a function of model parameters under equiaxial conditions. Finally, they studied the formation of polycrystalline growth morphologies (disordered dendrites, spherulites and fractal-like aggregates).

MAS-NMR STUDY OF THE CRYSTALLISATION PROCESS OF BARIUM FLUORPHLOGOPITE GLASS CERAMICS

Potassium fluorphlogopite glass ceramics are the basis of machinable ceramics. These materials can be machined to shape using tungsten carbide tooling. The crystallisation behaviour of 8SiO₂.YAl₂O₃.3.75MgO.2.25MgF₂.BaO glasses with Y varying between 1.5 and 3.5 were investigated by R G Hill, A Stamboulis, R V Law and J Hawes of the Department of Materials, Imperial College, London and J Henry, University of Limerick using differential scanning calorimetry, x-ray diffraction analysis and nuclear magnetic resonance spectroscopy. The objective was to develop new machinable glass ceramics based on barium fluorphlogopite, BFP (6SiO₂.Al₂O₃.4MgO.2MgF₂.BaO). In the original glasses the ²⁷Al MAS NMR showed the aluminium to be four-

coordinated, Al(IV). The ¹⁹F spectra indicated the presence of predominantly F-Mg(n) species. The Si spectra indicated the presence of Q³Al type species. None of the spectra of the glasses changed significantly on varying the alumina content. DSC showed the glasses to exhibit two crystallisation peaks, which decreased in temperature with decreasing alumina content. The first peak (Tp1) corresponded to the formation of BFP. The ²⁷Al spectra changed significantly on crystallisation with Al(V) and Al(VI) being detected. The Al(VI) is thought to be present as crystalline mullite and Al(V) in the residual glass. The ²⁹Si spectra of the glasses heat treated to confirmed the presence of BFP. The ¹⁹F spectra exhibited a new sharp peak with a similar chemical shift to the original glasses corresponding to F-Mg(3) species in the BFP. It appears that the structure of the glass is similar to that of the primary crystal phase that forms, BFP.

Recent studies of nucleation in silicate and metallic glasses and liquids are reviewed by K F Kelton of the Department of Physics, Washington University, St. Louis, Missouri, focusing on the nucleation barrier for crystallisation and on the formation of nanostructured materials. Local icosahedral order in amorphous metals is frequently invoked to explain the undercooling behaviour of liquids and the formation of a crystallisation nanostructure in those glasses that form quasicrystals. We present diffraction data that demonstrate the formation of icosahedral order with increased undercooling in a TiZrNi liquid, directly linking this to the nucleation barrier for the first time. We also demonstrate that icosahedral order alone cannot explain nanocrystal formation in devitrified metallic glasses. Long range diffusion during nucleation and growth is generally critically important. Predictions from a new model for nucleation that takes this into account are discussed. ■

TO BE CONTINUED IN SGT NEWS, GLASS MAY 2004.



Society of Glass Technology,
3rd Floor,
Don Valley House,
Savile Street East,
Sheffield S4 7UQ.
Tel 0114 263 4455.
Fax 0114 263 4411.

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Crystalline dots and lines such as $\text{Sm}_2\text{Te}_6\text{O}_{15}$ and $\beta\text{-BaB}_2\text{O}_4$ were written in Sm_2O_3 containing glasses by irradiation from a continuous Nd:YAG laser operating at a wavelength of 1064 nm, and their morphologies and nonlinear optical properties were examined by T Komatsu, S Kawasaki, T Honma, Y Benino and T Fujiwara of the Department of Chemistry, Nagaoka University of Technology and R Sato of Tsuruoka National College of Technology. It was found that the crystalline phases formed by YAG laser irradiations were the same as those in crystallised glasses obtained by heat treatment in an electric furnace. Crystalline dots with corn-like shapes were formed, and their size depended on laser power, laser irradiation time and Sm_2O_3 content in glass. A close relation between dot size/length(depth) and cube root of laser irradiation time was found, suggesting that the growth of crystalline dots is controlled by diffusion of ions. Crystal lines of $\beta\text{-BaB}_2\text{O}_4$ were written by scanning YAG laser, and it was demonstrated from second harmonic generation measurements that the lines are $\beta\text{-BaB}_2\text{O}_4$ single crystals with the c-axis orientation along the laser scanning direction. The present study proposes that Nd:YAG laser irradiations of Sm_2O_3 containing glasses has a great potential for spatially selected crystallisation.

WATER CONCENTRATION AND DIFFUSION COEFFICIENT

Water concentration, C_w , and diffusion coefficient, D_w , for silicate glass and crystal powders were quantitatively studied from water release experiments by isothermal vacuum hot extraction (VHE). Calibration was made with gypsum and the minimal water detection rate was found as 9 nmol/min. This is typical for powdered (40–50 μm)

soda–lime–silica glass containing 1 wt ppm water. The powder method utilised for calculation of D_w is applicable to glass and crystal powders and does not require expensive sample preparation, transparency or the knowledge of extinction coefficients. Limited by the minimum detection rate and by surface water desorption, powders of 40–80 μm in size turned out to be most useful, and D_w can be measured in the range of 10^{-8} – 10^{-12} cm^2s^{-1} . R Müller, M Gaber & P Gottschling of the Federal Institute for Materials Research and Testing BAM calculated values of D_w for soda–lime–silica and silica glasses that agree well with literature data. New results were obtained from potash–lime–silica, lamp bulb and cordierite glasses. For the sake of comparison, cordierite single crystals were also measured.

S Murugavel & B Roling of Westfälische Wilhelms-Universität Münster studied the ac ionic conductivity of $\text{Ag}_8\text{I}_4\text{V}_2\text{O}_7$ glass and glass ceramics at different stages of the crystallisation process. In the early stages of this process, the formation of nanocrystallites leads to an enhancement of the ionic conductivity, which is related to the large interface area between the nanocrystallites and the glassy phase. A brick layer model was used to separate and compare the bulk and the interfacial contributions to the ac conductivity spectra of the glass ceramic with the maximal conductivity, and it was found that the ionic mobility at the interfaces is about two to three orders of magnitude larger than in the bulk. The spectral shape of the interfacial contribution to the ac conductivity is similar to the bulk contribution, but the interfacial contribution is characterised by a larger mean square displacement of the mobile ions at the crossover from subdiffusive dynamics to diffusive dynamics.

FERROELECTRIC GLASS CERAMICS BASED ON THE BISMUTH GERMANATE SYSTEM

Glasses have been formed from the $\text{BiO}_{1.5}\text{-GeO}_2\text{-BO}_{1.5}$ and $\text{BiO}_{1.5}\text{-GeO}_2\text{-TeO}_2$ systems and glass ceramics produced by controlled devitrification. The ferroelectric phase, orthorhombic Bi_2GeO_5 , which crystallises in all of the borate glasses, was studied by K Pengpat of Department of Physics, Chiang Mai University, Thailand and D Holland of Department of Physics, University of Warwick. This is the dominant phase for the $60\text{BiO}_{1.5}:20\text{GeO}_2:20\text{BO}_{1.5}$ composition. The glass forming region of the $\text{BiO}_{1.5}\text{-GeO}_2\text{-TeO}_2$ system is quite narrow and, whilst Bi_2GeO_5 could be formed along with Bi_4TeO_8 at low TeO_2 contents, this was replaced by $\text{Bi}_4(\text{GeO}_4)_3$ at higher concentrations. On increasing the temperature, the Bi_2GeO_5 devitrification in the borate containing glass ceramics changes from spherulitic to surface crystallisation which can be used to produce oriented growth. Such Bi_2GeO_5 glass ceramics are ferroelectric at room temperature with $T_c = 407^\circ\text{C}$. The polarisation $P_s = 0.14 \text{ cm}^{-2}$ is comparable with that of BaTiO_3 ceramic but a high voltage is required for poling. The preferred orientation of the surface crystallisation in this glass ceramic is perpendicular to the Bi_2GeO_5 (311) planes but a -axis orientation may be preferable, in order to enhance the electrical properties.

CHANGES IN ELECTRICAL PROPERTIES

Impedance spectroscopy is used by C M Queiroz, F M Figueiredo, M H Fernandes and J R Frade of the Ceramics and Glass



LOCAL SECTION CONTACTS

For details of forthcoming local section events in your area, contact the following. All SGT members and non-members welcome.

London

– Mr M Holden, BH-F (Engineering) Ltd, 4A Churchward, Southmead Park, Didcot, Oxon OX11 7HB. Tel 01235 517202.

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– Mr R Nickels, 4 Boundary Way, Compton, Wolverhampton, West Midlands WV6 8DL. Tel 01902 762070.

North East

– Mr W Brookes, 82 Whitfield Crescent, Penshaw, Houghton Le Spring, Tyne & Wear DH4 7QY. Tel/Fax 0191 584 3100.

North West

– Dr D Martlew, Pilkington Technology Centre, Hall Lane, Lathom, Ormskirk, Lancs. Tel 01695 54210.

Scottish

– Mr D A Rennie, United Glass Ltd, Glasshouse Loan, Alloa FK20 1PD. Tel 01259 218822.

Yorkshire

– Miss R M Sales, 20 Blackbrook Drive, Sheffield S10 4LS. Tel 0114 2306179.

NORTH AMERICA

– Dr A G Clare, School of Ceramic Engineering and Sciences, New York State College of Ceramics at Alfred University, 2 Pine Street, Alfred, NY 4802-1296, USA. Tel 607 871 2392.

INDIA

– Dr J Mukerji, Central Glass and Ceramic Research Institute, PO Jadavpur University, Calcutta 777 032, India. Tel 473 3496.

Engineering Department, University of Aveiro to measure the changes in electrical properties during the crystallisation of a phosphate phase in a glass with nominal molar composition $0.45\text{SiO}_2 \cdot 0.405\text{MgO} \cdot 0.045\text{K}_2\text{O} \cdot 0.1(3\text{CaO} \cdot \text{P}_2\text{O}_5)$ being developed for biomedical applications. The results show that changes in electrical resistivity can be used to monitor the onset of crystallisation and the crystallisation peak in bulk samples.

CLASSICAL GIBBS APPROACH

J W P Schmelzer of Department of Physics, University of Rostock firstly presented a generalisation of Gibbs' approach to the description of heterogeneous systems allowing the description of the thermodynamic equilibrium and nonequilibrium states of interest in nucleation-growth processes, clusters in the ambient phase, in a self consistent way. Secondly, in application of the approach to the description of the properties of the critical clusters it is found, in wide agreement with the results of density functional computations and in contrast to Gibbs' classical theory, that the state parameters of the critical clusters may deviate significantly from the state parameters of both the ambient and the newly evolving phases. Thirdly, in contrast to the classical Gibbs' approach as well as to existing methods of density functional computations, the generalisation of Gibbs' theory allows also a determination of the state parameters of sub- and supercritical clusters. As a direct consequence it turns out that also a variety of other thermodynamic and kinetic parameters, determining the growth of the clusters, may depend on cluster size. This way, the properties of the critical clusters may be very different from the properties of clusters of smaller and larger sizes. The parameters in the set of kinetic equations, describing nucleation growth processes, may be different for clusters of critical sizes as compared with the respective properties of sufficiently large clusters. Moreover, these results may shed some new light on the widely discussed problem of the existence of metastable phases in

the crystallisation of some classes of glass forming melts. Following the above outlined results, such phases could be interpreted as transient states of the clusters evolving temporarily in the course of evolution to the new phase. This way it is believed that the method developed may give a new key for the resolution of the above mentioned and further related problems in the theoretical interpretation of nucleation and growth experiments in glass forming systems.

CRYSTALLATION OF GLASSES INVESTIGATED

A Stamboulis and R G Hill of Department of Materials and R V Law of the Department of Chemistry, Imperial College London and S Matsuya of the Faculty of Dental Science, Kyushu University looked at the crystallisation of $4.5\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3 \cdot 1.5\text{P}_2\text{O}_5 \cdot (5-z)\text{CaO} \cdot z\text{CaF}_2$ glasses with z between 0 and 3. They investigated this using differential scanning calorimetry (DSC), x-ray diffraction analysis and magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. The glasses showed two exothermic peaks at Tp1 and Tp2 due to crystallisation, which decreased in temperature with fluorine content. In the nonfluorine



containing glass ($z=0$), whitlockite ($\text{Ca}_3(\text{PO}_4)_2$) and anorthite ($2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{CaO}$) were the final crystallisation products. In the fluorine containing glasses ($z=2$ and 3), fluorapatite (FAP) ($\text{Ca}_5(\text{PO}_4)_3$), crystallised at Tp1 and mullite ($2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$) at Tp2. MAS-NMR results showed that a glass phase remained after crystallisation. The coordination state of the phosphate species in the glass drastically changed during crystallisation. Five coordinate Al, Al(V), in the glass containing fluoride, disappeared after crystallisation of mullite. The ^{27}Al and ^{29}Si MAS-NMR spectra did not change significantly during fluorapatite crystallisation, but changed markedly on mullite formation. ^{19}F MAS-NMR demonstrated the presence of FAP in the heat treated glasses. In the glasses with a higher fluorine content than that required to convert all the Ca and P to FAP a Al-F-Ca(n) type species remained in the residual glass phase.

There were also seven poster presentations from the meeting that are published in full. ■



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SOCIETY OF GLASS TECHNOLOGY

The objects of the Society of Glass Technology are to encourage and advance the study of the history, art, science, design, manufacture, after treatment, distribution and end use of glass of any and every kind. These aims are furthered by meetings, publications and the maintenance a library and the promotion of association with other interested people and organisations.

New Special Interest Groups are being launched this year within SGT. The first two, on the History & Heritage of Glass and on the Structure of Amorphous Materials, are running already and details are available on the SGT website www.sgt.org.

The website also contains details of the 2004 Undergraduate Project Prize, and of the 2004 Worshipful Company of Glass Sellers of London Awards.

SGT's annual conference in 2005 will take place at the University of Sheffield. The theme for this conference will be "Glass; past, present and future", and it will incorporate the New Researchers' Forum on Glass and on the History & Heritage of Glass. There will also be a series of special events to mark the centenary of the University of Sheffield.

The event will take place on September 7-10, 2005, at Halifax Hall of Residence at the University of Sheffield. An organising committee is already working to set up the programme. Committee members include Russell Hand, University of Sheffield; John Henderson, Henderson Technology; David Martlew, Pilkington plc; John Osborn, Beatson Clark; John Parker, University of Sheffield; Alan Reynolds, consultant; Rosemary Sales, Yorkshire Section SGT; Margaret West, West X-Ray Solutions; Adrian Wright, Reading University; and SGT staff Christine Brown and Sara Lindley.