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Probing crystallisation of a fluoro-apatite - mullite system using neutron diffraction

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ABSTRACT

Real-time small angle neutron scattering and wide angle neutron scattering studies were undertaken concurrently on a glass ionomer of nominal composition $4.5(SiO_2)$-$3(Al_2O_3)$-$1.5(P_2O_5)$-$3(CaO)$-$2(CaF_2)$. Neutron studies were conducted as a function of temperature to investigate the crystallisation process. No amorphous phase separation was observed at room temperature and the onset of crystallisation was found to occur at 650 °C, which is 90 °C lower than previously reported. The first crystalline phase observed corresponded to fluorapatite; it was only upon further heating was the mullite phase became present. The crystallite size at 650 °C was found to be ~115 Å and the result was consistent across all measurements.

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1. Introduction

Fluoro-apatite – mullite glasses are of considerable interest for dental applications [1]. Fluoride ions are essential for the formation of normal tooth and bone tissue [2]. Fluoride ions also prevent dental caries by enhancing mineralization, reducing demineralization and inhibiting bacterial enzymes [3]. Accordingly, fluorine has been incorporated into bioactive glass for dental cement applications [4]. For fluorine-containing cements fluorapatite is formed, rather than hydroxyapatite, under physiological conditions. Fluorapatite is known to be more chemically stable, particularly under acid attack which is of further benefit in dental applications [3]. Additional benefits of the incorporation of fluorine include the lowering of the glass transition temperature and extending the working time of the cement [5]. Consequently, these materials have been studied using a range of techniques including: scanning electron microscopy (SEM) [6], Dynamic Mechanical Thermal Analysis (DMTA) [7], computer modelling [8], NMR [9], Fourier transform infrared spectroscopy (FTIR), solid state MAS-NMR spectroscopy [9] and neutron diffraction [10]. Glass transition results showed two transition temperatures and demonstrated that the parent glass phase separates into two amorphous glass phases. The SEM results indicate that these phases are not interconnected and instead sparse calcium and fluoride rich droplets, on the scale of 20–100 nm, are dispersed in the matrix of enriched in aluminium and silicon and depleted in calcium and fluoride glass. There are well-defined interfaces which indicate no interconnectivity, and a random distribution which may possibly indicate phase separation [6].

The first step of crystallisation can be thought of as a nucleation phase [11]. The nucleation process tends to occur at temperatures only slightly higher than the glass transition temperature. However, nucleation has been observed to occur at lower temperatures if the length of time maintained at this temperature is extended; and as such a time dependence has been inferred for the process of nucleation [7]. In some homogeneous glasses the nucleation process begins with the separation into several phases. These phases have different compositions, and the separation of these phases may aid crystallisation. This glass has previously been reported to undergo bulk nucleation after amorphous phase separation [12].

The present study investigates the structure and the crystallisation process of $4.5(SiO_2)$-$3(Al_2O_3)$-$1.5(P_2O_5)$-$3(CaO)$-$2(CaF_2)$, also known as LG26, as a function of temperature using simultaneous small and wide angle neutron diffraction. The conventional wide angle scattering was used to detect the onset of crystallisation by the emergence of Bragg peaks. Small angle scattering was used to observe the changing macrostructure.

2. Method

2.1. Sample preparation

Amorphous $4.5(SiO_2)$-$3(Al_2O_3)$-$1.5(P_2O_5)$-$3(CaO)$-$2(CaF_2)$ was synthesized via the melt quench method. In brief, the precursors SiO_2

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Table 1
Composition of the fabricated glass (molar percent), estimated errors are ~±2%. Oxygen and fluorine compositions are inferred on the basis of charge-balancing the sample, and the ratio of CaO:CaF_2 maintained at the batch value.

	Nominal composition	Measured composition
SiO_2	32.1	30.6
P_2O_5	10.7	10.9
Al_2O_3	21.4	19.1
CaO	21.4	23.6
CaF_2	14.3	15.8

(Sigma Aldrich, 99.8%), Al_2O_3 (Sigma Aldrich, 99.99%), P_2O_5 (Sigma Aldrich, 99.99%), $CaCO_3$ (Alfa Aesar, 99.95%), $SrCO_3$ (Sigma Aldrich, 99.9%) and CaF_2 (Fisher Scientific, 99%), were weighed in the appropriate molar ratios and thoroughly mixed. The precursors were then placed in a Pt/Rh crucible and thence into a preheated furnace at 1450 °C for 1 h. The melt was cast into a preheated graphite mould at 450 °C and then annealed overnight at this temperature before being slowly cooled to room temperature.

2.2. Sample characterisation

X-ray diffraction was undertaken (using a Bruker D8 instrument) to ensure the samples were amorphous and that no crystallisation had occurred during their fabrication. X-ray fluorescence was undertaken (PANalytical Epsilon 3) to determine the relative concentration of elements present in the sample; it must be noted that oxygen and fluorine cannot be detected using conventional benchtop X-ray florescence due to their low atomic number. We therefore assigned O and F to charge balance the measured values of P, Si, Ca and Al atoms that are detectable. In the case of Ca we assigned this to a mixture of CaO and CaF_2 whilst maintaining the initial starting ratio of fluoride to oxide. It is assumed, and has been confirmed in studies of glasses of similar composition, that the calcium carbonate decompose upon heating to give calcium oxide and that the calcium fluoride remains intact [12]. Weight loss measurements confirm the loss of carbonates from the melt derived sample. The sample densities were measured using helium pycnometry (Quantachrome Multi-Pycnometer). The glass transition temperature was measured using a NETZSCH STA 409 PG (TG/DSC) simultaneous thermal analysis, thermogravimetry, differential scanning calorimetry. Samples of ~30 mg were heated in sealed aluminium pans at a rate of 5 °C/min up to 1000 °C under standard atmosphere. Bioactive glasses are typically used in particulate form as filling agents. Our diffraction studies were undertaken on similarly powdered samples. Samples were ground using an agate pestle and mortar immediately prior to the diffraction studies to minimise any potential surface hydration effects.

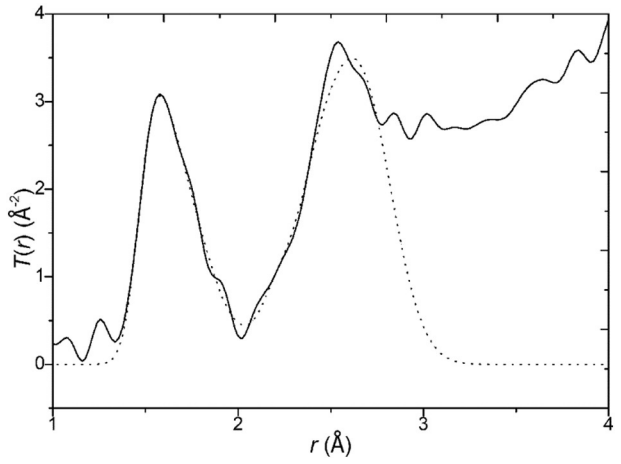

Fig. 1. The real space diffraction data obtained for fluoro-apatite – mullite glass at room temperature. The solid curve shows the experimental data and the dashed curve the fit.

2.3. Neutron diffraction

Datasets were collected using the *Near and InterMediate Range Order Diffractometer* (NIMROD) [13] and the GEneral Materials diffractometer (GEM] [14] at the ISIS pulsed neutron source, Rutherford Appleton Laboratory. Diffraction datasets were collected at a series of temperatures using the instrument NIMROD, whilst room temperature measurements were conducted, for a series of pre-heat treated samples, using GEM.

2.4. NIMROD

The powdered samples were placed into thin walled flat-plate vanadium containers and heated *in situ* using the RAL-4 63 mm bore furnace with vanadium windows mounted directly on the diffractometer. Diffraction patterns were collected at room temperature and at a series of predetermined elevated temperatures. The furnace was heated at a rate of 10 °C/min until the sample was 10 °C from the required temperature. To ensure the required temperature was not exceeded the heating rate was then reduced to 1 °C/min for the final 10 °C. In addition to the interference patterns collected for the samples, interference patterns were also collected for the empty instrument, empty sample container, a vanadium plate, and empty furnace to enable background corrections and normalisation of the sample data to be achieved. Data reduction and normalisation were undertaken using the program *Gudrun* [15]. The Bragg peak free room temperature spectrum was Fourier transformed to give a real space function, D(r), and fitted using *NXFit* [16]. The corrected small angle scattering datasets were investigated using Guinier and Porod analysis [19].

2.5. GEM

Neutron datasets were collected for heat-treated samples using the GEM diffractometer. The samples were placed in cylindrical vanadium containers with inside diameter of 5.0 mm and a wall thickness of 0.025 mm. interference patterns for the empty instrument, vanadium rod and empty container were collected to allow for background and normalisation corrections. The datasets were corrected and normalised using *Gudrun* [15]. Bragg peaks were indexed using the Chemical Database Service database [17] to identify the crystal phases present in this system.

3. Results and discussion

The resultant glass was optically transparent and visibly homogenous with no visible sign of crystallisation. X-ray diffraction data confirmed that the glasses were indeed amorphous. It is worth noting that previous studies traditionally quench these types of glasses into water to avoid crystallisation [12]. However, due to the need to undertake neutron diffraction experiments on these samples, all efforts were undertaken to ensure minimal surface hydration given that hydrogen is a strong inelastic scattering atom. This result demonstrates that these types of glasses can be prepared via conventional air quenching. The resulting composition, as determined by fluorescence spectroscopy, is given in Table 1. As seen there is reasonable agreement between the expected nominal composition and the experimentally measured composition (given an estimated 2% experimental error). The density of the fluoro-apatite – mullite glass was found to be 2.70 $g \cdot cm^{-3}$ which is in agreement with the previously reported value of 2.73 $g \cdot cm^{-3}$ [18].

The real space data obtained from NIMROD, formed after applying background corrections and Fourier transforming the interference function $i(Q)$, is shown in Fig. 1. As shown, there are no Bragg peaks present and the sample is fully amorphous prior to heat treatment. A

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