Iron phosphate glasses: Bulk properties and atomic scale structure

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1. Introduction

Iron phosphate glasses are of interest for application in the field of radioactive waste immobilisation due to their high chemical durability [1–6]. Among the various Fe/P atomic ratio, the glass with 40 mol% Fe2O3-60 mol% P2O5 (IPG) (where the Fe/P atomic ratio = 0.67) is found to be more chemically durable [3]. As indicated by Jantzen [5,6], excellent chemical durability, high solubility for heavy metals, low melting temperatures, rapid melting rates, low corrosion of oxide refractories and inconel alloys and higher (25–50 mass %) waste loading are certain salient features of iron phosphate glass. The glass forming characteristics of iron phosphate glass are demonstrated by immobilizing waste rich in Cs, Mo, U, and Cr [3,7,8] which are poorly soluble in borosilicate glass [9]. In our earlier studies [10], we had demonstrated IPG as a promising matrix for the immobilisation of Cs with respect to higher loading (50 ± 2 wt. % Cs2O) and also due to its low (<0.5 wt. %) volatilisation loss during homogenisation of the melt in contrast to ~10 wt. % loss of Cs during immobilisation in borosilicate glass used for clinical applications [11]. Sealed radioactive Cs source is not only used for clinical application, it has other industrial, research and medical applications. Reference [12] contains a good summary of these applications. Because radioactive caesium decays to barium, it is essential to understand the change in the bulk properties (such as density, glass transition temperature, linear thermal expansion) of caesium loaded IPG when the Cs is partly or completely replaced with Ba. In order to understand the effect of complete conversion to Ba loaded iron phosphate glass, the said bulk properties were studied for iron phosphate glass containing 10 and 20 wt. % BaO. As the maximum composition of Cs2O loaded in IPG was 50 ± 2 wt. % (labelled as IPCs50 henceforth), bulk properties were determined with partial replacement of Cs2O with 5 wt. % BaO and 25 wt. % BaO. Various other combinations and compositions of Cs/Ba loaded iron phosphate glasses are not part of the present study. A study such as this is essential before immobilizing 137Cs in IPG, since 137Cs loaded IPG can serve as a γ source for medical application.

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2. Experimental

2.1. Glass preparation

Batches of iron phosphate glasses were prepared by mixing various amounts of Cs₂CO₃ (99.9% Aldrich), Fe₂O₃ (99.5%, Fisher Scientific), NH₄H₂PO₄ (ADP) (99% Ranbaxy) and Ba(OH)₂·8H₂O (99.9% Loba Chemie). The mixture was homogenized by grinding in a mortar and pestle in an inert argon glove box. The mixture was taken in a high density re-crystallized alumina crucible and calcined at 523 K for 1 h prior to melting. Each calcined sample was melted inside an electric furnace in air. The batch composition of each mixture was such that the melted material was air quenched on a stainless steel plate. The air quenched bulk materials were ball milled and powder samples were used for all the characterization studies except for density measurements. As-quenched granules were used for the density measurements. The percentage weight loss during glass preparation of each glass batch is presented in Table 1. The error in weight measurement was ± 0.001 g. A mixture of Fe₂O₃ and NH₄H₂PO₄ maintaining a Fe/P atomic ratio of 0.67 was heated in a similar alumina crucible and air quenched at 1423 K for the preparation of un-doped IP9. No measurable corrosion was observed when heated in a high density re-crystallized alumina crucible. The glass inside the alumina crucible could be removed. Fig. 1 shows a photograph of the crucible before and after removal of the IPBa10 glass.

2.2. Characterization

2.2.1. X-ray diffraction

Samples were characterised by XRD (X-ray diffraction) by using a Siemens D500 X-ray diffractometer (equipped with secondary beam curved graphite monochromator) employing Cu Kα radiation. Scans were performed with the step size of 0.05° over a range of 2θ = 5°—80° with 1 s counting time per step.

2.2.2. Density measurements

The density of each glass was determined by using the Archimedes principle utilising dibutyl phthalate as the liquid medium. Randomly chosen pieces of glasses were subjected to density measurements. The error in the density measurements was ± 5 kg m⁻³.

2.2.3. Differential thermal analysis (DTA)

The DTA was carried out using TG-DTA Setsys Evolution 16/18, M/s. Setaram, France. The instrument was calibrated for temperature as explained previously [10]. A differential thermal analysis measurement was used to determine the glass transition temperature (T_g) of the glasses under present study. The T_g of all the glasses were determined in flowing argon (rate: 20 ml min⁻¹) using Pt crucibles at a heating rate of 10 K min⁻¹. Blank runs were carried out under similar conditions and the data presented are the blank corrected ones. The glass transition temperature (T_g) is defined as the midpoint temperature of the extensions of the pre and posttransition baselines of the DTA curve. The error in the temperature measurement was ±1 K.

2.2.4. Dilatometry

Thermal expansion studies were carried out by means of a home-built push rod dilatometer [14] in air up to 700 K at a heating rate of 2 K min⁻¹ using a LVDT (linear variable differential transformer) sensor and quartz push rod. Specimen temperature was measured by a chromel–alumel thermocouple placed very near the specimen. High density thoria pellets were used as standards. The faces of the glass rod (graphite moulded with dimension of 15 mm in height and 10 mm in diameter) were made parallel by polishing with SiC paper (grit 240 and 600). These rods were used for the thermal expansion measurements using the dilatometer. The maximum relative error in the dilatometric measurements was ± 2%.

2.2.5. Mössbauer spectroscopy

Room temperature ⁵⁷Fe Mössbauer measurements were carried out using a Wissel spectrometer. Finely powdered specimens were analysed in transmission mode, using a 50 mCi ⁵⁷Co source embedded in a Rh matrix. Calibration of the data was made relative to α-Fe and the spectra were measured using a constant acceleration waveform at a velocity range of ± 10 mm s⁻¹. Spectral deconvolution was performed using the commercially available software RECOIL [15] by assigning doublets with an extended Voigt-based fitting (xVBF) profile to represent the different Fe oxidation states and coordination environments in the samples. xVBF lineshapes are a convolution of Lorentzian and Gaussian components which represent both the natural lineshape of the emission/absorption process and the site distribution characteristics of amorphous materials [16].

2.2.6. XAS studies

XAS data were acquired on the beam line B18 at Diamond Light Source, Harwell, UK, and beamline X23A2 of the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY, USA. Beamline B18 utilises a collimating mirror, a fixed-exit double crystal Si(111) monochromator and a double toroidal focussing mirror. Beamline X23A2 utilises an upwards reflecting, fixed exit, piezo-feedback stabilised Si (311) double crystal monochromator of a Golovchenko-Cowan design, and a single bounce harmonic rejection mirror. Fe K-edge XAS data were acquired on B18 and X23A2 in transmission mode using finely ground specimens dispersed in polyethylene glycol to achieve a thickness of one absorption length. P K-edge XAS data were acquired on B18 in fluorescence mode, under He atmosphere, using finely ground specimens dispersed in a mixture of polyethylene glycol and graphite, oriented at 45° to the incident X-ray beam and detector.

| Sample | Batch Composition ± 0.5 (wt. %) | % weight loss | Density ± 5 (kg m⁻³) | Molar volume (m⁻³) | Glass transition temperature ± 1 (K) |
|--------|---------------------------------|---------------|----------------------|-------------------|-----------------------------------|
| IPBa10 | 38.6 34.3 21.5                  | 51.4 45.7 28.6 | 10.0 20.0 24.9      | 0.0 0.0 0.0       | 0.85 0.75 0.84                   |
| IPBa20 | 0.0 0.0 0.0                      | 0.0 0.0 0.0   | 0.0 0.0 0.0         | 0.0 0.0 0.0       | 0.0 0.0 0.0                      |
| IPBa25 | 31.9 34.3 21.6                  | 47.1 45.7 28.8 | 10.0 20.0 24.9      | 0.0 0.0 0.0       | 0.85 0.75 0.84                   |
| IPBa30 | 31.9 34.3 21.6                  | 47.1 45.7 28.8 | 10.0 20.0 24.9      | 0.0 0.0 0.0       | 0.85 0.75 0.84                   |

Table 1

Batch composition, observed percentage of weight loss during glass preparation, and the properties measured for the glasses under present study.
Incident and transmitted beam intensities were measured using ionization chambers, filled with mixtures of He and Ar or N₂, operated in a stable region of their I/V curve. Fluorescence emission was detected using a four channel Si-drift detector, with appropriate dead time correction as described previously [17]. An iron foil was used as an internal energy calibration where the first inflection point was defined to be 7111.0 eV. Data reduction and analysis was performed using the programmes Athena, Artemis and Hephaestus [18].

3. Results and discussion

3.1. Glass preparation and amorphous nature

The percentage weight loss observed during the preparation of the glasses is shown in Table 1. The weight loss observed was < 1% and thus the batch composition was taken as the glass composition (Table 1). Bulk glass samples were characterised by XRD. The prepared glasses were found to be X-ray amorphous as shown in Fig. 2. The XRD pattern of un-doped IPG [13] is also added in Fig. 2 for comparison. The quenching temperature (Table 1) of either Ba loaded or Ba/Cs loaded IPG was lower than that of un-doped IPG, indicating the effect of addition of modifiers such as Cs₂O or BaO during the synthesis of glass. This is similar to that reported in the literature for Cs loaded IPG [10]. Although the quenching temperature plays an important role in maintaining the redox (Fe⁺/ΣFe) ratio in glass, the effect of quenching temperature on the iron redox ratio is more predominant only when quenched at a temperature higher than 1473 K [19]. As the quenching temperature of the glasses under present study was 1323 K, the reduction in quenching temperature is due to the addition of glass modifiers such as Cs₂O and/or BaO.

3.2. Density and molar volume

Table 1 shows the densities of the iron phosphate glasses under present study. Since the density of glass is sensitive to both the volume occupied by the atoms and to their atomic weight, molar volume is often used to compare the behaviour of glasses [20]. The molar mass of IPBa10 and IPBa20 are 149.5 and 149.9 g mol⁻¹ respectively, the increase being only about 0.3%. However, a greater decrease in molar volume (about 10%) was observed with increasing barium content in the glass; thus molar volume is more sensitive to change in the Ba content. Better glass network connectivity in IPBa20 compared to IPBa10 can reduce the molar volume in IPBa20. The decrease in molar volume is in agreement with similar iron phosphate glasses reported in the literature [21]. Similarly, the molecular weight of IPCs45Ba5 and IPCs25Ba25 were
189 and 170.3 g mol$^{-1}$. Although Cs and Ba have similar atomic weight, the reduction in molecular weight in IPCs25Ba25 is due to replacement of one unit of Cs$_2$O by a BaO. However, the density of the glass increases from IPCs45Ba5 to IPCs25Ba25, resulting in the reduction of molar volume. The molar volume of iron phosphate glass [10] containing 50 wt. % of Cs$_2$O (labelled as IPCs50) was 5.33 $\times 10^{-5}$ m$^3$. Comparing the molar volume of IPCs50, IPCs45Ba5 and IPCs25Ba25, it is evident that the molar volume decreases when Cs is replaced by Ba, indicating the better connectivity due to better cation field strength of Ba$^{II}$ as explained below.

### 3.3. Glass transition temperature

The DTA curves showing the glass transition temperature of IPBa10 and IPBa20 are shown in Fig. 3. The glass transition temperature of these glasses is also presented in Table 1. The glass transition temperature ($T_g$) of un-doped IPG was 783 K [13]. As the concentration of Ba increases in IPG, the glass transition temperature also increases indicating improved thermal stability. The observed increase in glass transition temperature is similar to that observed for caesium loaded IPG [10]. The $T_g$ of 20 wt. % Cs$_2$O loaded IPG was 790 K. Although an increase in $T_g$ is observed with addition of either BaO or Cs$_2$O, the magnitude of increase is higher (63 K) compared to that (7 K) reported for equivalent concentration of Cs$_2$O loaded IPG. Both Cs and Ba act as modifier in IPG but the higher glass transition temperature observed for Ba loaded IPG clearly indicates that Ba$^{II}$ is a better glass modifier compared to Cs$^{I}$. It is well known that greater cation field strength [22] (cation charge/(radius)$^2$) leads to a better glass network connectivity. Ba$^{II}$ ions with cation field strength of 0.26 would have better glass network connectivity compared to Cs$^{I}$ with cation field strength of 0.1. Thus, a higher glass transition temperature is observed for IPG containing Ba compared to IPG containing a similar concentration of Cs. The Crystallisation behaviour of IPBa10 is different from that of IPBa20. Multiple crystallisation exotherms are observed for IPBa10, whereas IPBa20 shows a single crystallisation peak under similar experimental conditions. The onset temperature of the first crystallisation peak is considered as the temperature of crystallisation for IPBa10. The crystallisation temperature ($T_x$) of IPBa10 and IPBa20 are 910 and 923 K respectively. The observed liquidus temperatures ($T_L$) are 1225 and 1237 K for IPBa10 and IPBa20.
The glass transition temperature of IP5Cs5 was 743 K [10]. The glass transition temperature of 5 wt. % BaO added glass (IP5Cs5Ba5) showed a marginal increase in glass transition temperature, i.e., 752 K. The glass transition temperature of IPCs25Ba25 was 856 K. The increase in glass transition temperature is another indication of the better glass network connectivity or rigidity of the glass network. The increase in density (thus reduction in molar volume) and increase in glass transition temperature is a positive change in the network. The increase in density (thus reduction in molar volume) and increase in glass transition temperature is a positive change when Cs is replaced by Ba. In the same way, the onset of crystallisation temperature and liquidus temperature increases when Cs is replaced by Ba. The onset of crystallisation of IPCs45Ba5 and IPCs25Ba25 were 1142 and 1254 K respectively. The crystallisation temperature and liquidus temperatures increases when Cs is replaced by Ba. In the same way, the onset of crystallisation of IPCs45Ba5 and IPCs25Ba25 were 1142 and 1254 K respectively as shown in Fig. 3. The increase in crystallisation temperature and liquidus temperature, when Cs is replaced by Ba, also signifies the strength of the phosphate network. However, the delineation of the crystallisation behaviour of the glasses is not part of the present study.

3.4. Thermal expansion

The percentage of linear thermal expansion of IPBa10 and IPBa20 is shown in Fig. 4. The expansion behaviour of IPG [23] is also added in Fig. 4 for comparison. The thermal expansion behaviour was experimentally determined up to 700 K, which is well below the glass transition temperature of the glasses under present study. The thermal expansion data were fitted to the quadratic equation:

\[
\frac{\Delta L}{L} \times 100 = A_1 + A_2T + A_3T^2
\]

where \(A_1, A_2, A_3\) are coefficients of the quadratic equation and \(\Delta L\) is the change in length of the glass sample of length “L”. The values of the coefficients, \(A_1, A_2, A_3\) along with \(R^2\) values are presented in Table 2 for IPBa10 and IPBa20.

The average thermal expansion coefficient was evaluated for each glass from the plot of thermal expansion vs. Temperature as follows:

\[
a_{\text{avg}} = \frac{\Delta L}{L_{300K} - \Delta L_{700K}} \times \frac{100}{\Delta T}
\]

where \(L_{300K}\) and \(L_{700K}\) are the length of sample as a function of temperature at 300 and 700 K respectively. Whenever alkali oxide [21,23] or alkaline earth oxide [21] are added as modifiers in IPG, the average thermal expansion coefficient of such glass would increase compared to un-doped IPG. The values of the average thermal expansion coefficient \(a_{\text{avg}}\) of IPBa10 and IPBa20 are \(8.22 \times 10^{-6} \text{ K}^{-1}\) and \(9.31 \times 10^{-6} \text{ K}^{-1}\) respectively. The \(a_{\text{avg}}\) of IPG was \(6.77 \times 10^{-6} \text{ K}^{-1}\) [21]. The expansion behaviour of Ba doped

| Sample | \(\delta (\text{mm s}^{-1})\) | \(\Delta (\text{mm s}^{-1})\) | \(\Gamma (\text{mm s}^{-1})\) | \(A (%)\) | Site | \(\text{Fe}^{II}/\text{Fe}^{VI}\) | \(N_0\) |
|--------|----------------|----------------|----------------|---------|------|----------------|------|
| IPG    | 0.33 ± 0.02    | 0.81 ± 0.02    | 0.19 ± 0.02    | 33      | FeII(V) | 0.20           | 5.3  |
| IPBa10 | 1.00 ± 0.02    | 2.51 ± 0.02    | 0.19 ± 0.02    | 20      | FeII(VI)|               |      |
| IPBa20 | 0.47 ± 0.02    | 0.83 ± 0.02    | 0.20 ± 0.02    | 52      | FeII(VI)|               |      |

| Sample | \(\delta (\text{mm s}^{-1})\) | \(\Delta (\text{mm s}^{-1})\) | \(\Gamma (\text{mm s}^{-1})\) | \(A (%)\) | Site | \(\text{Fe}^{II}/\text{Fe}^{VI}\) | \(N_0\) |
|--------|----------------|----------------|----------------|---------|------|----------------|------|
| IPCs45Ba5 | 0.47 ± 0.02   | 0.83 ± 0.02   | 0.22 ± 0.02   | 61      | FeII(VI)| 0.22           | 5.7  |
| IPCs25Ba25 | 0.98 ± 0.02  | 2.58 ± 0.02   | 0.22 ± 0.02   | 22      | FeII(VI)|               |      |

Table 3
Room temperature Mossbauer parameters for iron phosphate glass (IPG) and Ba loaded IPG; \(\delta\) – isomer shift, \(\Delta\) – quadrupole splitting, \(\Gamma\) – full width half max, \(A\) – relative spectral area, \(\text{Fe}^{II}/\text{Fe}^{VI}\) – fraction, \(N_0\) – average coordination number. \(\delta\) is given relative to metallic Fe at room temperature. Site assignment for each spectral contribution indicated. (IV) and (VI) indicate the coordination number of the Fe ion.

Table 4
Pre-edge parameters for reference compounds, iron phosphate glass (IPG) and Ba loaded IPG. A (the summed area from all the contributions), the \(\text{Fe}^{II}\) fraction (\(\text{Fe}^{II}/\text{Fe}^{VI}\)) and the average coordination number \(N_0\) are also reported.
glasses are higher than that of un-doped IPG, but similar to that of Cs loaded IPG reported by us earlier [21]. The average thermal expansion coefficient determined in the present study is in agreement with that reported for similar iron phosphate glasses [23]. The linear thermal expansion of IPCs45Ba5 and IPCs25Ba25 as a function of temperature is also shown in Fig. 4 along with that of IPCs50. It is apparent from the plot that as Ba replaces Cs in Cs loaded IPG, the linear thermal expansion decreases and the coefficient of the quadratic fit of these glasses are also presented in Table 2. Average thermal expansion coefficients of IPCs45Ba5 and IPCs25Ba25 are 15.3 × 10⁻⁶ K⁻¹ and 13.4 × 10⁻⁶ K⁻¹ respectively. These values are lower than that of IPCs50 (19.8 × 10⁻⁶ K⁻¹) reported earlier [21]. Similar expansion characteristics (when Ba replaces Cs completely) and reduction in thermal expansion behaviour (when Cs loaded glass is partially replaced by Ba) represent a desirable property because of the conversion of 137Cs to 137Ba during radioactive decay of 137Cs loaded IPG. Sealed radioactive source used for clinical application would show no adverse effect due to change in thermal expansion behaviour.

3.5. ⁵⁷Fe Mössbauer spectroscopy

⁵⁷Fe Mössbauer spectra for the IPG (undoped), IPBa10 and IPBa20 are shown in Fig. 5 along with the fitted contributions to the spectral envelope. For each glass, three contributions were fitted, indicating the presence of three distinct Fe environments which are shown as solid grey lines (Fe⁰⁰) or dashed grey lines (FeIII) in Fig. 5 (the overall fit is shown by the solid black line). The fitted Mössbauer parameters (isomer shift – δ, quadrupole splitting – Δ, and relative spectral area - A) are shown in Table 3. In glasses, well-defined ranges of isomer shift are observed for Fe in a particular combination of oxidation state and coordination environment, allowing specific contributions to be assigned to different Fe sites [24]. Quadrupole splitting can also be used as a diagnostic for specific coordination environments, although the broad range of quadrupole splitting reported for amorphous materials, means that careful interpretation is required [24]. Ferrous ions have larger isomer shifts and quadrupole splitting than ferric ions and so are readily distinguished. Initial fitting was performed using two contributions to represent the presence of Fe⁰ and FeIII species. However, more satisfactory fits were obtained by including a second FeIII species, consistent with previous studies of related iron phosphate glasses, which suggested that the FeIII adopts both tetrahedral and octahedral coordination [25]. The doublet centred at approximately 1.00 ± 0.02 mm s⁻¹ was assigned to Fe⁰ in octahedral coordination and the doublets centred at 0.33 ± 0.02 and 0.47 ± 0.02 mm s⁻¹ were assigned to FeIII in tetrahedral and octahedral co-ordination, respectively. Although the measured isomer shift and quadrupole splitting for a specific combination of oxidation state and coordination number can occur over a range of values, the assignments given above are supported by published Mössbauer parameters for relevant Fe containing minerals with very well characterised structures [26–28]. The fitted ⁵⁷Fe Mössbauer parameters are also consistent with those previously reported in the literature for similar iron phosphate glasses [29–33]. The Fe⁰ content and the average Fe coordination numbers (NFe) were estimated, by considering the relative area of all contributions from the Fe⁰ and FeIII species. In order to accurately determine the Fe⁰/FeIII ratio the respective recoil free fraction ratio for ferrous (f₅) and ferric iron (fₛ) need to be known. It has been assumed previously that this value is close to unity but this leads to an overestimation of the FeIII content [34]. Eckhout and Grave [35] reported recoil free fraction ratios (f₅/fₛ) of 0.734 for anapate, Ca₂Fe(PO₄)₂·4H₂O, and 0.824 for strunzite, [MnFe]₂(PO₄)₂(OH)₂·6H₂O. In this study corrections were made using a value of 0.769 based on previous work on IPG systems [36]. The isomer shift and quadrupole splitting did not vary appreciably with increasing Ba content and only a small increase in Fe⁰⁰ iron content was observed. The estimated average Fe coordination number increased from 5.3 ± 0.2 to 5.7 ± 0.2, with increasing Ba content, consistent with the results from the Fe K-edge XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) analysis as shown in Tables 4 and 5. The presence of a contribution from five-fold coordinated FeIII, was ruled out based on the reported large quadrupole splittings.

Table 5

|       | IPG | IPBa10 | IPBa20 |
|-------|-----|--------|--------|
| E₀ (eV) | 1.1 | 1.5 | 4.1 | 1.4 | 3.0 | 1.9 |
| Rₑ₋₀₁ (Å) | 1.90 | 0.01 | 1.93 | 0.01 | 1.95 | 0.01 |
| Nₑ₋₀₁ | 4.5 | 0.8 | 4.4 | 0.7 | 4.7 | 0.8 |
| Rₑ₋₀₂ (Å) | 2.21 | 0.05 | 2.18 | 0.05 | 2.21 | 0.06 |
| Nₑ₋₀₂ | 0.6 | 0.8 | 0.9 | 0.4 | 1.0 | 0.7 |
| Total Nₑ | 5.1 | 1.1 | 5.3 | 0.8 | 5.7 | 1.1 |
| Avg. Rₑ | 1.93 | 0.05 | 1.97 | 0.05 | 1.99 | 0.06 |
| σₑ₋₀ (Å²) | 0.008 | 0.002 | 0.009 | 0.002 | 0.009 | 0.002 |
| Rₑ₋₀ₓ | 0.12 | 0.10 | 0.17 | 0.10 | 0.18 | 0.10 |
| Rₑ₋₁₁₀ | 2.73 | 0.15 | 2.89 | 0.02 | 2.88 | 0.04 |
| Nₑ₋₁ | 0.5 | * | 0.5 | * | 0.5 | * |
| σₑ₋₁ (Å²) | 0.021 | 0.018 | 0.004 | 0.005 | 0.004 | 0.004 |
| Rₑ₋₁₁₀ | 3.15 | 0.02 | 3.26 | 0.18 | 3.27 | 0.41 |
| Rₑ₋₁₁₀ | 3 | * | 3 | * | 3 | * |
| Nₑ₋₁₁₀ | 3.39 | 0.02 | 3.40 | 0.16 | 3.39 | 0.42 |
| σₑ₋₁₁₀ (Å²) | 0.009 | 0.002 | 0.016 | 0.027 | 0.017 | 0.053 |
| Rₑ₋₁₁₀ | 3 | * | 3 | * | 3 | * |
| σₑ₋₁₁₀ (Å²) | 0.006 | 0.008 | 0.005 | 0.005 | 0.006 |
| R-factor | 0.008 | – | 0.003 | – | 0.028 | – |
| BVS (v.u.) | 3.1 | 0.6 | 2.9 | 0.6 | 2.9 | 0.6 |

Fig. 6. Normalised Fe K-edge XANES data for IPG, IPBa10 and IPBa20. Spectra for reference materials are included. The pre-edge region is shown magnified on the left hand side of the figure.
observed for square pyramidal and trigonal bipyramidal FeIII in a range of synthetic [37–40] and mineral [41,42] samples.

3.6. Fe K-edge X-ray absorption spectroscopy

3.6.1. Analysis of Fe K-edge XANES

Fig. 6 shows the Fe K-edge XANES data for the glasses under present study together with data from selected well characterised mineral and synthetic reference compounds in which the Fe oxidation state and coordination environment are known. The Fe oxidation state in the glass samples was estimated from the precise energy of the absorption edge (E0) and interpolating between the energies measured for a set of reference compounds; a thorough treatment of this approach is given by Wong et al. [43]. In this study E0 was set to be the energy corresponding to a normalised absorption of 0.5, after the background subtracted absorption data were normalised to a unit edge step. The measured absorption edge of the IPG glasses was $E_0 = 7122.8$ eV identical to that of the FeIII reference compounds, and distinct from the absorption edge of FeII reference compounds at $E_0 = 7119.4$ eV (precision ± 0.2 eV). It is therefore clear that FeIII is the dominant speciation in the IPG glasses, in agreement with analysis of $^{57}$Fe Mössbauer data. Fine structure in the pre-edge region of the IPG glasses is damped compared to the crystalline reference compounds, consistent with FeIII in an amorphous matrix [44], where the lack of long range order reduces coherent scattering effects.

The intensity and position of features in the pre-edge region of Fe K-edge XANES spectra, at ca. 7113 eV, provides information on both the oxidation state and the local coordination environment of Fe [44–46]. Although the area under the pre-edge peaks is strictly dependent on site symmetry, rather than coordination number, it has been shown to follow a linear relationship with average coordination number for a given Fe oxidation state [44,47]. Fitting of the pre-edge feature of the IPG glasses and reference compounds was performed in the energy range 7104 eV−7120 eV, according to the methodologies proposed by Farges and Wilke [44,46]. The background subtracted absorption data were normalised to a unit edge step using Athena [18], and the rising edge background was fitted using a spline function interpolated across the pre-edge region, as described previously [46]. Gaussian components were then fitted to the data using a least squares minimisation routine. The total area under the pre-edge feature was derived by summing the integrated intensity under each pre-edge component. In order to ensure the robustness of this fitting procedure, the values obtained for the centroid position and the integrated area of the standard compounds were compared with data previously reported by Wilke et al. [46] and Jackson et al. [48]. The validity of the fitting process used in this work was evidenced by the fact that our values and those reported in the literature were the same within experimental precision.

Table 4 summarises the fitted parameters and centroid position of the pre-edge feature (i.e. the intensity-weighted average of the energy positions of the fitted Gaussian components) for the reference compounds and the glass samples. Energy calibration was performed with respect to a Fe foil in the reference channel, with the first derivative in the edge step set to 7111.0 eV, to ensure calibration with previous studies of Fe coordination in minerals and glasses [44,46]. The centroid position of the pre-edge feature in the spectra of the iron phosphate glasses at 7131.3 ± 0.2 eV is consistent with dominant FeIII speciation, when compared with the average centroid position of the FeIII (7113.4 ± 0.2 eV) and FeII (7111.9 ± 0.2 eV) reference compounds, as shown in Table 4. The FeII fraction for the glass samples was estimated by interpolation between the averaged centroid positions for the FeII and FeIII reference compounds. This yielded FeII contents of between 13 ± 5% and 20 ± 5% consistent with the values obtained from the Mössbauer analysis (Table 3), which is acknowledged as a more accurate probe for determination of Fe speciation [31]. Similar FeII contents (ca. 20–25%) have been reported for iron phosphate glasses of the same nominal composition; slight variations in FeII content can be attributed to the differences in melt temperature and annealing conditions employed therein [25,29,49]. In general, it is assumed that the value of $S_0$ (the amplitude reduction factor) is fixed in the model. The re

### Table 4

| Compound | R-factor ± | ΔE0 | ± | $R_{Fe}$ | ± | σ² | ± | $N_{Fe}$ | ± | BVS | ± |
|----------|------------|-----|---|---------|---|-----|---|----------|---|-----|---|
| FeO1     | 0.017      | 0.001 | 1.77 | 1.23 | 2.11 | 0.01 | 0.009 | 0.002 | 6 | -- | 1.8 | 0.4 |
| Fe-C     | --         | --   | -- | -- | 2.96 | 0.03 | 0.004 | 0.003 | 6 | -- | -- | -- |
| Fe-O2    | --         | --   | -- | -- | 3.14 | 0.03 | 0.009 | 0.002 | 6 | -- | -- | -- |
| Fe-Fe1   | --         | --   | -- | -- | 3.73 | 0.02 | 0.010 | 0.002 | 6 | -- | -- | -- |
| Fe-O3    | --         | --   | -- | -- | 3.95 | 0.02 | 0.009 | 0.002 | 12 | -- | -- | -- |
| Fe-O4    | --         | --   | -- | -- | 4.39 | 0.05 | 0.009 | 0.002 | 6 | -- | -- | -- |
| Fe-Fe2   | --         | --   | -- | -- | 4.63 | 0.03 | 0.006 | 0.003 | 6 | -- | -- | -- |

The local co-ordination environment of Fe in the iron phosphate glasses was further investigated by analysis of the Fe K-edge EXAFS data. Accurate determination of first shell coordination number ($N_0$) in amorphous materials requires independent determination of the amplitude reduction factor ($S_0$), since this is directly correlated with $N_0$ [50]. In general, it is assumed that the value of $S_0$ is transferable between materials for a given element studied at the same beamline [50]. Consequently we independently determined a value for $S_0$ = 1.03 for fitting EXAFS data acquired for FeCO3.
(siderite) using the structural model reported by Effenberger [51]; the fitted model parameters are reported in Table 6. The refined Fe-O contact distance, $2.11 \pm 0.01 \AA$, was in agreement with that reported by Effenberger, and the determined bond valence sum (BVS, [52]) was $1.8 \pm 0.4$ v.u., consistent with speciation as Fe$^{II}$.

Inspection of the extracted EXAFS data from the iron phosphate glasses (Fig. 7) showed a simplified and damped waveform, consistent with an amorphous material [50]. The model elaborated to fit the Fe K-edge EXAFS data comprised several distinct scattering paths, based on the crystal structure of Fe$_3$(P$_2$O$_7$)$_2$ [53] which has been shown to crystallise as the primary phase from these IPG glasses upon heat treatment [19,32,49]. Previous X-ray and neutron scattering studies of IPG have shown the average local Fe environment to be approximated by those in Fe$_3$(P$_2$O$_7$)$_2$ [54].

All Fe K-edge EXAFS data were modelled using an amplitude reduction factor of $S_0^2 = 1.03$, as noted above. The $k^2\chi(k)$ waveforms and FT $k^2\chi(k)$ plots, together with theoretical fits, are shown in Fig. 7. The refined structural parameters for all the glasses are

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Fig. 7. $k^2\chi(k)$ and FT of $k^2\chi(k)$ Fe K-edge EXAFS data of IPG and Ba loaded IPG (uncorrected for phase shift). Solid black lines represent experimental data and dashed black lines represent theoretical fits. Fitting windows are indicated by solid grey lines.
summarised in Table 5. Taking the analysis of IPBa10 as an example, the most significant modelled contributions to the EXAFS data were associated with two distinct Fe-O contact distances at \( r_{Fe-O} = 1.93 \pm 0.01 \ \text{Å} \) (with \( N_{Fe-O} = 4.4 \pm 0.7 \)) and \( r_{Fe-O} = 2.18 \pm 0.05 \ \text{Å} \) (with \( N_{Fe-O} = 0.9 \pm 0.4 \)). These two Fe-O contact distances are characteristic of Fe\(^{\text{III}}\) and Fe\(^{\text{II}}\) species, respectively. The estimated Fe\(^{\text{III}}\) : Fe\(^{\text{II}}\) ratio (0.17 \pm 0.10), calculated from the EXAFS contact distances, is in good agreement with that determined from analysis of XANES, FePO\(_4\) and Mössbauer data (0.21 \pm 0.01). The average Fe-O co-ordination number determined from modelling the EXAFS data was 5.3 \pm 0.8, again in good agreement with that estimated from analysis of XANES, Mössbauer and EXAFS data (5.5 \pm 0.2) and Mössbauer data (5.5 \pm 0.2). The crystal structure of Fe\(_3\)(P\(_2\)O\(_7\))\(_2\) is characterised by an Fe\(_{12}\)O\(_{32}\) cluster consisting of a Fe\(^{\text{II}}\) trigonal prism (Fe-O, ca. 2.11 \Å) and two Fe\(^{\text{III}}\) octahedra (Fe-O ca. 2.00 \Å) connected by a pyrophosphate (P\(_2\)O\(_7\))\(^4\) group [49,53]. Our EXAFS determined Fe-O contact distances are therefore in reasonable agreement with those reported for the model Fe\(_3\)(P\(_2\)O\(_7\))\(_2\) compound; the shorter Fe-O contact distance for Fe\(^{\text{III}}\) reported here is consistent with the observation of ferric iron tetrahedra in our glasses.

Previous studies of glasses with similar compositions, have reported models based on three distinct Fe-O contact distances representing both tetrahedral and octahedral Fe\(^{\text{III}}\) and octahedral Fe\(^{\text{II}}\) [25,30,31,34,49]. Attempts to model our data using three Fe-O contact distances proved unsuccessful. Our average Fe-O contact distances were validated by calculation of the bond valence sum [52], using the refined coordination number \( \langle N_0 \rangle \), giving values of ca. 3.0 \pm 0.6 v.u., consistent with the presence of majority Fe\(^{\text{III}}\) in the glass samples.

As shown in Fig. 7, the FT \( k^2 \chi(k) \) data show significant features in the range \( R = 2.1-3.9 \ \text{Å} \), uncorrected for phase shift. For all of these glasses, these features were fitted by one Fe-Fe path at \( r_{Fe-Fe} \approx 2.8 \ \text{Å} \) (with \( N_{Fe-Fe} = 0.5 \)) and two Fe-P paths, one each at \( r_{Fe-P} \approx 3.2 \ \text{Å} \) and \( r_{Fe-P} \approx 3.4 \ \text{Å} \) (with \( N_{Fe-P} = 3.0 \) and \( N_{Fe-P} = 3.0 \)). An attempt to fit a single Fe-P path at an intermediate distance was unsuccessful; the relative precision on the determined Fe-P contact distances confirms the presence of two distinct contributions, at least for the Ba free composition. The refined Fe-P and Fe-Fe contact distances are commensurate with those reported in Fe\(_3\)(P\(_2\)O\(_7\))\(_2\) [53], which are distributed about values of ca. 3.3 \Å and 2.9 \Å, respectively. Addition of these paths typically reduced the residual R-factor by ca. 75\%, associated with satisfactory fitting of the weak but significant FT \( k^2 \chi(k) \) features in the range \( R = 2.1-3.9 \ \text{Å} \). In the case of Ba doped compositions, it was possible to fit an additional Fe-Ba path at ca. 3.0 \Å with \( N_{Fe-Ba} = 0.5 \), which further improved the fit to FT \( k^2 \chi(k) \) features in the range \( R = 2.1-3.9 \ \text{Å} \). Attempts to refine the weighting of the Fe-P, Fe-Fe and Fe-Ba path lengths, even under heavy damping, were unsuccessful, but this is understandable given the amorphous nature of the material. Adjustment of the constrained weighting of these paths, in steps of \( N = 0.5 \), afforded a progressive increase in the residual R-factor and ultimately an implausible model.

3.7. P K-edge X-ray absorption spectroscopy

3.7.1. Analysis of P K-edge XANES

Fig. 8 shows the P K-edge XANES data for the IPG glasses together with data from the synthetic FePO\(_4\) reference compound for which the P oxidation state and co-ordination environment are known. The absorption edge of the iron phosphate glasses was determined to be \( E_0 = 2152.7 \ eV \), close to that of the P\(^\text{IV}\) reference compound (FePO\(_4\)) at \( E_0 = 2152.5 \ eV \). The P K-edge XANES spectra of Fe-phosphate minerals have a very distinct pre-edge feature on the low energy side of the intense white line at ca. 2150 eV [55–57] which is clearly apparent in our reference data (labelled feature 1 in Fig. 8). In the iron phosphate glass samples this pre-edge feature is present as a broad shoulder rather than as a distinct and well-defined feature. Additionally, the features in the XANES region (labelled features 2 and 3) are weaker, relative to the absorption edge, than in the crystalline reference material. This damping of the fine structure in the glass samples is consistent with P in an amorphous matrix [44] and similar spectra have been reported in the literature for sodium polyphosphate glass [58] and amorphous SiO\(_2\)-P\(_2\)O\(_5\) materials [59]. Comparison with the FePO\(_4\) reference, presented here, and also reference spectra for Na\(_2\)P\(_2\)O\(_5\) and Na\(_3\)P\(_3\)O\(_9\) [58] indicate that the IPG glass structure consists of a network of pentavalent phosphorus tetrahedra, most likely speciated as pyrophosphate (P\(_2\)O\(_5\))\(^4\) groups.

Table 7

| FePO\(_4\) | R-factor | \( \pm \) | \( \Delta E_0 \) | \( \pm \) | \( R_{Fe} \) | \( \pm \) | \( \sigma^2 \) | \( \pm \) | \( N_0 \) | \( \pm \) | BVS | \pm |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| P-O      | 0.162    | 0.006    | 3.57     | 4.91     |          |          |          |          |          |          |          |          |
| P-O-P    |          |          |          |          |          |          |          |          |          |          |          |          |
| P-Fe     |          |          |          |          |          |          |          |          |          |          |          |          |
| P-O3     |          |          |          |          |          |          |          |          |          |          |          |          |
| P-P      |          |          |          |          |          |          |          |          |          |          |          |          |
3.7.2. Analysis of P K-edge EXAFS

The local co-ordination environment of P in the iron phosphate glasses was investigated by analysis of the P K-edge EXAFS data. A value for $S_0^2 = 0.785$ was determined from fitting EXAFS data acquired for FePO$_4$ using the structural model reported by Labeguerie [60]; the fitted model parameters are reported in Table 7. The refined P-O contact distance, 2.51 ± 0.01 Å, was in agreement with that reported by Labeguerie; the calculated BVS was 5.3 ± 1.0 v.u. consistent with speciation as P$^{V}$.

Inspection of the extracted EXAFS data from the IPG, and Ba loaded IPG glasses (Fig. 9), showed a simplified and damped waveform, with no distinct features corresponding to medium range order, consistent with an amorphous material [50]. The model elaborated to fit the EXAFS data comprises several distinct scattering paths, based on the crystal structure of Fe$_2$(P$_2$O$_7$)$_2$ [53] which contains pyrophosphate (P$_2$O$_7$)$^{4-}$ groups. The EXAFS data
were modelled using an amplitude reduction factor of $S_0^* = 0.785$, as noted above. The $k^2\chi(k)$ waveforms and FT $k^2\chi(k)$ plots, together with theoretical fits, are shown in Fig. 9 and the refined structural parameters for all the glasses are summarised in Table 8. A single P-O shell was used to model the intense feature in the EXAFS envelope. Parameters for all the glasses are summarised in Table 8. A single P-Fe path at ca. 3.1 Å (uncorrected for phase shift). Refinement of the contact distance yielded a value of ca. 3.1 ± 0.02 Å and a corresponding coordination number (NP-Fe1) of 4.1 ± 0.8. The crystal structure of Fe3(P2O7)2 is characterised by Fe3O12 clusters connected by a pyrophosphate (P2O7)6 group (with a P-O bond length of 1.53 Å). Our EXAFS determined P-O contact distances are in good agreement with each other. The average coordination number for IPG was 5.3 ± 0.0 v.u. as expected for PV. Small but significant improvement was achieved by the inclusion of two additional shells; a P-Fe path at ca. R_P-Fe = 3.1 Å (with NP-P-Fe = 4) and an additional P-O path at ca. R_P-O2 = 3.3 Å (with NP-P-O2 = 6). Attempts to refine the weightings for these paths proved unsuccessful.

### 4. Conclusions

Iron phosphate glasses containing either BaO loaded or Cs2O/BaO were synthesised without phase separation or crystallisation. An increase in glass transition temperature with the addition of BaO in IPG or Cs2O loaded IPG indicates the better glass rigidity or glass network connectivity compared to that of un-doped IPG. Similar thermal expansion behaviour of IPG loaded with either Cs or Ba suggest that no adverse effect would result when caesium loaded iron phosphate glass is completely converted to barium loaded iron phosphate glass, a promising result for the use of 137Cs loaded IPG as radioactive source for medical applications. Investigation of the glass structure by Mössbauer, EXAFS and XANES also rules out any drastic modification as a result of large scale Ba doping in IPG. The isomer shift and quadrupole splitting did not vary appreciably with increasing Ba content and only a small increase in FeIV content was observed. The average coordination number for IPG was 5.3 ± 0.2 and increased to 5.7 ± 0.2 with increasing Ba content. The average coordination number, FeIV content in these iron phosphate glasses obtained by various techniques (Mössbauer and X-ray absorption spectroscopy) were found to be in good agreement with each other.

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### Table 8

| Parameter       | IPG IPBa10 | IPBa20 |
|-----------------|------------|--------|
| E0 (eV)         | 0.4        | 4.5    | 3.1 |
| R_P-O1 (Å)      | 1.51       | 1.51   | 1.53 |
| σ_P-O1 (Å²)     | 4.1        | 0.8    | 4.1 |
| R_P-Fe (Å)      | 3.12       | 0.05   | 3.17 |
| σ_P-Fe (Å²)     | 0.005      | 0.003  | 0.018 |
| R_P-O2 (Å)      | 3.27       | 0.07   | 3.82 |
| σ_P-O2 (Å²)     | 0.005      | 0.003  | 0.018 |
| R-NP (Å)        | 6.0        | 6.0    | 6.0 |
| R-factor        | 0.052      | 0.059  | 0.045 |
| BVS (v.u.)      | 5.3        | 5.0    | 5.1  |
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