Thermal and Crystallisation Kinetics of Yttrium-Doped Phosphate-Based Glasses

Abul Arafat¹, Sabrin A. Samad¹, Matthew. D. Wadge¹, Md Towhidul Islam¹, Andrew. L. Lewis², Emma R. Barney¹ and Ifty Ahmed¹

¹Faculty of Engineering, Advanced Materials Research Group, University of Nottingham, Nottingham, UK
²Biocompatibles UK Ltd., a BTG International group company, Lakeview, Riverside Way, Watchmoor Park, Camberley, Surrey, GU15 3YL, UK

Correspondence: Ifty Ahmed, Email:ifty.ahmed@nottingham.ac.uk

Abstract

Yttrium doped glasses have been utilised for biomedical applications such as radiotherapy especially for liver cancer treatment. In this paper, the crystallisation behaviour of phosphate-based glasses doped with yttrium (in the system 45P₂O₅-(30-x) Na₂O-25CaO-xY₂O₃ – where x = 0, 1, 3 and 5) have been investigated via Differential Scanning Calorimetry (DSC) using non-isothermal technique at different heating rates (5°C, 10°C, 15°C and 20°C/min). The glass compositions were characterised via EDX, XRD, Density and Molar volume analysis. The Moynihan and Kissinger methods were used for the determination of glass transition activation energy (Eₔ) which decreased from 192 kJ/mol to 118 kJ/mol (Moynihan) and 183 kJ/mol to 113 kJ/mol (Kissinger) with increasing yttrium oxide content. Incorporation of 0 to 5 mol% Y₂O₃ revealed an approximate decrease of 71 kJ/mol (Ozawa and Augis) for onset crystallisation (Eₓ) and 26 kJ/mol (Kissinger) for crystallisation peak activation energies (Eₐ). Avrami index (n) value analysed via Matusita-Sakka equation suggested a one-dimensional crystal growth for the glasses investigated. SEM analysis explored the crystalline morphologies and revealed one-dimensional needle-like crystals. Overall, it was found that
these glass formulations remained amorphous with up to 5 mol% $\text{Y}_2\text{O}_3$ addition with further increases in $\text{Y}_2\text{O}_3$ content resulting in significant crystallisation.

**Keywords:** Yttrium phosphate glass, DSC, Crystallisation kinetics, Crystal growth
1. Introduction:

Phosphate-based glasses have been widely investigated for biomedical applications and can provide highly useful properties such as low glass transition and melting temperatures, high thermal expansion coefficients, biocompatibility, high refractive indices and one of their most unique offerings is their controlled dissolution properties. (1). The structural, chemical and physical durability of phosphate glasses has been shown to be improved by the inclusion of several oxide additions such as ZnO (2,3), Fe$_2$O$_3$ (4,5), Y$_2$O$_3$ (6,7), Al$_2$O$_3$ (8,9), TiO$_2$ (10,11) and Bi$_2$O$_3$ (12,13).

Amongst these, yttrium oxide containing glasses are an area of interest due to their characteristic structural and physical properties such as high refractive index, high thermal expansion coefficient, density and excellent infrared transmission (14). Moreover, it has also demonstrated highly useful application in radiotherapy (15–17) due to the relatively short half-life and beta emission properties of the $^{90}$Y isotope (18–20).

Y$_2$O$_3$ plays a vital role in improving the properties of glasses. Within glass systems, yttrium oxide can act as a network modifier or as a network former depending on glass composition and the amount of Y$_2$O$_3$ within the glass (14,21,22). Singh et al. investigated the 55 SiO$_2$–30 B$_2$O$_3$–x Li$_2$O–(15-x) Y$_2$O$_3$ glass system and reported that Y$_2$O$_3$ changed its role from glass former to network modifier as its concentration exceeded 5 mol% (14). Furthermore, incorporation of Y$_2$O$_3$ into the zinc borosilicate glass system was reported to increase glass stability by 20°C with increasing yttria content from 0 to 3 mol% (23). Mahdy et al. investigated yttrium aluminosilicate glasses and stated that the glass stability increased due to replacing Al$_2$O$_3$ with Y$_2$O$_3$ resulting in greater strength of the cross-links between the Y$^{3+}$ cation and oxygen atoms, leading to an increase in the structural rigidity of the glasses (22).
This increase in stability can be related to the crystallisation kinetics and activation energy of the glass systems (24) which also correlates with the crystallisation behaviour of the glasses. The higher the activation energy, the less prone the glass will be to crystallise (25).

Crystallisation kinetics of yttrium silicate glasses have been reported in the literature (26–29). Wang et al. studied yttrium zinc borosilicate glasses and stated that addition of Y$_2$O$_3$ enhanced the glass thermal stability and addition of more than 8 mol% of Y$_2$O$_3$ revealed that the glass began to crystallise due to tendency of supersaturation in the glassy state (30). Vishal et al. studied the crystallisation behaviour of a yttrium and lanthanum calcium borosilicate glass to explore the suitability of this glass as a sealant and they found that this glass was a good candidate as compared to yttrium calcium borosilicate glass due to higher thermal expansion coefficient, low fragility index value and viscosity profile (26). Studies on crystallisation kinetics of lithium (31), copper (32), calcium (33) and aluminium (9) phosphate glasses have been reported. Limited studies have been reported on the crystallisation behaviour of yttrium phosphate glasses. Petra et al. studied on crystallisation kinetics of erbium doped yttrium phosphate glasses based on particle size of the powder and bulk sample (34).

In order to explore crystallisation kinetics and thermal stability of glasses, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are popular methods for studying the kinetics of non-isothermal data (35,36). These methods are relatively straight-forward to carry out, requiring only small sample volumes and possessing flexibility in the ability to vary the heating rates. Between these two techniques, DSC is widely used due to its simplicity and sensitivity (37,38). Isothermal and non-isothermal methods are the two basic methods in DSC analysis. For the isothermal method, the sample is heated up to a temperature above glass transition ($T_g$) and the heat evolution during the crystallisation process is recorded as a
function of time where the temperature is kept constant. For non-isothermal analysis, the sample is heated at a fixed rate and the heat evolved is recorded as a function of temperature and time (39) and is more widely used due to its simplicity and rapid method (40,41).

In the present investigation, the glass transition temperature and crystallisation kinetics were studied as a function of the $Y_2O_3$ content in phosphate glasses using non-isothermal DSC analysis. The Moynihan (42), Kissinger (43), Ozawa (44), Augis-Bennette (45) and Matusita–Sakka (46) equations were used for the determination of crystallisation kinetics and activation energies for glass transition, onset crystallisation and crystallisation temperature.
2. Materials and Methods:

2.1 Glass synthesis:

Four different glass compositions were prepared using sodium dihydrogen phosphate (NaH$_2$PO$_4$), calcium hydrogen phosphate (CaHPO$_4$), yttrium oxide (Y$_2$O$_3$) and phosphorous pentoxide (P$_2$O$_5$) (Sigma Aldrich, UK) as starting materials. The precursors were mixed together and transferred to a 10%Rh/Pt crucible (Birmingham Metal Company, UK) which was placed in a furnace preheated to 350°C for half an hour and 500°C for an hour depending on the glass compositions for the removal of H$_2$O. The mixtures were then heated at 1150°C for the yttrium free glass and 1300°C for the yttrium containing glasses, for 2 hours as shown in Table 1. The resultant melts were poured onto a steel plate and left to cool to room temperature. The glass was then crushed using a planetary ball mill (Retsch PM100) and sieved to obtain a glass particle size range of between 25-45 µm.

2.2 Powder X-ray diffraction analysis:

The as-quenched glass was used for XRD analysis to investigate the amorphous nature of the glass compositions produced. The data was collected on a Bruker AXS–D8 Advance powder diffractometer in flat plate geometry using Ni-filtered Cu-Kα radiation (λ=0.15418 nm), operated at 40kV and 35mA. The angular range 2θ for each scan was from 10° to 70° with a step size of 0.1° and a step time of 5s. The phases were identified using the EVA software via Crystallographic Search-Match icon (DIFFRACplus Suite, Bruker-AXS) and the International Centre for Diffraction Data (2005).
2.3 Energy dispersive X-ray analysis:

Portions of the glass samples from each composition were polished using SiC paper and diamond cloths with industrial methylated spirit (IMS) as eluent. The samples were then dried and cleaned by air dry spray before being carbon coated. Energy dispersive x-ray (EDX) analysis was performed on an EDAX model DX 4 using ZAF quantitative analysis. The accelerating voltage was maintained at 15 kV and the system resolution was 60 eV with a live time of 120 seconds. Jadeite (for Na), gallium phosphide (for P), wollastonite (for Ca) and yttrium (for Y) were used as a standard for analysis. The working distance was 10 mm and the EDX spectrometer was connected to the Philips XL30 SEM. An average of five separate areas were analysed for the final composition of the materials.

2.4 Helium pycnometry:

Density measurements were conducted using a Micromeritics AccuPyc 1330 helium pycnometer (Norcross, GA, USA). ‘Archimedes’ principle of fluid displacement was employed to determine the volume of the solid objects. Calibration of the equipment was conducted using a standard calibration ball (3.18551 cm³) with errors of ±0.05%. Approximately 3.5 g of the samples were used for measurement and the process was repeated three times. For each formulation the molar volume was calculated using the equation 1:

\[ V_m = \frac{\sum x_i M_i}{\rho} \]  

(1)

where \( x_i \) is the molar fraction of the \( i \)th component, \( \rho \) is the density, and \( M_i \) is the molecular weight of the \( i \)th component.
2.5 Thermal analysis:

Approximately 10 mg samples of the glass powders (size range of 25 and 45 µm) were tested to determine the thermal properties such as glass transition (T\(_g\)), onset of crystallisation (T\(_x\)), crystallisation (T\(_c\)) and melting (T\(_m\)) temperature using a simultaneous thermal analysis (TA Instruments SDT Q600, USA). Glass particles were placed into a platinum pan and heated from room temperature to 1100°C at different heating rates (i.e. 5, 10, 15 and 20°C/min) under argon gas flow (50 ml/min). A blank run was carried out to determine the baseline which was then subtracted from the plot obtained using TA universal analysis 2000 software. The thermal stability of the glasses was measured in terms of the processing window by taking the temperature difference between the glass transition temperature (T\(_g\)) and the onset of crystallisation temperature (T\(_x\)) as shown in the following:

\[
\text{Processing window} = T_x - T_g
\]  

(2)

2.6 SEM analysis:

For imaging analysis, a JEOL 7100F Field-Emission Gun Scanning Electron Microscope (FEG-SEM) and scanning electron microscope (SEM, Phillips FEI XL30, USA) utilising a 15 kV beam set at a working distance of 10 mm, were used to investigate the glass formulations produced and the samples which crystallised. Prior to acquisition, the samples were mounted in an epoxy resin block, which were ground using varying grits (P240-P1200), followed by polishing on 6 and 1 µm diamond polishing pads respectively. The polished blocks were then eroded in 4 % (mass concentration) HF for 20 s each. The etched samples were subsequently cleaned with deionised water and air dried. A conductive carbon coat of ca. 10 nm was applied before SEM analysis.
3. Results:

3.1 EDX analysis:

EDX analysis was performed to confirm the compositions of the different glass formulations prepared in comparison with expected formulations (see Table 2). All the compositions were found to be close to the expected compositions (within a 2 % error margin). Figure 1 represents the 8 mol% and 10 mol% Y₂O₃ containing glass sample where 8 mol% glass became crystalline and the glass did not melt for 10 mol% glass sample.

3.2 XRD analysis:

The X-ray diffraction spectra of the different glass compositions are presented in Figure 2. Absence of any sharp crystalline peaks suggested that the glasses as prepared were amorphous. A single broad halo shaped peak was observed between 20° to 40° diffraction angle for Y0, Y1, Y3 and Y5 formulations. Tetragonal yttrium phosphate (YPO₄) crystal peaks were observed for Y8 glass formulation.

3.3 Density and Molar volume analysis:

The density and molar volume for the multicomponent glasses are presented in Figure 3. The density of glass particles increased from 2.56 to 2.74 g/cm³ with the incorporation of 0 to 5 mol% Y₂O₃ into the glass system. In contrast, the change observed in molar volume was from 37.65 cm³ mol⁻¹ to 38.1 cm³ mol⁻¹ for the same glasses across the compositional variation.
3.4 Thermal analysis:

Figure 4 shows the DSC scans obtained for 0 to 5 mol% yttrium containing phosphate glass system at different heating rates (i.e. 5°C/min⁻¹, 10°C/min⁻¹, 15°C/min⁻¹ and 20°C/min⁻¹). The DSC traces exhibited clear endothermic and exothermic peaks at glass transition (T_g) and crystallisation (T_c) temperature, respectively. The onset crystallisation temperature (T_x) has been defined as temperature corresponding to the intersection of the two linear portions of the transition between glass transition and crystallisation temperature. The values of T_g, T_x, T_c and processing window (i.e. T_x-T_g) at different heating rates are summarised in Table 3. As can be seen in Table 3, the T_g at different heating rates was similar for the yttrium free phosphate glass (355°-361°C) whereas the T_g at different heating rates increased from 368°-376°C, 386°-399°C and 415°-429°C for the glasses investigated with increasing Y_2O_3 content.

The variation of shifts in T_x for the varying glass formulations at different heating rates are presented in Figure 5. The T_c at different heating rates increased from 471°C to 537°C for 5°C, 480°C to 552°C for 10°C, 485°C to 564°C for 15°C and 492°C to 571°C for 20°C, with increasing (0 to 5 mol%) Y_2O_3 content, respectively as shown in Figure 4. The values of T_x and T_c are listed in Table 3.

The processing window (T_x-T_g) was also evaluated for the different compositions investigated which is an indication of their thermal stability (47). From Figure 6, it was seen that the processing window values increased as the Y_2O_3 concentration increased to 3 mol% and further addition of Y_2O_3 to 5 mol% showed a slight reduction in the thermal stability. It was also observed that the values of processing window were seen to increase with increase of heating rates for each formulation.
To validate the results, the glass formulations were heat-treated at two different temperature regimes; a) between 24-50°C above \( T_g \) to avoid crystallisation and explore any physical changes in their properties and b) between \( T_x \) and \( T_c \) to deliberately crystallise the samples and observe the crystal morphology formed.

“From Figures 7 (a-d), it was observed that needle shaped crystals had nucleated near to the glass surface. However, fewer needle shaped crystals were observed on the glass surface for the 5 mol % \( Y_2O_3 \) samples as seen in Fig. 7 (d).”

A heat treatment process (between \( T_x \) and \( T_c \)) at a heating rate of 10°C/min was applied to the different glass formulations investigated to explore the growth and morphology of the crystals observed. However, it was also observed that the needle like crystalline morphologies formed decreased in width with the addition of yttrium oxide.

### 3.6 Activation energies:

The activation energies for the \( T_g \), \( T_x \), \( T_c \) and overall crystallisation (E) region of the glasses were determined by utilising the equations outlined in supplementary section S1.

**Activation energy of glass transition temperature:**

The glass transition activation energies (\( E_g \)) obtained using equation 3 in supplementary section S1 are represented in Figure 9 and highlight the plots of \( \ln \alpha \) versus \( 1000/T_g \). The \( E_g \) values obtained from the slope of the straight lines are also highlighted in Figure 9. As can be seen, the \( E_g \) obtained using the Moynihan equation decreased from 191.82 to 118.12 KJ/mol with increasing \( Y_2O_3 \) from 0 to 5 mol%.

The \( E_g \) can also be determined utilising the Kissinger equation (see equation 4 in S1). A plot of \( \ln (\alpha/T_g^2) \) versus \( (1000/T_g) \) is depicted in Figure 9. The activation energies here were also
observed to decrease from 183.68 to 113.40 KJ/mol with increasing Y$_2$O$_3$ content (0 to 5 mol%). The $E_g$ values obtained from Kissinger equation were very similar to those obtained by Moynihan equation.

**Onset crystallisation temperature activation energy:**

The values of the onset crystallisation activation energy ($E_x$) were obtained using the Ozawa equation (see equation 5) based on the slope of ln$\alpha$ vs 1000/$T_x$ as shown in Figure 10. The values of $E_x$ decreased from 189.74 to 118.27 KJ/mol with the incorporation of Y$_2$O$_3$ into the glass system.

The onset of crystallisation activation energies using Augis and Bennett method was also determined (based on equation 6 in S1). The $E_x$ of the glasses estimated from plots of ln ($\alpha$/$T_x$) versus 1000/$T_x$ are shown in Figure 10. The values of $E_x$ were seen to decrease from 184.26 to 114.88KJ/mol with the incorporation of Y$_2$O$_3$ in the glass system.

**Peak crystallisation activation energy:**

The activation energy of crystallisation peak temperature ($E_c$) was also explored based on the Kissinger equation (see equation 7 in S1). The plot of ln ($\alpha$/$T_c^2$) versus 1000/$T_c$ for the samples explored are shown in Figure 11. The value of $E_c$ was calculated from the slope of each curve. It was clear from Figure 10 that the activation energy of crystallisation ($E_c$) decreased from 120.34 to 94.27 KJ/mol with increasing Y$_2$O$_3$ content.

**Overall crystallisation activation energy:**

The overall non-isothermal crystallisation activation energy (E) was calculated using the Matusita-Sakka equation, which represents the volume fraction of crystals (X) precipitating in a glass heated at a constant rate ($\alpha$). From equation 8, the nucleation parameter (n) was determined by plotting ln[-ln(1-X)] versus ln$\alpha$ for three selected temperatures (within the
crystallisation peaks of the DSC traces obtained at each of the heating rates explored) as shown in Figure 12. The slope of the straight lines provided the value of nucleation and growth parameters \((n)\) and the corresponding values are listed in Table 4. The nucleation parameters or Avrami exponent \((n)\) were almost similar for the glass formulations tested. The dimensionality of crystal growth \((m)\) depends on the Avrami exponent \((n)\) and usually the dimensionality of crystal growth \(m\) is equal to \(n-1\) (23). As such, a one-dimensional crystal growth was suggested based on the Avrami exponent values obtained for the glasses investigated (see Table 4).

With the order parameter \(n\), \(m\) and plots of \(\ln [\ln(1-X)]\) versus \(1000/T\) at different heating rates, the overall crystallisation activation energy \((E)\) of the glass formulations was estimated from Equation 9. These plots are presented in Figure 13. Overall the crystallisation activation energy decreased from 253.46 to 205.52 KJ/mol with the incorporation of \(Y_2O_3\) in the glass system (see Table 4).
4. Discussion:

Yttrium containing phosphate-based glasses (PBGs) could be promising materials for biomedical applications such as radioembolisation therapy (48). However, from the glass formulations investigated, compositions above 5 mol% yttrium oxide content showed strong tendency towards crystallisation. The crystallisation kinetics and activation energy can provide a better understanding about the glass formability and thermal stability of glasses. In this study, the effect of Y_2O_3 incorporation into PBGs (upto 5 mol%) on crystallisation kinetics was investigated. Glasses containing more than 5 mol% yttrium oxide content (in this series) were not considered for analysis as these formulations rapidly crystallised (see Figure 1) and confirmed via XRD as shown in Figure 2.

Compositional analysis was confirmed via EDX and revealed that the respective oxide contents for the glasses investigated were within 2 mol% of their predicted values (see Table 2). The reduction of small amount of P_2O_5 content was observed and this was attributed to the effect of its volatilisation (49).

In general, for PBGs the density and molar volume are usually inversely related (50). However, in the present study for the glasses investigated, the density and molar volume increased with increasing yttrium oxide from 0-5 mol% (see Figure 3). Shaharuddin et al. reported that the density of phosphate glass was dependent on the atomic weight of the components added as well as compactness of the glass structure (51). The increase in density was attributed to the replacement of lower molar mass (61.97 g/mol) and density (2.27 g/cm^3) of Na_2O with higher molar mass (225.81 g/mol) and density (5.01 g/cm^3) of Y_2O_3 (11,14). Ebrahim et al. also found an increase in density (from 2.78 - 3.01 g/cm^3) for calcium magnesium aluminosilicate glass due to the addition of Y_2O_3 (from 0 to 3 mol%) in place of Al_2O_3 (22). Structural NMR analysis
on phosphate based glasses were studied by different authors in the literature (52–54) and reported that Q¹ and Q² structures were found for compositions with fixed P₂O₅ at 45 mol%. Fu et al. investigated the structural analysis on yttrium containing phosphate based glasses and they reported that yttrium acts as a network modifier (7). Mitang et al. stated that generally rare earth oxides acts as a network modifiers in the glass structure and the introduction of the modifier oxide into the glass structure breaks the glass network, which subsequently creates a Non Bridging Oxygen (NBO) (23). The increase of molar volume with increasing Y₂O₃ content was attributed to the increase in number of non-bridging oxygens which decreased the compactness of the glass structure subsequently leading to increase in molar volume. This increase in molar volume could also be attributed to the larger atomic radii of Y (240 pm) and bond length of Y-O (2.2 Å°)(7) compared to the smaller atomic radii of Na (227 pm) and bond length of Na-O (2.051 Å°) (55). Mi et al. studied the incorporation of Y₂O₃ in soda lime silicate glass and reported that the molar volume increased from 24.03 to 24.15 cm³/mol with increasing Y₂O₃ content from 0 to 1 mol% due to an increase in the number of non-bridging oxygens, which subsequently decreased the compactness of the glass structure (56).

The thermal profiles of PBG are strongly dependent on their structure and composition (50). A gradual increase in glass transition temperature (T₉) for glass particles were observed with increasing yttrium oxide (from 0 to 5 mol%) content and with different heating rates (5°, 10°, 15° and 20°C / min) as shown in Figure 4. The T₉ increased by ~60°C for 5°C and 10°C heating rate, ~65°C for 15°C heating rate and ~68°C for 20°C heating rate for 0, 1, 3 and 5 mol% Y₂O₃ respectively. This increase in T₉ was attributed to the fact that the Y-O bond strength is greater than that of the Na-O bond as Y-O has greater bond dissociation energy (715 KJ/mol) compared to Na-O (257 KJ/mol). Constantini et al. investigated the thermal properties of
calcium yttrium silicate glass and found that the $T_g$ value increased from 810° to 840°C with the incorporation of $Y_2O_3$ in place of $CaO$ (from 0 to 0.33 mol%). They reported that this was due to replacement of the lower field strength of $Ca^{2+}$ (2.04 Å$^2$) and lower bond ($Ca-O$) strength (130 KJ/mol) with higher field strength of $Y^{3+}$ (3.76 Å$^2$) and greater single bond ($Y-O$) strength in the oxide structure (210 KJ/mol) (57,58).

In this study, the $T_g$ values were also found to increase with increasing heating rates (see Table 3). This was attributed due to the decrease of structural relaxation which subsequently increase the glass transition temperature with increasing heating rates. Benson et al. stated that structural relaxation time of lithium phosphate glasses decreased with higher heating rates and was inversely proportional to the glass transition temperature (31). A similar study conducted by Kawamoto et al. found that the $T_g$ decreased with the addition of $MoO_3$ into a ternary sodium borosilicate glass formulation (59). They reported that the decrease in $T_g$ was due to the lowering of the viscosities and the increase of driving force with $MoO_3$ addition (59).

The onset crystallisation ($T_x$) and crystallisation peak ($T_c$) temperatures of the glass particles were also seen to increase with incorporation of yttrium oxide at different heating rates (see Table 3). The shift of $T_x$ and $T_c$ to higher temperature with different heating rate may be attributed to the easier relaxation of randomly arranged structures at slower heating rates where relaxation time is inversely proportional to the heating rate. Kasyap et al. studied the heating rate dependence of crystallisation temperature on Cu-Based metallic glass and found that metallic glass starts crystallising at lower temperatures as the structural relaxation happens more easily at slow heating rates (60). They also suggested that heating rate is inversely proportional to relaxation time and proportional to $T_x$ and $T_c$ (60). With increasing heating rates, the shift of $T_c$ to higher temperature was observed which is mainly attributed
to the induction time associated with the nucleation process and crystallisation is controlled by nucleation. Khan *et al.* studied chalcogenide glasses and stated that $T_c$ increased from 397°C to 440°C with increasing heating rate from 5 K to 25 K/min (61). They also mentioned that as the heating rate increases, the temperature at which induction time becomes zero increases leading to shift of $T_c$ to higher temperatures. In addition, the $T_c$ also increased with increasing $Y_2O_3$ content and this was ascribed to the heat flow of the samples increasing with increasing heating rate (62,63). Al-noaman *et al.* investigated the effect of MgO on bioactive glasses and reported that the $T_c$ increased from 880°C to 920°C with increasing heating rates from 5°C to 20°C/min (64). Similar results were also found by Clupper and Hench (65) and Bretcanu *et al.* (66).

The thermal stability of the glass particles in terms of their processing window increased with the addition of yttrium oxide up to 3 mol% (see Table 3). This was suggested to be due to the replacement of P-O-P bonds (bond energy, 680 KJ/mol) by Y-O-P bonds which have a higher bond energy (1054 KJ/mol) (67). As a result, the cohesive energy increased with increasing $Y_2O_3$ content which increased thermal stability. However, further addition of $Y_2O_3$ decreased the thermal stability and this could be attributed due to the formation of quasicrystal which in turn decreases the glass forming ability (68). Zhuohao *et al.* studied $Y_2O_3$ doped germanate oxyfluoride glass ceramics and reported that their thermal stability decreased when yttrium content increased from 0 to 9.30 mol% due to their tendency to crystallise (69). Mehta *et al.* studied thermal stability of Se-Sb glassy alloys and reported an increase up to 4 mol% Sb content which decreased for 6, 8 and 10 mol % additions due to the decrease of bond energies (70). Similar results were also reported by Abhay *et al.* chalcogenide glass system (71) Furthermore, a lower atomic radius of yttrium (0.1801 nm) compared to sodium (0.1857 nm)
could have formed more dense atomic packing and consequently, improve thermal stability of the lower Y$_2$O$_3$ doped glasses (72).

Differential scanning calorimetry (DSC) has been widely used for investigating the crystallisation kinetics of glasses. Activation energy and crystallisation kinetics are important parameters and can be obtained using the equations proposed from the interpretation of non-isothermal data. For the different methods of analysis applied for the determination of activation energies of $T_g$, $T_x$ and $T_c$ for the four different glass formulations investigated, see supplementary section S1.

Moynihan and Kissinger equations were used for the determination of activation energy at glass transition temperature ($E_g$). Although the Moynihan and Kissinger equations are based on different theoretical models, the values of $E_g$ were close to each other and the differences in values were within the experimental errors (see Figure 9). The $E_g$ value decreased from 191 to 118 KJ/mol (via Moynihan method) and from 183 to 113 KJ/mol (via Kissinger method) with increasing Y$_2$O$_3$ content from 0 to 5 mol% (see Figure 9). $E_g$ is directly related with the relaxation energy of glass structure. The relaxation energy is the amount of energy needed to overcome the barrier between different quasi-stable regions during the preparation of glass. Mitang et al. studied yttrium oxide containing silicate glass and reported that $E_g$ was linked with to the structural relaxation energy and as such, $E_g$ was inversely proportional to the stability of the glass structure (23). In addition, they stated that Y$_2$O$_3$ acts as a network modifier and its introduction into the glass structural network creates non-bridging oxygen’s (NBOs), which can increase the disorder and entropy of the glass structure. Three types of activation energy can be involved in the crystallisation process, including activation energy for onset of crystallisation ($E_x$), for peak crystallisation ($E_c$) and for the overall crystallization ($E$). The $E_x$ decreased from 189.74 to 118.27 KJ/mol (using Ozawa model) and
from 184.26 to 114.88 KJ/mol (using Augis-Bennette model) with increasing yttrium oxide content from 0-5 mol% (see Figures 10). Moreover, $E_c$ decreased (from 120.34 to 94.27 KJ/mol) with increasing $Y_2O_3$ content via Kissinger method (see Figure 11). The reduction of $E_s$ or $E_c$ could be attributed to an increase in the number of non-bridging oxygens by the addition of $Y_2O_3$ acting as a network modifier (7,73). Therefore, the movement of atoms in glass structure was easier for the formation of crystal nucleation and growth. Zarabad et al. studied addition of $Y_2O_3$ on crystallisation kinetics of oxyfluoride glass ceramics and found the opposite results where the activation energy of crystallisation increased with incorporation of $Y_2O_3$ (74). They reported that $Y_2O_3$ acted as a network former and consequently, the formation of bridging oxygens which makes the movements of atoms difficult for crystallisation and as a result, an increase in the activation energy of crystallisation was observed.

The theory of transformation of crystallisation kinetics was developed by Johnson and Mehl (75) and Avrami (76). Matusita et al. developed a method of crystallization based on nucleation and growth processes (46,77). Crystallisation mechanisms such as bulk or surface crystallisation should be considered when investigating the activation energy. The Avrami exponent ($n$) can be used to understand the crystallisation process in glassy materials. The value of the dimensionality of growth ($m$) is related to the nucleation parameter/Avrami exponent ($n$) value. Usually, the dimensionality of crystal growth ($m$) is reported to be equal to $n-1$ (23). When surface crystallisation predominates; the value of the nucleation and growth parameters are equal to 1 (40). In our study, the nucleation or Avrami parameter ($n$) was found to be approximately 2 for all the glass formulations investigated (see Table 4). This suggested that one-dimensional crystal growth was occurring for the glasses investigated, which could be explained by the small addition of yttrium oxide in the glass system (78). SEM
analysis confirmed that the crystalline morphologies observed resembled one-dimensional structures in the form of needle-like arrays, for all glass formulations investigated (as shown in Figure 8 (a-d). Mitang et al. studied yttrium doped zinc borosilicate glasses and found that one-dimensional crystal growth formed from the surface to the inside of the glass structure (23). From Figure 12d, deviations from the straight lines for Y5 glass formulation was observed at high temperature (550°C, 554°C and 558°C) which could be attributed to the saturation of nucleation sites during the latter stages of the crystallisation process (79). In addition, restriction of crystal growth by small size particles may also be responsible for the deviations observed at high temperature (80). The overall crystallisation activation energy (E) also decreased from 253 to 205 KJ/mol with increasing yttrium oxide content. Similar trends were also observed for other T₉, Tₓ and Tᶜ activation energy values. The decrease of overall activation energy could also be attributed to the network modifying effect of Y₂O₃ forming NBOs.

In general, the E₉ was higher than Eₐ due to the molecular motion around the T₉ (81). A similar behaviour was noted for lithium ions in bismuthate glasses (82). In this study higher Eₓ value was found compared to Eₓ (see Figures 10 and 11) and this was attributed to the effect of bulk nucleation and crystal growth processes. Huan et al. also found higher Eₓ value compared to Eₓ for amorphous Zr-Cu-Ni alloys and suggested that the nucleation process of amorphous Zr₇₀Cu₂₀Ni₁₀ alloy was more difficult than the growth process (41).

In summary, the incorporation of Y₂O₃ into the glass system investigated decreased E₉, Eₓ and Eₓ and increased their thermal stability. Differences of activation energy values using Moynihan, Ozawa, Augis and Bennette, Kissinger and Matusita-Sakka plots were observed and attributed to the different temperatures involved in the various equations. The reduction in activation energy with incorporation of Y₂O₃ into the glass system implied that Y₂O₃ acted
as a nucleating agent promoting crystallisation effects. On the basis of activation energy values for this glass family series (with fixed 45 mol% P₂O₅), it could be suggested that yttrium containing PBGs with more than 5 mol% Y₂O₃ would crystallise as the activation energy reduced to lower than 200 KJ/mol.
5. Conclusions:

In this study, crystallisation kinetic studies were carried out for \(45\text{P}_2\text{O}_5-(30-x) \text{Na}_2\text{O}-25\text{CaO} -x\text{Y}_2\text{O}_3\) glass system using non-isothermal DSC measurements, which indicated that the glass transition and crystallisation temperatures were influenced by the heating rates. The activation energy of \(T_g\), \(T_x\) and \(T_c\) was determined by five different methods. The \(T_g\), \(T_x\) and \(T_c\) increased with the addition of \(\text{Y}_2\text{O}_3\) into glass system while the \(E_g\), \(E_x\), \(E_c\) and \(E\) decreased. The Avrami parameter \((n = 2)\), revealed the crystallisation kinetics to be controlled by bulk nucleation with one-dimensional growth predicted and observed via SEM analysis. It is suggested that \(\text{Y}_2\text{O}_3\) acted as a nucleating agent in this glass family series and glasses with yttrium oxide content above 5 mol% would crystallise. The overall activation energy data also revealed that values close to or lower than 200 KJ/mol would very likely results in crystallisation of phosphate-based glasses in this family series.

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**Supplementary Figure:**

**Figure S1**: A schematic diagram of differential scanning calorimetry curve for the determination of crystallised volume fraction X at specific temperature T
**Table 1: Glass codes, drying, melting and casting temperature used throughout the study**

| Glass Code | P\(_2\)O\(_5\) content (mol\%) | CaO content (mol\%) | Na\(_2\)O content (mol\%) | Y\(_2\)O\(_3\) content (mol\%) | Drying temp./time (°C/hr) | Melting temp./time (°C/hr) | Casting temp./time (°C/hr) |
|------------|-------------------------------|---------------------|---------------------------|-------------------------------|--------------------------|--------------------------|--------------------------|
| Y0         | 45 / 45                       | 25 / 25             | 30 / 30                   | ---                           | 350 / 0.5                | 1150 / 2                 | 374 / 1                  |
| Y1         | 45 / 45                       | 25 / 25             | 29 / 29                   | 1 / 1                         | 500 / 1                  | 1300 / 2                 | 385 / 1                  |
| Y3         | 45 / 46                       | 25 / 25             | 27 / 27                   | 3 / 3                         | 500 / 1                  | 1300 / 2                 | 406 / 1                  |
| Y5         | 45 / 43                       | 25 / 25             | 25 / 25                   | 5 / 5                         | 500 / 1                  | 1300 / 2                 | 433 / 1                  |

**Table 2: Elemental composition for different phosphate-based glass formulations investigated using EDX analysis**

| Sample | P\(_2\)O\(_5\) (Expected/Actual value) (mol\%) | CaO (Expected/Actual value) (mol\%) | Na\(_2\)O (Expected/Actual value) (mol\%) | Y\(_2\)O\(_3\) (Expected/Actual value) (mol\%) |
|--------|-----------------------------------------------|------------------------------------|------------------------------------------|-----------------------------------------------|
| Y0     | 45 / 43.9±1.4                                 | 25 / 25.5±1.8                      | 30 / 30.6±1.8                            | 0 / 0                                         |
| Y1     | 45 / 43.2±1.9                                 | 25 / 26.9±1.9                      | 29 / 29.1±1.4                            | 1 / 0.8±0.4                                   |
| Y3     | 45 / 46.2±1.3                                 | 25 / 25.9±2.1                      | 27 / 25.9±1.5                            | 3 / 2±1.2                                     |
| Y5     | 45 / 43.8±1.8                                 | 25 / 26.2±1.7                      | 25 / 26.3±1.9                            | 5 / 3.7±1.5                                   |
| Y8     | Glass became crystalline during cooling (see Figure 2) |
| Y10    | Glass did not melt at all (see Figure 1b)     |
Table 3: Glass transition temperature $T_g$, onset crystallisation temperatures $T_x$, crystallisation temperature $T_c$ and processing window of yttrium phosphate glasses

| Sample | Heating rate (°C/min) | Glass transition $T_g$ (°C) (±1) | Onset crystallisation $T_x$ (°C) (±1) | Crystallisation temperature $T_c$ (°C) (±1) | Processing window $T_x-T_g$ (°C) |
|--------|-----------------------|----------------------------------|-------------------------------------|---------------------------------|-------------------------------|
| Y0     | 5                     | 355                              | 442                                | 471                             | 87                            |
|        | 10                    | 356                              | 446                                | 480                             | 90                            |
|        | 15                    | 360                              | 450                                | 485                             | 90                            |
|        | 20                    | 361                              | 454                                | 492                             | 93                            |
| Y1     | 5                     | 368                              | 462                                | 495                             | 94                            |
|        | 10                    | 370                              | 469                                | 507                             | 99                            |
|        | 15                    | 375                              | 473                                | 513                             | 98                            |
|        | 20                    | 376                              | 480                                | 520                             | 104                           |
| Y3     | 5                     | 386                              | 500                                | 531                             | 114                           |
|        | 10                    | 391                              | 515                                | 549                             | 124                           |
|        | 15                    | 396                              | 518                                | 558                             | 122                           |
|        | 20                    | 399                              | 523                                | 564                             | 124                           |
| Y5     | 5                     | 415                              | 520                                | 537                             | 105                           |
|        | 10                    | 417                              | 534                                | 552                             | 117                           |
|        | 15                    | 425                              | 540                                | 564                             | 115                           |
|        | 20                    | 429                              | 549                                | 571                             | 120                           |
Table 4: Values of overall crystallisation activation energy, nucleation parameter (n) and dimension parameter (m) for 45P_{2}O_{5}-(30-x) Na_{2}O-25CaO -xY_{2}O_{3} (where x= 0, 1, 3 and 5) glass system

| Sample | Overall crystallisation activation energy (KJ/mol)-Matusita-Sakka equation | Avrami index/Nucleation and growth parameter (n) | Dimensionality of growth (m) |
|--------|-------------------------------------------------|-----------------------------------------------|-------------------------------|
| Y0     | 253                                             | 2.0                                           | 1                             |
| Y1     | 216                                             | 2.1                                           | 1                             |
| Y3     | 211                                             | 2.2                                           | 1                             |
| Y5     | 205                                             | 2.1                                           | 1                             |
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Figure 2: X-ray diffraction pattern for glasses in the system of 45P$_2$O$_5$-(30-x) Na$_2$O-25CaO -xY$_2$O$_3$ (where x= 0, 1, 3, 5 and 8)
Figure 3: Density and Molar volume of phosphate glass particles as a function of Y$_2$O$_3$ content; error bars represent standard error of mean where $n = 3$.

Figure 4: DSC traces for glass particles investigated in the glass system 45P$_2$O$_5$-(30-x) Na$_2$O-25CaO-xY$_2$O$_3$ (where x=0, 1, 3 and 5) at different heating rates (5°C, 10°C, 15°C and 20°C/min$^{-1}$)
Figure 5: Variation of onset crystallisation temperature ($T_x$) with $Y_2O_3$ content at different heating rates.

Figure 6: Variation of processing window ($T_x-T_g$) with $Y_2O_3$ content at different heating rates.
Figure 7: SEM micrographs of surface microstructure in glass samples-(a) Y0 and (b) Y1 heat treated at 406°C for 5h, (c) Y3 and (d) Y5 heat treated at 441°C for 5h

Figure 8: SEM micrographs exploring crystal growth formation for-(a) Y0 and (b) Y1 heat treated at 476°C for 5h, (c) Y3 heated at 535°C and (d) Y5 heat treated at 545°C for 5h
Figure 9: Plots of a) $\ln \alpha$ versus $1000/T_g$ and b) $\ln (\alpha/T_g^2)$ versus $1000/T_g$ for 45P$_2$O$_5$-(30-x) Na$_2$O-25CaO -xY$_2$O$_3$ (where $x$ = 0, 1, 3 and 5) glass system

Figure 10: Plot of a) $\ln \alpha$ as a function of $1000/T_x$ and b) $\ln (\alpha/T_x)$ as a function of $1000/T_x$ for 45P$_2$O$_5$-(30-x) Na$_2$O-25CaO -xY$_2$O$_3$ (where $x$ = 0, 1, 3 and 5) glass system
Figure 11: Plots of ln (α/Tc²) versus 1000/Tc for 45P₂O₅-(30-x) Na₂O-25CaO -xY₂O₃ (where x=0, 1, 3 and 5) glass system

Figure 12: Plots of ln[-ln(1-X)] versus lnα at different temperatures for different compositions
Figure 13: Matusita plots of $\ln[-\ln(1-X)]$ versus $1000/T$ at different heating rates for $45P_2O_5$-(30-x) $Na_2O$-25$CaO$-x$Y_2O_3$ (where $x=0,1,3$ and 5) glass system

Figure S1: A schematic diagram of differential scanning calorimetry curve for the determination of crystallised volume fraction $X$ at specific temperature $T$