THERMAL STABILITY OF Na_2O – FeO – Fe_2O_3 – P_2O_5 GLASSES

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Abstract:

The crystallization tendencies of five series of Na_2O – FeO – Fe_2O_3 – P_2O_5 (NFP) glasses with different O/P (3.0–3.5) and Fe/P (0.13–0.67) ratios were studied. Characteristic temperatures, including the glass transition temperature (T_g) and crystallization temperature (T_x^h), were obtained using differential thermal analysis (DTA), and liquidus temperatures (T_L) were determined by microscopic evaluation of heat-treated samples. The compositional dependence of glass structure and the characteristic temperatures are discussed. The glass stability (GS) against crystallization is described using parameters based on the characteristic temperatures. For the glass series with O/P ratios near the pyrophosphate composition (O/P ~3.5), the glass stability goes through a minimum value around Fe/P ~ 0.3 to 0.4, which corresponds to the crystalline phase NaFeP_2O_7 and $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$.

Keywords:

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ABSTRACT

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1. Introduction

As potential hosts to vitrify high-level nuclear waste (HLW), some phosphate minerals and iron phosphate glasses have advantages that include their chemical stability, resistance to radiation damage, and solubility for substantial quantities of actinides [1]. The excellent chemical durability of iron phosphate glasses is often equivalent to or better than many other nuclear waste storage hosts, including borosilicate glasses [2,3,4,5]. In addition, iron phosphate glasses can tolerate high concentrations of waste components, including alkali oxides (up to 20 wt%) and chromium oxide (up to 4.5 wt%) without deterioration of their good chemical durability [5,6]. Iron phosphate glasses with PbO have been developed for radiation shielding applications, including gamma-radiation [2,7]. Iron phosphate glasses have also been developed as biomaterials with tailored rates of degradation in aqueous environments and as corrosion-resistant, reinforcing fibers for composite materials [8,9,10,11]. Phosphate glasses containing divalent iron cations exhibit interesting semiconducting properties, magneto-optical properties and magnetic transition properties [12,13,14,15,16].

The fraction of ferrous ions in an iron phosphate glass varies with the initial batch materials and preparation conditions, increasing when ferrous raw materials are used and when melts are processed under reducing conditions [16,17,18]. The fraction of $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ is typically about 20% for glasses made by conventional melting (in air) and quenching techniques [4,17,19].

The structural complexity of iron phosphate glasses is increased by the distortion of Fe-polyhedra and by disproportionation reactions of phosphate anions in the melts [20,21,22,23,24]. The structural complexity further changes the ability of an iron phosphate glass to incorporate a variety of elements into its structure, and affects the thermal stability of super-cooled iron phosphate melts against crystallization. Understanding the thermal stability of a glass against

crystallization on heating is useful for sintering glass powders and designing nuclear waste storage hosts that may heat as a result of radioactive decay and geological thermal cycles [9,25]. Glass forming ability indicates the likelihood of cooling a melt from above the liquidus temperature to the glass transition temperature without crystallization [26]. Structural and kinetic approaches are used to understand the concepts of thermal stability and glass forming ability, and efforts have been made to relate these two concepts [26,27,28].

Several parameters regarding glass stability on heating are obtained from differential thermal analysis (DTA) or differential scanning calorimetry (DSC) experiments, which provide characteristic temperatures, including the glass transition temperature (T_g), the crystallization onset temperature on heating (T_x^h), and the crystallization peak temperature on heating (T_c^h) [28]. The melting point (T_m), solidus temperature (T_s) and liquidus temperature (T_L) of a composition are also important characteristic temperatures. From DSC/DTA data, the T_s and T_L values can be determined for some glasses from the beginning (onset) and the end (offset) of the melting endotherms, if the endotherm also corresponds the first exotherm on the cooling curve [25,29,30]. For glasses without clear melting peaks, hot stage microscopy or the gradient furnace method has been used to measure the liquidus temperature [25,31].

Several important glass stability parameters that utilize the characteristic temperatures are given in Table 1, in which characteristic temperatures are in absolute temperature scale. An increase in each of these parameters, for example the increase in the difference between crystallization temperatures and T_g , indicates a greater resistance to crystallization on heating a glass or quenching a melt (better stability). For silicate glasses, studies have shown that an increase in glass stability parameters indicates a decrease in the critical cooling rate for glass formation, and so an increase in glass forming ability [26,27]. Nascimento et al.[28] compared

and evaluated these and other glass stability parameters and found that the Weinberg and Hrubý parameters, which include three characteristic temperatures, have the best empirical correlations with glass-forming ability.

The $\text{Na}_2\text{O}\text{--}\text{FeO}\text{--}\text{Fe}_2\text{O}_3\text{--}\text{P}_2\text{O}_5$ (NFP) glass system is a model for iron phosphate compositions used to vitrify high alkaline nuclear waste streams [32]. The glass-forming region and thermal properties of sodium iron phosphate and sodium-free iron phosphate glasses have been reported [18,33,34,35], but less is known about the compositional effects of glass structure and iron redox on thermal stability or crystallization behavior of these glasses. In the present work, five series of $\text{Na}_2\text{O}\text{--}\text{FeO}\text{--}\text{Fe}_2\text{O}_3\text{--}\text{P}_2\text{O}_5$ glasses with different O/P (3.0–3.5) and Fe/P (0.13–0.67) ratios that cover the broad glass-forming range were prepared by conventional melting (in air) and quenching techniques. Glass stability against crystallization are described using the parameters in Table 1, and the effects of composition on thermal stability are discussed in terms of the network structure, stable crystalline phases and iron redox. Studies of the phosphate anion distributions and iron coordination sites in these same NFP glasses are presented elsewhere [22,23].

2. Experimental Procedures

The experimental procedures for preparing and analyzing the sodium iron phosphate glasses used in this study have been described in a previous study [22,23]. Briefly, glasses were made from batches of raw materials including Na_2CO_3 (Alfa Aesar, $\geq 98\%$), Fe_2O_3 (Alfa Aesar, $\geq 99\%$) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Alfa Aesar, $\geq 98\%$) that were melted in fused SiO_2 crucibles (Leco #728-701) between 1000 °C and 1250 °C in air for two hours. Glass compositions, including some silica transferred from the crucibles, were determined by inductively-coupled plasma

optical emission spectroscopy (ICP-OES, PerkinElmer Optima 2000 DV, Norwalk, USA), and the fraction of iron present as Fe^{2+} was determined by a wet chemical technique [36].

Compositional series with similar O/P ratios, from 3.0 to 3.5, are labeled from A to E as defined in a previous study [23]. For example, glass E-0.66 is a sample in the E-series with a batched O/P ratio of 3.5 and an analyzed Fe/P ratio of 0.66.

Differential thermal analysis (Perkin Elmer, 7 series/UNIX DTA 7, Norwalk, Connecticut USA) was used to determine the characteristic temperatures, including T_g (onset), T_x^h and T_c^h (crystallization exotherm onset and peak, respectively). About 30 mg of glass powder with particle sizes ranging between 75 and 150 μm were heated in an alumina crucible at 15 $^{\circ}\text{C}/\text{min}$ under a nitrogen atmosphere (flow rate 30 cm^3/min) from room temperature until melting was complete. For most of the sodium iron phosphate glasses in this study, the characteristic temperatures for melting, T_m , T_s and T_L , could not be accurately determined from the DTA scans because of small and diffuse changes in heat associated with crystal melting [25]. The liquidus temperatures (T_L) were determined instead by crystallizing the glass powders (75–150 μm) in air by holding them for nine hours at the offset temperature of the DTA crystallization peaks. The crystalline phases in these samples were identified by X-ray diffraction (XRD) with a Philips X'pert multipurpose diffractometer with PIXcel detector, using $\text{Cu K}\alpha$ radiation and Ni filter, at 45 kV and 40 mA. The crystallized samples were then heated in air in a platinum boat for up to 30 minutes at increasing temperatures, and then quenched and analyzed by optical microscopy (Hirox KH-8700 digital microscopy with MXG-2500 REZ zoom lens) and Raman spectroscopy (Horiba Jobin Yvon LabRAM Aramis μ -Raman with a 632.8 nm He-Ne laser and a 10 $\times$ objective). The apparent T_L was determined to be the midpoint between the highest temperature where crystals were observed and the lowest temperature where no crystals were observed [37].

3. Results

3.1. Characteristic temperatures

Fig. 1 (a) shows a DTA scan for the E-0.23 glass to indicate how the characteristic temperatures were determined. Fig. 1 (b) shows the DTA patterns for the E-series ($O/P = 3.49 \pm 0.01$) glasses. Similar DTA data were collected for the other glasses and the characteristic temperatures, T_g , T_x^h and T_c^h ($^{\circ}C$), are given in Table 2. These temperatures were reproducible to $\pm 3^{\circ}C$ based on at least three DTA runs of selected samples. For a glass series with similar O/P ratios, the replacement of Na^+ ions by Fe^{2+} and Fe^{3+} ions affects the T_g and the crystallization behavior of the glasses. Fig. 2 shows a systematic increase in T_g with increasing $Fe/(Na+Fe)$ ratio, although glasses with $O/P \geq 3.4$ exhibit maxima in T_g for $Fe/(Na+Fe)$ ratios near 0.5–0.7. A decrease in T_g is observed (Table 2) for the sodium-free iron phosphate glasses with increasing O/P ratio, from $576^{\circ}C$ for glass A-0.37 to $487^{\circ}C$ for glass E-0.66.

The crystalline phases that form when the E-series glasses were held for nine hours at the offset temperatures of the respective DTA exothermic peaks were determined by XRD and are shown in Fig. 3 (a). The O/P ratio of this series is near the pyrophosphate stoichiometry ($O/P = 3.5$), and as the Fe/P ratio increases from 0.15 to 1.00, the dominant crystalline phases are the related pyrophosphates that appear in the order $Na_4P_2O_7$ (PDF 71-1631), $Na_7Fe_3(P_2O_7)_4$ [38], $NaFeP_2O_7$ (PDF 36-1454) and $Fe_4(P_2O_7)_3$ [39]. For the Na-free iron phosphate glasses, the crystalline phases evolve from $Fe(PO_3)_3$ (PDF 38-109), for glasses with $O/P < 3.3$, to $Fe_4(P_2O_7)_3$ with increasing O/P ratios (Fig. 3 (b)) [35].

3.2. Thermal stability

Fig. 4 shows an example of how the liquidus temperatures, T_L , were determined in this study. The E-0.23 glass was held for nine hours at 557 °C, the offset temperature of the DTA crystallization exotherm (Fig. 1 (a)), and the crystallized sample was then heated to the higher temperatures, held for 30 min, then cooled to room temperature and analyzed by optical microscopy and Raman spectroscopy. Crystals could be detected on the surface of the glass cooled from 830 °C (Fig. 4 (a)). Raman spectra of these crystals (Fig. 4 (b)) indicate that they are likely $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ [21,23]. No crystals were detected in the sample quenched from 847 °C and this sample has a Raman spectrum similar to that for the sample quenched from 1100°C (Fig. 4 (b)). Therefore, for the crystallized E-0.23 samples, 830 °C is the highest temperature where crystals were observed and 847 °C is the lowest temperature where no crystals were observed, and so the T_L for the E-0.23 glass is taken as the midpoint, 839 °C. The liquidus temperatures were measured by the same technique for the other glasses in this study, and are summarized in Table 2.

Glass stability parameters K_A , K_W and K_H (Table 1) were calculated from the characteristic temperatures, converted to the absolute scale (K), and are given in Table 2. The compositional dependences of these three parameters are similar. Fig. 5 (a) shows a minimum in the stability parameters for the series E glasses (O/P ~3.49) at $\text{Fe}/(\text{Na}+\text{Fe}) = 0.33$. Minima in the glass stability parameters also occur for the series of sodium-free iron phosphate glasses around O/P 3.3–3.4 (Fig. 5 (b)).

4. Discussion

4.1. Glass transition temperature

Fig. 6 (a) shows that the glass transition temperatures of the Na-free iron phosphate glasses decrease with increasing O/P ratio, consistent with literature [9]. A similar decrease in T_g with increasing O/P ratio was also noted for ZnO–P₂O₅ polyphosphate glasses [40]. The differences between the values of T_g measured in this study and those reported in the literature are most likely due to differences in composition, including the degree of iron reduction, Al₂O₃ contamination [9,24] or SiO₂ contamination (this study), arising from differences in melting conditions.

For phosphate glasses with O/P ratios in the range 3.0–3.5, the ratio of the bridging oxygen (BO) connecting two phosphate tetrahedra to the nonbridging oxygen (NBO) that link one P-tetrahedron to the modifying metal ion (Me) polyhedra, BO/NBO, can be calculated from [41],

$$\frac{BO}{NBO} = \frac{4 - (\frac{O}{P})}{2(\frac{O}{P} - 2)} \quad (1)$$

The predicted ratios of BO/NBO for NFP glasses in this study are consistent with the BO/NBO ratios determined by HPLC analyses, as described in a previous study of phosphate anion distributions [22]. With an increase in O/P ratio, the number of relative longer (P–O)–Me bonds increases, and the relative numbers of shorter (P–O)–P bonds decreases, as does the average phosphate chain length. The shorter chains and weaker P–O bonds correlate with the decrease in T_g values for the Na-free iron phosphate glasses.

For glasses with similar O/P ratios but different modifying oxides, the bonds between the metal polyhedra and phosphate anions determine the compositional dependence of the glass properties, like T_g . In general, cations with greater field strengths increase the structural rigidity

of the network, which increases the temperature required to activate rotational motions, and so increase T_g [41,42]. For a series of NFP glasses with similar O/P ratios, the replacement of lower field strength Na ions by Fe ions generally increases the glass transition temperature, as shown in Fig. 2 and Fig. 6 (b). For the NFP glasses with compositions near the pyrophosphate stoichiometry, however, there is a maximum in T_g with increasing iron content, as seen in the present study and reported in the literature (Fig. 6 (b)). Similar observations of a maximum T_g were also made for mixed alkali $x\text{Na}_2\text{O}-(20-x)\text{R}_2\text{O}-32\text{Fe}_2\text{O}_3-48\text{P}_2\text{O}_5$ ($\text{R} = \text{K}$ and Cs) glasses [33]. Such behavior cannot be explained by the simple modifier field strength argument outlined above.

In the previous Raman spectroscopic study of these NFP glasses [23], it was shown that the frequency of the symmetric stretching modes of non-bridging oxygens (O_{nb}) generally increased with an increase in iron content for glasses with similar O/P ratios. Fig. 7 shows some results from that study; here, the $(\text{PO}_3)_{\text{sym}}$ modes are associated with non-bridging oxygens on Q^1 tetrahedra and the $(\text{PO}_2)_{\text{sym}}$ are associated with NBOs on Q^2 tetrahedra. The shifts to greater Raman frequencies can be associated with shorter average $\text{P}-\text{O}_{\text{nb}}$ bond lengths [21] or narrower average $\text{O}_{\text{nb}}-\text{P}-\text{O}_{\text{nb}}$ bond angles [23,43,44], indicating that stronger $\text{P}-\text{O}_{\text{nb}}$ bonds may then be correlated with greater values for T_g . Supporting this correlation are the maxima in the $(\text{PO}_3)_{\text{sym}}$ Raman frequencies for the glasses with $\text{O/P} = 3.40$ and 3.49 in the same compositional ranges, $\text{Fe}/(\text{Na}+\text{Fe}) = 0.45-0.70$, where there are maxima in the values of T_g .

4.2. *Glass forming ability and thermal stability*

Glass forming ability describes the ease of vitrification of a melt on cooling from T_L to T_g , and so is affected by thermodynamic and structural factors as well as the kinetic process of glass

formation [26,45]. Glasses that have two modifying cations with large differences in ionic field strengths will have large negative exothermic enthalpies of mixing for their melts ($\Delta H_{\text{mix}} < 0$) [46], and so will favor homogeneous melts instead of phase separated ones [47]. Compared to Na^+ , iron cations are less basic and have greater electronegativity, and so the enthalpy of the formation of Fe–O bonds is more negative than that of the formation of Na–O bonds. At the same time, as the Fe content increases, the distribution of phosphate chains in a melt becomes broader, and the enthalpy for the endothermic disproportionation reactions (ΔH_n) decreases [46]. These enthalpy changes indicate that the replacement of Na by Fe should improve the glass forming ability of a phosphate melt and this is consistent with the laboratory observation that sodium-free iron phosphate melts near the pyrophosphate composition are much better glass formers than are Na-pyrophosphate melts.

From a structural view, a greater degree of P–O–P connectivity in a glass melt could provide steric inhibition to crystallization [40]. Therefore, vitrification may be easier if there are relatively greater concentrations of longer phosphate chains or wider distributions of phosphate anions in the melts. The increased structural complexity that results from disproportionation reactions leads to good glass forming ability for pyrophosphate melts with high field strength cations (e.g., Fe, Zn, Cd, and Bi), compared to melts with K, Na, or Li [40].

Even though glass formation is favored by the presence of complex anionic structures in a phosphate melt, the stability of the competing crystalline phases also influences glass formation and needs to be taken into consideration [45]. Studies have shown that glass-forming ability can be estimated by several thermal stability parameters (e.g., Table 1) defined by three characteristic temperatures [28]. Greater thermal stability is associated with lower critical cooling rates (q_{cr}) [28], and thus with greater glass forming ability.

Thermal stability indicates the ability of glass to resist crystallization on heating. The compositional dependence of the thermal stability parameters can be used to indicate trends in glass-forming ability. A ternary contour map of the compositional dependence of the Hrubý thermal stability parameter, K_H , is shown in Fig. 8, where K_H is calculated from the measured characteristic temperatures shown in Table 2. Glasses with long phosphate chains (lower O/P ratio) or with low sodium contents generally have better thermal stability. Glass compositions with the lowest K_H are similar to the compositions of the stable crystalline phase $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ and NaFeP_2O_7 .

For the E-series, near the pyrophosphate stoichiometry, thermal stability shows a minimum value between the Fe/P ratios 0.3 and 0.4 (Fig. 5 (a)), and the corresponding glass composition around the minimum in thermal stability readily crystallized on heating to form NaFeP_2O_7 (Fig. 3 (a)). Compositions of the crystalline phases identified by XRD (Fig. 3) are indicated in Fig. 8. Melts with compositions near other stable intermediate compounds are also associated with the lower glass forming ability [34].

The glass forming region for the Na_2O – Fe_2O_3 – P_2O_5 system determined by Parsons et al [34] shows a discontinuity around compositions similar to crystalline $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ (crystal 2 in Fig. 8) and NaFeP_2O_7 (crystal 3 in Fig. 8). The crystalline phase NaFeP_2O_7 was observed in iron phosphate glass with 5 wt% Na_2O and 30 wt% simulated Japanese HLW (Fe/P ~0.43) [48]. Bingham et al. [49] report a limit to glass formation in the $[(1-x)(0.6\text{P}_2\text{O}_5-0.4\text{Fe}_2\text{O}_3)] + x\text{Na}_2\text{SO}_4$ system at 30–40 mol% Na_2O with a Fe/(Na+Fe) ratio ~0.38, similar to the minimum in glass forming ability near ~43 mol% Na_2O and Fe/(Na+Fe) ~0.33 in Fig. 5 (a). Dissolution studies have shown that glassy iron phosphate wastefoms have better chemical durability than

crystallized wasteforms [5,6], and thus compositions with the lowest thermal stability should be avoided when designing waste glasses with greater chemical durability.

The effect of the stability of the competing crystalline phases on glass formation cannot be ignored [45], which may mean that the best glass-forming compositions in a system are not necessarily the eutectic compositions with the lowest liquidus temperatures. A study of the thermal stability of glasses from the ferric $\text{Fe}(\text{PO}_3)_3\text{--Fe}_4(\text{P}_2\text{O}_7)_3$ system shows that the K_A and K_w parameters continuously decrease with increasing O/P ratio, and reaches the minimum value for iron phosphate glasses with O/P ratio ~ 3.40 [9], which is very close to the eutectic point in the system of $\text{Fe}(\text{PO}_3)_3\text{--Fe}_4(\text{P}_2\text{O}_7)_3$ [37], and similar to the minimum values in stability parameters near O/P ~ 3.36 noted in Fig. 5 (b); here, $\text{Fe}_4(\text{P}_2\text{O}_7)_3$, $\text{Fe}_3(\text{P}_2\text{O}_7)_2$ and $\text{Fe}(\text{PO}_3)_3$ were identified in crystallized sample (Fig. 3 (b)).

4.3. *Effects of iron redox*

Phosphate melts prepared with Fe_2O_3 will partially reduce to form Fe^{2+} under most circumstances. The difference in electron density and chemistry between Fe^{3+} and Fe^{2+} affects the physical and chemical properties of glass melts, including structure, viscosity, and the behavior of volatile components [50].

Under reducing conditions [16,17], the extent of Fe^{3+} reduction is determined by the partial pressure of oxygen or oxygen fugacity during melting [50]. For glasses melted in air, the melting temperature determines the ratio of $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$, and the following reaction is endothermic [17,51,52],

For iron pyrophosphate glasses melted in air, the equilibrium constant K of reaction (2) depends on the temperature according to [52,53],

$$\ln(K) = 9.40 - 1.58 \times 10^4/T \quad (3)$$

and the enthalpy (ΔH) of reaction (2) is calculated to be 131 ± 9 kJ/mol. For silicate glasses with iron less than 1 mol%, the enthalpy of reaction (2) was determined to be 144~171 kJ/mol, which is larger than that for phosphate glass [51,53]. This is consistent with the observations that the relative amount of Fe^{3+} reduced to Fe^{2+} is smaller in silicate glasses than that in phosphate glasses melted at the same temperature [50,54].

The distribution of phosphate anions will also be affected by the iron redox because the phosphate anions in the glass melts are in equilibrium with O^{2-} as shown by reaction (4) [46],

Zhang et al [9] report an increase in the $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ratio with an increase in the O/P ratio for glasses melted at the same temperature, indicating that reaction (4) is favored for glasses with greater O/P ratios. The reduction of ferric ions to ferrous ions reduces the oxygen available to form smaller phosphate anions, and this in turn will affect the equilibrium between phosphate anions, as represented by [46,55],

As indicated by the equilibrium states of reactions (2) and (4), the reduction of Fe^{3+} to Fe^{2+} will result in greater amount of pyrophosphate anions in the glass network because of the shift of the equilibrium of reactions (2) and (4) to the right. Studies have shown that the glass forming ability of the pyrophosphate melts deteriorates as the fraction of Fe^{2+} increases [18].

The liquidus temperatures of the Na-free iron phosphate glass melts in this study are 40–260 °C greater than the corresponding liquidus surface reported by Zhang et al. in a recent

study of the $\text{Fe}(\text{PO}_3)_3\text{--Fe}_4(\text{P}_2\text{O}_7)_3$ system [37]. This may be because the glasses in the present study are more reduced ($\text{Fe}^{2+}/\text{Fe}_{\text{tot}} \sim 0.19 \pm 0.05$ [23]) than the ferric materials studied by Zhang et al. [37], and are consistent with the increase in melting temperatures for sodium-free iron pyrophosphate glasses with an increase in $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ratio reported by Bingham et al. [56].

5. Summary

The thermal stability and crystallization behavior of several series of $\text{Na}_2\text{O--FeO--Fe}_2\text{O}_3\text{--P}_2\text{O}_5$ (NFP) glasses with different O/P (3.0–3.5) and Fe/P (0.13–0.67) ratios were studied. The glass transition temperatures were related to the nature of the P–O_{nb} bonds with the Na and Fe ions that link neighboring phosphate anions. The thermal stability against crystallization of sodium-free iron phosphate glasses is generally better than that of the sodium-containing iron phosphate glasses, and decreases with O/P ratio in the range 3.04~3.36. The minimum values of the thermal stability parameters correspond to the compositions of the stable crystalline compounds. The redox behavior of iron in the glass melts affects the glass thermal stability and the liquidus temperature, in part by affecting the phosphate anion distributions in the glass melts.

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Table 1 Thermal stability parameters reported in the literature.

Parameters	Equations
Angell[57,58]	$K_A = T_x^h - T_g$
Weinberg[59]	$K_W = \frac{T_c^h - T_g}{T_m}$
Hruby[60]	$K_H = \frac{T_x^h - T_g}{T_m - T_x^h}$

Table 2 Summary of characteristic temperatures and thermal stability parameters from the DTA data. Compositional information is from Ref. [23]. The error of T_g , T_x^h and T_c^h is ≤ 3 °C, the error for measured T_L is listed in the table, and the errors for $K_A \leq 4$ K, for $K_W \leq 6\%$, for $K_H \leq 8\%$.

Batched		Analyzed				Characteristic temperatures (°C)				Thermal stability parameters		
O/P	Fe/P	O/P	Fe/P	Fe ²⁺ /Fe _{tot}	Fe/(Na+Fe)	T _g	T _x ^h	T _c ^h	T _L	K _A (K)	K _W	K _H
A-Series	0.33	3.04	0.37	0.24	1.00	576	748	780	1210 ± 7	172	0.14	0.37
	3.0	0.23	3.04	0.23	0.31	447	562	591	1142 ± 7	115	0.10	0.20
	0.13	3.03	0.13	0.13	0.18	353	451	571	880 ± 5	98	0.19	0.23
B-Series	0.40	3.15	0.42	0.14	1.00	572	730	779	1208 ± 5	158	0.14	0.33
	3.1	0.33	3.10	0.32	0.26	500	605	622	1099 ± 5	105	0.09	0.21
	0.23	3.12	0.22	0.26	0.29	403	592	714	930 ± 6	189	0.26	0.56
	0.13	3.13	0.12	0.24	0.13	344	411	455	961 ± 4	67	0.09	0.12
C-Series	0.50	3.28	0.49	0.15	1.00	527	657	693	1229 ± 5	130	0.11	0.23
	3.25	0.40	3.25	0.38	0.22	489	577	601	1080 ± 8	88	0.08	0.17
	0.33	3.24	0.32	0.22	0.39	443	595	618	1029 ± 6	152	0.13	0.35
	0.23	3.27	0.23	0.27	0.23	382	495	512	1004 ± 9	113	0.10	0.22
	0.13	3.30	0.15	0.12	0.12	360	427	454	865 ± 9	67	0.08	0.15
D-Series	0.60	3.36	0.58	0.11	1.00	497	620	645	1187 ± 6	123	0.10	0.22
	3.4	0.50	3.38	0.49	0.16	513	645	669	1043 ± 5	132	0.12	0.33
	0.40	3.40	0.39	0.18	0.39	476	537	555	1040 ± 6	61	0.06	0.12
	0.33	3.42	0.32	0.21	0.28	433	503	515	1064 ± 9	70	0.06	0.12
	0.23	3.43	0.23	0.19	0.17	395	513	530	920 ± 6	118	0.11	0.29
	0.13	3.44	0.13	0.12	0.08	357	431	456	691 ± 8	74	0.10	0.28
E-Series	0.67	3.48	0.66	0.17	1.00	487	664	713	1138 ± 8	177	0.16	0.37
	3.5	0.60	3.48	0.58	0.20	502	642	666	1167 ± 5	140	0.11	0.27
	0.50	3.48	0.48	0.18	0.49	523	603	615	1095 ± 5	80	0.07	0.16
	0.40	3.50	0.39	0.20	0.33	467	516	537	1080 ± 5	49	0.05	0.09
	0.33	3.50	0.34	0.19	0.26	438	530	544	956 ± 5	92	0.09	0.22
	0.23	3.51	0.23	0.14	0.15	403	489	510	839 ± 9	86	0.10	0.24

Fig. 1. DTA data for glass powders (75–150 μm) heated in nitrogen at 15 $^{\circ}\text{C}/\text{min}$. (a) E-0.23 glass, showing the determination of the characteristic temperatures, the onset glass transition temperature (T_g), the onset crystallization temperature (T_x^h), the crystallization peak temperature on heating (T_c^h) and melting point (T_m); (b) E-series NFP glasses ($\text{O}/\text{P} = 3.49 \pm 0.01$).

Fig. 2. The dependence of T_g , determined by DTA (75–150 μm glass powder, heated at 15 $^{\circ}\text{C}/\text{min}$), on $\text{Fe}/(\text{Na}+\text{Fe})$ for each series of NFP glasses.

Fig. 3. X-ray diffraction patterns of glasses heated for nine hours above their respective DTA exothermic crystallization peaks. (a) E-series glasses ($O/P = 3.49 \pm 0.01$); (b) Sodium-free iron phosphate glasses with increasing O/P ratios. The identified crystalline phases are 1: $\text{Na}_4\text{P}_2\text{O}_7$ (PDF 71-1631); 2: $\text{Na}_7\text{Fe}_3(\text{P}_2\text{O}_7)_4$ [38]; 3: NaFeP_2O_7 (PDF 36-1454); 4: $\text{Fe}_2\text{Fe}(\text{P}_2\text{O}_7)_2$ [61]; 5: $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ [39]; 6: $\text{Fe}(\text{PO}_3)_3$ (PDF 38-109).

Fig. 4. (a) Optical image ($\times 600$) of crystals on the surface of E-0.23 glass, initially crystallized at 557 °C for 9 hours, then reheated to 830 °C for 30 minutes before quenching; (b) Raman spectra of the crystallized E-0.23 glass after reheating to the temperatures indicated. The points where the spectra were collected from the 830 °C sample are indicated on the optical image.

Fig. 5. Thermal stability parameters, K_A , K_W and K_H (heating rate 15 °C/min), presented (a) as a function of Fe/(Na+Fe) ratio for the E-series glasses ($O/P = 3.49 \pm 0.01$); (b) as a function of O/P ratio for the sodium-free iron phosphate glasses.

Fig. 6. T_g values. (a) changing with O/P ratio for Na-free iron phosphate glasses; (b) changing with the Fe/(Na+Fe) ratio for several series sodium iron phosphate glasses with similar O/P ratios. Reference data from Fang (2003) [33], Šantić (2007) [24], Parsons (2008) [34], Bingham (2009) [32], and Zhang (2010) [9].

Fig. 7. Raman peak position (cm^{-1}) of the PO_2 symmetric stretching mode and the PO_3 symmetric stretching mode depends on the $\text{Fe}/(\text{Na}+\text{Fe})$ ratio for the five glass series in this study, from reference [23].

Fig. 8. Compositional dependence of the thermal stability parameter, K_H (heating rate 15 °C/min). Crystalline phases marked by numbered stars are, 1: $Na_4P_2O_7$; 2: $Na_7Fe_3(P_2O_7)_4$; 3: $NaFeP_2O_7$; 4: $Fe_2Fe(P_2O_7)_2$; 5: $Fe_4(P_2O_7)_3$; 6: $Fe(PO_3)_3$.

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