Assessment of glass-forming ability and the effect of La_2O_3 on crystallization mechanism of barium–lead–zinc phosphate glasses

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Abstract

Differential scanning calorimetry (DSC) was used in this work to study the effect of La_2O_3 addition on crystallization mechanism of barium–lead–zinc phosphate glasses. Bulk glasses from two different routes (using P_2O_5 and H_3PO_4 as starting materials) presented only one crystallization peak. An assessment of glass-forming ability (GFA) was performed from recent theory that is connected to glass stability (GS), and is also correlated to critical cooling rate, q_{cr}. Systems with high La_2O_3 content presented some of the highest GS values and estimated critical cooling rates (q_{cr}) lower than 0.079 K/s. For both routes were determined the activation enthalpies for crystallization, that were 126 ± 12 kJ/mol (for P_2O_5) and 110 ± 32 kJ/mol (for H_3PO_4). The calculated Avrami n parameters, based on exothermic crystallization peaks, were 3.50 ± 0.33 (for P_2O_5) and 3.09 ± 0.91 (for H_3PO_4), considering data from the lowest heating rate (5 K/min). These values suggest that the DSC peaks should be associated to volume crystallization, due to La_2O_3 influence, and crystallization did not change significantly using different routes.
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1. Introduction

Phosphate glasses doped with rare earths are of technological interest owing to their unique properties such as optical quality, relative chemical stability, wide glass-forming range, low-melting, softening and glass transition temperatures, making then appropriate in optical fibers and amplifiers [1].

The determination of the ideal conditions to fabricate glasses destined for optical applications requires knowledge related to the nucleation and crystallization mechanisms. Thus, stability against crystallization is a key parameter. It is important to know if the glass is stable or tends to crystallize and to identify an eventual re-crystallization phenomenon, which could take place during the fiber drawing process. Therefore, it is important to know physical and thermal characteristics of interest. The application of thermal analysis techniques, such as differential scanning calorimetry (DSC) or differential thermal analysis (DTA) has been shown to be a simple and useful method to obtain information about nucleation and crystallization mechanisms in glassy systems [2,3]. In this way, the activation enthalpy for crystal growth and the kinetics of the nucleation and crystallization can be deduced through the formal kinetics theory of Johnson–Mehl–Avrami–Kolmogorov (JMAK) [4–8].

Glass-forming ability (GFA) is the ease to vitrify a liquid on cooling, while glass stability (GS) is the glass resistance against devitrification on heating. Recent studies showed that there exists direct relationship between these two parameters through quantitative criteria using JMAK [9]. For example, Cabral et al. [10] and Avramov et al. [11] presented recent experimental and theoretical studies on GFA and GS, respectively.

GFA accounts for the easy vitrification of a melt when cooled from above the liquidus T_l (or melting point, T_m) to the glass transition temperature (T_g). This parameter is characterized by the critical cooling rate, q_{cr}, which is the lowest cooling rate at which the final degree of crystallinity of the frozen liquid will not exceed

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a critical value, X_c, normally assumed to be $\approx 0.1\%$ [9–11]. According to stability, there are many definitions for GS, and they involve characteristic temperatures such as glass transition (T_g), crystallization onset (T_x), peak crystallization (T_c) or the melting point (T_m). Eqs. (1) and (2) present the GS parameter of Weinberg [12] and Lu and Liu [13], respectively.

$$K_W = \frac{T_x - T_g}{T_m} \quad \text{(Weinberg)} \tag{1}$$

$$K_{LL} = \frac{T_x}{T_g + T_m} \quad \text{(Lu and Liu)} \tag{2}$$

As most of the GS parameters that consist of three characteristic DSC temperatures show excellent correlation with GFA, it is possible to use them to estimate the GFA from the systems in study. To obtain the experimental GS parameters were carried out DSC runs using bulk glasses [9].

Recently, the DTA and DSC techniques were applied with success for nucleation and crystallization studies on different phosphate glasses [14–18]. Reynoso et al. [14] studied the effect of PbS on crystallization of $50 P_2O_5 \cdot 27.8 Na_2O \cdot 16 ZnO \cdot 6.2 Al_2O_3$. Yung et al. [15] analyzed the crystallization kinetics of a low-melting $40 P_2O_5 \cdot 10 ZnO \cdot 50 PbO$. Hassan and Hafid [16] verified the properties of $50 P_2O_5 \cdot xZnO \cdot (50-x)BaO$ with $0 \leq x \leq 50$. Harada et al. [17] studied the effect of small amounts of B_2O_3 in $xB_2O_3 \cdot (100-x)[49.5 P_2O_5 \cdot 50.5 BaO]$, where $0 \leq x \leq 3$. Ouchetto et al. [18] investigated the chemical durability of lanthanum–zinc phosphate glasses.

In this work, the crystallization mechanisms of phosphate glasses using two different starting materials were studied using the DSC technique. In addition, La_2O_3 was used as impurity and its effect on crystallization mechanism was investigated. Evaluations of GFA from selected systems are presented and discussed.

2. Experimental

Two phosphate series were used: one using P_2O_5 and other H_3PO_4 as starting materials (named series PZnBaPbAl·x and PZnBaPbAl·xH, respectively). In each series six phosphate glasses of composition $(65-x)P_2O_5 \cdot 14 ZnO \cdot 10 BaO \cdot 10 PbO \cdot 1 Al_2O_3$, both doped with xLa_2O_3 (where $x = 0, 2, 4, 6, 8$ and 10 mol%), were prepared by conventional melt-quenched method. Commercial reagents of zinc oxide (ZnO), lead oxide (PbO), barium carbonate (BaCO$_3$) and aluminum oxide (Al$_2$O$_3$) were mixed in appropriate proportions and melted in porcelain crucibles in an electric furnace at 1000–1200 °C for 1 h. The melt was then poured into a stainless steel mold and pressed between two stainless steel plates. All melt-quenched samples were transparent.

DSC 404 from Netzsch Instruments was used to determine physical characteristics of the studied glass. The DSC has a temperature accuracy of ±5 °C. Physical characteristics include parameters such as T_g, T_x, T_c and T_m. Based on these results, activation enthalpy of crystallization could be determined. The DSC measurements were performed in air using approximately 20 mg samples for all measurements. To study the crystallization mechanism, DSC measurements were performed on bulk

samples only, in a similar way as a recently published work [9], to achieve reasonable estimations on GFA.

3. Results and discussion

The DSC curves obtained from some bulk PZnBaPbAl·x and PZnBaPbAl·xH glasses series are shown in Table 1. Based on this table, La_2O_3 substitution caused significant changes on characteristic glass temperatures, as increasing T_g by ≈ 90 °C, T_x and T_c by ≈ 140 °C and T_m by ≈ 75 °C in both series. From the literature, Yung et al. [15] noted that $40 P_2O_5 \cdot 10 ZnO \cdot 50 PbO$ glasses show significant improvement in durability while maintaining low T_g (338 °C). Ouchetto et al. [18] affirmed that chemical durability increases with lanthanum content (from 4 up to 17 La_2O_3 mol%). Considering a fixed lanthanum content in both series, glasses made with P_2O_5 presented something higher T_g values than using H_3PO_4, suggesting that first route produces more rigidity phosphate structures. T_x and T_c presented not conclusive results comparing both series, but the melting point near coincides for odd compositions. It is important to note that all compositions show $T_x - T_g > 250$ °C, that could be viewed as another GS parameter. Particularly, sample PZnBaPbAl.10 presented $T_g = 451$ °C, $T_x = 771$ °C and $T_c = 859$ °C while T_g, T_x and T_c values for sample PZnBaPbAl·10H were 446, 746 and 889, respectively.

DSC crystallization peaks of the PZnBaPbAl.10 and PZnBaPbAl.10H glasses are shown in Fig. 1a–b, for several heating rates (5, 10, 15 and 20 K/min). The maximum temperature of the PZnBaPbAl·10 crystallization peak (T_c) increases from 770 to 859 °C and the PZnBaPbAl·10H crystallization peak increases from 781 to 889 °C, when the heating rate increases from 5 to 20 K/min. In both cases the crystallization peak temperatures shifts to lower temperatures with decreasing heating rate and its intensities decrease, causing the broadening of the peak shape.

As shown in Fig. 1a–b, an asymmetric and broad crystallization peak was observed in both series. This fact is due to the presence of just one phase transformation or crystallization mechanism. This influence was not investigated because the main purpose of the present work is to study the crystallization mechanism on bulk phosphate glass and assess the GFA considering the best GS parameters.

Comparing bulk glass samples of Fig. 1a–b, the T_g and T_x presented essentially the same values (within error, ±5 °C), at around 446–450 °C and 767–772 °C. On the other hand, T_c is greater at PZnBaPbAl·10H glass. This fact may be associated with hydroxyl presence. Further transmittance studies should corroborate (or not) this assumption.

Table 1
Characteristics DSC temperatures (T_g, T_x, T_c and T_m) of PZnBaPbAl·x and PZnBaPbAl·xH glass series at heating rate of 20 K/min (bulk glasses)

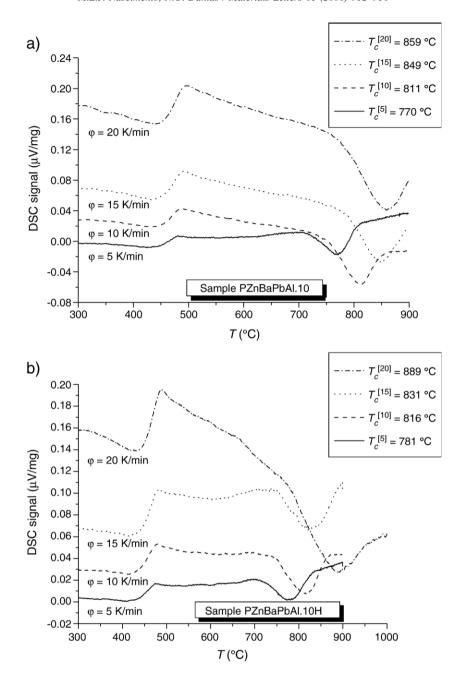| Composition (x)	T_g (°C)	T_x (°C)	T_c (°C)	T_m (°C)
0	367	636	845	942
2	402	658	*	980
4	405	711	876	1006
6	443	736	924	1016
8	458	780	890	1018
10	451	771	859	999
0H	349	650	744	966
2H	366	673	868	990
4H	390	678	869	1025
6H	436	758	884	1008
8H	464	722	808	1036
10H	446	746	889	1001

(*) Temperature not determined.

Fig. 1. DSC crystallization peak of 55 $P_2O_5 \cdot 14$ $ZnO \cdot 10$ $BaO \cdot 10$ $PbO \cdot 1$ Al_2O_3 (in mol%), with 10 La_2O_3 mol%, samples PZnBaPbAl.10 (a) and PZnBaPbAl·10H (b) at different heating rates (bulk glass).

An evaluation of GFA could be obtained using parameters presented of Fig. 1a–b. Nascimento et al. [9] showed that strong correlation exists between GS and GFA by four orders of magnitude in q_{cr} using bulk samples. One should use these parameters to estimate GFA from q_{cr}:

$$\log_{10}q_{cr} = 4.44 - 21.4K_W \quad \text{(Weinberg)} \tag{3}$$

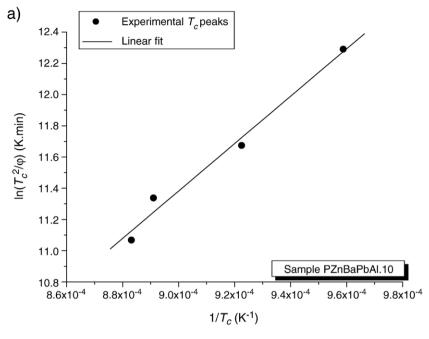$$\log_{10}q_{cr} = 17.7 - 34.6K_{LL} \quad \text{(Lu and Liu)} \tag{4}$$

The calculated q_{cr} using data measured at 10 K/min (see Fig. 1a–b) are presented in Table 2. For GFA assessment was used T_c instead of T_x, according to Eqs. (1) and (2) and analysis recently published [9].

The low q_{cr} results on Table 2 establish that both systems are easy to produce glasses.

When crystallization mechanisms are studied in glasses, it is important to know the activation enthalpies involved on crystallization processes.

Table 2
Characteristics DSC temperatures (T_g, T_x, T_c and T_m) of PZnBaPbAl·10 and PZnBaPbAl·10H glasses at heating rate of 10 K/min and respective GS and GFA parameters (bulk glasses)

Composition (x)	T_g (°C)	T_x (°C)	T_c (°C)	T_m (°C)	K_{LL} (K/K)	K_W (K/K)	q_{cr}^{LL} (K/s)	q_{cr}^{W} (K/s)
10	450	751	811	999	0.543	0.284	0.079	0.023
10H	431	738	816	1001	0.551	0.302	0.045	0.010

Fig. 2. Kissinger plots for the exothermic crystallization peaks of 55 $P_2O_5 \cdot 14$ $ZnO \cdot 10$ $BaO \cdot 10$ $PbO \cdot 1$ Al_2O_3 with 10 La_2O_3 (in mol%): PZnBaPbAl·10 (a) and PZnBaPbAl·10H (b).

To determine the activation enthalpy (E_A) for crystallization, the results from Fig. 1a–b were analyzed using the Kissinger equation [19]:

$$\ln\left(\frac{T_c^2}{\varphi}\right) = \frac{E_A}{RT_c} + C \tag{5}$$

where T_c is the temperature of the maximum DSC crystallization peak, φ is the heating rate, and R is the universal gas constant. The activation enthalpy (E_A) was calculated from a plot of $\ln(T_c^2/\varphi)$ versus $1/T_c$. Frequently, similar procedure has been used by other researchers to study the crystallization kinetics of glasses [14,15].

Fig. 2a–b shows Kissinger plots for PZnBaPbAl·10 and PZnBaP-bAl·10H bulk glasses. The activation enthalpies were calculated from the slopes of the linear fits to the experimental data in Fig. 2a–b using Eq. (5). From Fig. 2a, the activation enthalpy was 126 ± 12 kJ/mol,

calculated based on crystallization peak of PZnBaPbAl·10 glass. Similarly, from Fig. 2b, the activation enthalpy of 110 ± 32 kJ/mol was obtained for crystallization peak of PZnBaPbAl·10H glass. In both glasses the activation enthalpies are analogous, within error.

Finally, the crystallization mechanism may be correlated with the Avrami parameter n using the equation [20]:

$$n = \frac{2.5}{\Delta T} \frac{RT_c^2}{E_A}, \tag{6}$$

where ΔT is the width of the crystallization peak at half maximum.

Based on Eq. (6) and the obtained activation enthalpies, Avrami parameters n were determined for PZnBaPbAl·10 and PZnBaPbAl·10H glasses based on deconvolution of both crystallization peaks. For PZnBaPbAl·10 and considering 5 and 10 K/min DSC scans, the obtained

Avrami parameters were $n_5 = 3.50 \pm 0.33$ and $n_{10} = 3.28 \pm 0.31$, respectively. And for PZnBaPbAl.10H considering 5 and 10 K/min DSC scans, the obtained Avrami parameters were $n_5 = 3.09 \pm 0.91$ and $n_{10} = 3.00 \pm 0.89$, respectively. The errors on n are related to errors on E_A.

The crystallization mechanism of glasses is produced throughout two stages: nucleation and crystal growth [21]. Nucleation can occur in the volume or on glass surface only. From Eq. (6), a value of n close to 3 denotes volume crystallization [19]. Thus, based on n values obtained in this work, it is reasonable to say that the crystallization peaks in PZnBaPbAl·10 and PZnBaPbAl·10H glasses should be associated with bulk crystallization and related to La_2O_3 addition (10 mol%) on glass matrix.

4. Conclusions

Crystallization mechanisms in phosphate glasses were studied based on DSC results. The influence of route, using P_2O_5 and H_3PO_4 as starting raw materials, and also La_2O_3 addition on glass matrix were also investigated (considering only thermal properties). Only one distinct exothermic crystallization peak was observed on bulk glasses from both routes. Choosing systems with high lanthanum content, in both glasses the activation enthalpies obtained were equal within error. Based on Avrami n parameter, the DSC peak could be associated with volume crystallization in both glasses. Then crystallization did not change significantly using different routes. Assessments of critical cooling rates were found to be lower than 0.079 K/s on these systems, that showed high glass stability parameters.

Acknowledgements

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