



Crystallization of barium magnesium phosphate glasses determined by differential thermal analysis and X-rays diffraction

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ARTICLE INFO

Article history:

Available online 2 September 2008

PACS:

64.70.P–
81.70.Pq
64.70.dg
61.05.C

Keywords:

Phosphate
Glasses
Thermal analysis
Thermal stability

ABSTRACT

The scope of this work is to determine the crystalline phases of devitrified barium magnesium phosphate glasses and the glass composition which presents the best resistance to crystallization. Barium magnesium phosphate glasses with composition $x\text{MgO} \cdot (1-x)(60\text{P}_2\text{O}_5 \cdot 40\text{BaO})$ mol% ($x = 0, 0.15, 0.3, 0.4, 0.5, \text{ and } 0.6$) were analyzed by differential thermal analysis (DTA) to evaluate the thermal stability against crystallization, and X-ray diffraction (XRD) to identify the crystalline phases formed after devitrification. The glass transition temperature (T_g) increases as the MgO content increases. The maximum temperature attributed to the crystallization peak in the DTA curve (T_c) increases when x increases in the range $0 \leq x \leq 0.3$, and it decreases for $x > 0.3$. The most thermally stable glass composition against crystallization is for $x = 0.3$. After the devitrification, the number of coexisting crystalline phases increases as the MgO content increases. For $x = 0.3$ there is the coexistence of $\gamma\text{Ba}(\text{PO}_3)_2$ and $\text{Ba}_2\text{MgP}_4\text{O}_{13}$ phases for devitrified glasses. The trend of the T_c is explained based on the assumptions of changes in the Mg^{2+} coordination number and the amphoteric features of MgO.

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1. Introduction

Magnesium phosphate glasses present discontinuities in the behavior of some properties such as density, refractive index, and cut off wavelengths when the magnesium content is varied in the glass composition; this behavior was attributed to changes in the coordination number of the Mg ion from 6 to 4 [1]. Later that effect was attributed to changes in the short and intermediate range structure [2]. Phosphate glasses containing relatively high amounts of magnesium and calcium oxide were previously studied and it was shown that glasses containing magnesium are easier to be formed than glasses containing calcium due to the existence of ionic bonds between oxygen and magnesium [3], and the average coordination number of magnesium is 5, while the average coordination number for calcium is 6. Does variation in the MgO content cause any change in the thermal stability against crystallization of phosphate glasses? In the present work metaphosphate glasses containing magnesium and barium were analyzed by differential thermal analysis (DTA) to evaluate the thermal stability against crystallization. XRD was used to identify the crystalline phases formed after the devitrification as a function of the MgO content. A barium metaphosphate glass was chosen as base glass composition, and MgO was added in a composition range where glasses are formed.

2. Experimental procedure

Glasses with composition $x\text{MgO} \cdot (1-x)(60\text{P}_2\text{O}_5 \cdot 40\text{BaO})$ mol% ($x = 0, 0.15, 0.3, 0.4, 0.5, \text{ and } 0.6$) were produced by melting mixtures of reagent grade $\text{NH}_4\text{H}_2\text{PO}_4$ (Merck), BaCO_3 (CAAL), and MgO (Merck) at $1400^\circ\text{C}/12$ min (for bubbles removal) followed by $1300^\circ\text{C}/1$ h (for homogenization) in a crucible-type electric furnace (Lindberg Blue M) in air. An alumina crucible was used and batches of 20 g were obtained.

The liquid was cast in an aluminum mold, and annealed in the temperature range of $520\text{--}590^\circ\text{C}$ for 2 h. Samples were obtained as powders for XRD and DTA analyses. Glass powders were heat treated in air at the maximum crystallization temperature determined by the DTA curves for 0.25 h, and 10 h, and cooled down to room temperature; the crystalline phases were identified by XRD and the JCPDS files.

XRD patterns were obtained at room temperature in the 2θ range of $10^\circ\text{--}80^\circ$ at $2^\circ/\text{min}$ using a $\text{CuK}\alpha$ radiation (Philips, model PW 1700). DTA (Setaram) were performed in the temperature range of $20\text{--}950^\circ\text{C}$, at $10^\circ\text{C}/\text{min}$, in a dynamic synthetic air flow condition.

3. Results

Fig. 1 shows the DTA curves for different glass compositions in the temperature range where the exothermic peak (T_c) attributed to the crystallization process is observed. Table 1 presents the glass

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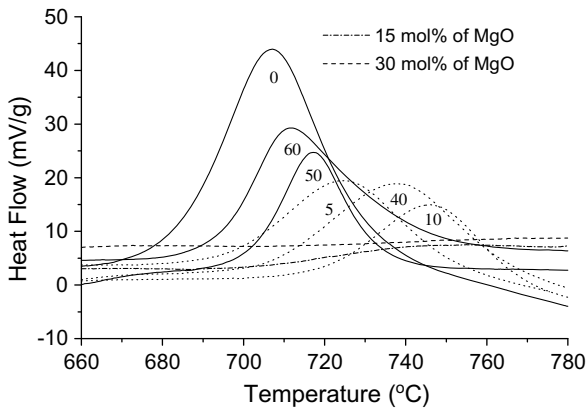


Fig. 1. DTA curves in the region of the crystallization maxima for glasses $x\text{MgO} \cdot (1-x)(60\text{P}_2\text{O}_5 \cdot 40\text{BaO})$ mol% ($x = 0, 0.15, 0.3, 0.4, 0.5, \text{ and } 0.6$).

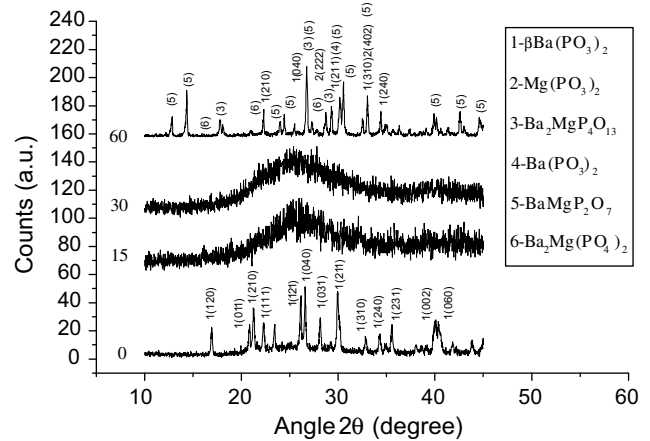


Fig. 3. XRD patterns of glasses treated at T_c for 15 min.

Table 1
Glass transition temperature and maximum crystallization temperature

Mol% MgO	T_g (°C)	T_c (°C)
0	517 ± 5	707 ± 5
5	519 ± 5	733 ± 5
10	528 ± 5	736 ± 5
15	540 ± 5	750 ± 5
30	564 ± 5	787 ± 5
40	578 ± 5	741 ± 5
50	582 ± 5	717 ± 5
60	589 ± 5	712 ± 5

transition temperature (T_g) and the maximum crystallization temperature (T_c) for each glass composition.

Fig. 2 shows $T_c - T_g$ and the crystallization peak amplitude as a function of the MgO content. Fig. 3 shows the XRD patterns for glasses after heat treating for 0.25 h, and Fig. 4 shows the XRD patterns for glasses after heat treating for 10 h. The identified crystalline phases are shown in the inset caption. Table 2 presents the crystalline phases identified for each devitrified glass composition.

4. Discussion

To improve the thermal stability against crystallization of phosphate glasses, which is basically formed by chains of $(\text{PO}_4)^{3-}$ tetrahedral, earth-alkaline metals such as Ba and Mg are added to promote crosslink between the $(\text{PO}_4)^{3-}$ chains. Since the Ba^{2+} ionic radius is larger than the one of Mg^{2+} , the Ba–O and Mg–O bond

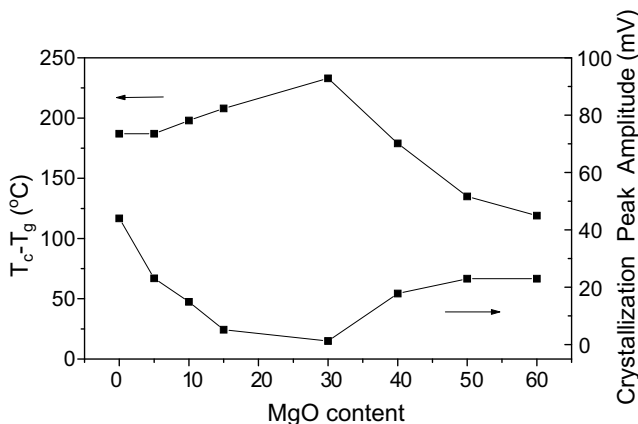


Fig. 2. $T_c - T_g$ and amplitude of the crystallization peak for glasses with different amounts of MgO.

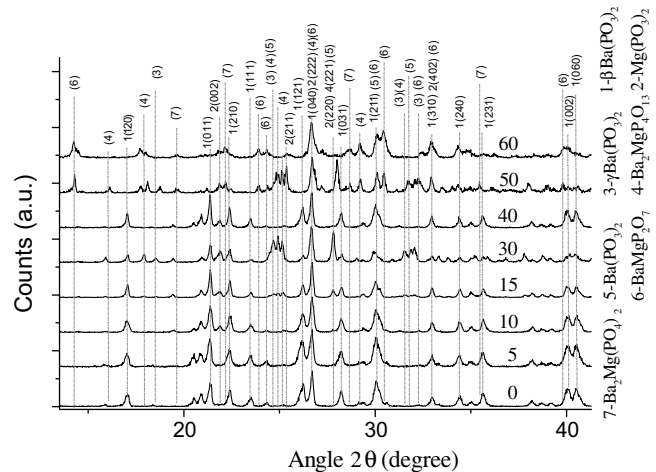


Fig. 4. XRD patterns of glasses treated at T_c for 10 h.

lengths are different, so it will be the crosslink. As the amount of MgO increases the number of crosslink will increase, however nearest-neighbor crosslink will be more difficult to be found. The devitrified $60\text{P}_2\text{O}_5 \cdot 40\text{BaO}$ glass presents only the crystalline phase $\text{Ba}(\text{PO}_3)_2$, as previously determined by XRD [4], so the glass network contains chains of $(\text{PO}_3)^-$. Ba^{2+} ions bind to neighbor oxygen by ionic bonding maintaining the coordination number (CN) 8 in the $(\text{PO}_3)^-$ network, and forming $\beta\text{Ba}(\text{PO}_3)_2$ when devitrified. Therefore, both the coordination number and the charge balance required by the presence of Ba^{2+} affect the thermal stability against crystallization. By adding MgO to the $60\text{P}_2\text{O}_5 \cdot 40\text{BaO}$ glass composition, the structure stability against crystallization is even improved. Fig. 1 and Table 1 show that the temperature for the maximum of the crystallization peak (T_c) increases up to 787°C as the amount of MgO increases in the range of $x = 0$ to 0.3 . For larger amounts of MgO ($0.4 \leq x \leq 0.6$) T_c decreases. It is our assumption that this effect is related to changes in the glass structure caused by the variation of the number of NBO due to the presence of modifying Mg^{2+} . In case this tendency is related with the previously reported 'unusual trend in the variation of physical properties', we could attribute this behavior to a transition in the Mg–O coordination number from 6 to 4 or to changes in the short- and intermediate range order [2].

In Table 1 it is also noticed that T_g increases as the MgO content increases. In this case covalent P–O–P bonds are being replaced by ionic bonds between oxygen and magnesium. It is expected that an

Table 2

Crystalline phases after heat treatment for 10 h

%MgO	$\beta\text{Ba}(\text{PO}_3)_2$	$\text{Mg}(\text{PO}_3)_2$	$\gamma\text{Ba}(\text{PO}_3)_2$	$\text{Ba}_2\text{MgP}_4\text{O}_{13}$	$\text{Ba}(\text{PO}_3)_2$	BaMgP_2O_7	$\text{Ba}_2\text{Mg}(\text{PO}_4)_2$
0	Yes	No	No	No	No	No	No
5	Yes	No	No	No	No	No	No
10	Yes	Yes	No	No	No	No	No
15	Yes	Yes	No	No	No	No	No
30	Yes	Yes	Yes	Yes	No	No	No
40	Yes	Yes	No	Yes	No	Yes	Yes
50	Yes	Yes	No	Yes	Yes	Yes	Yes
60	Yes	Yes	No	Yes	Yes	Yes	Yes

open structure is replaced by a more compact structure, since polyhedral of Mg ions coordinated with oxygen are possibly sharing corners, edges, and faces in the glass structure [5]. As earth-alkaline metals are added, the number of NBO increases, and two situations can occur: the number of NBO is larger than the CN of the alkaline metal, or the number of NBO is smaller than the CN of the alkaline metal. For instance, in case of Mg^{2+} assuming the coordination number 4, for the $\text{MgO} \cdot \text{P}_2\text{O}_5$ glass, the number of NBO (2) will be lower than the CN of Mg^{2+} (4). For 67 mol% of MgO, the transition between the two situations described above will occur because the NBO is 4 and CN is also 4.

The glass composition with $x = 0.3$ is the most thermally stable against crystallization. The increase of T_c , as noticed in Table 1, might be an indication of a barrier for crystallization. For glasses with MgO in the range of $0 \leq x \leq 0.3$, it is still possible to have neighbor crosslink among the phosphate chains, however for higher concentrations of MgO it will be more difficult to have such neighborhood and the crystallization will be enhanced.

Fig. 2 shows that as $T_c - T_g$ increases, the crystallization peak amplitude decreases, and the thermal stability against crystallization is improved.

Fig. 3 shows that only glasses with 15 and 30 mol% of MgO do not show any evidence of crystalline phases on the XRD patterns. For other compositions, XRD peaks corresponding to crystalline phases were observed, and no diffraction halos corresponding to amorphous phases could be detected.

From Table 2 and Fig. 4 it is noticed that as the MgO content increases, the number of crystalline phases also increases after devitrification.

The Mg^{2+} electronegativity (1 and 2) is larger than the one for Ba^+ (0.9), therefore, the electronic distribution in a O–Mg bond will be different than in a O–Ba bond. The tendency for devitrification will be affected and it will be reduced as the amount of MgO is added. After a limited value, the composition will be in the region of the phase diagram where crystalline phases are predicted and the material is prone to be devitrified. Since magnesium has a CN that differs from barium, there is a large tendency to accommodate oxygen atoms, promoting the approximation of the phosphate chains and consequently, a more compact glass structure. The maximum stability of the present glasses is reached when the MgO content is added and the Mg^{2+} coordination number changes from 4 to 6, as it has been previously reported for silicate glasses containing MgO [6]. This is a possible explanation for the trend of T_c as a function of MgO concentration.

The second assumption to explain the T_g and T_c variation is based on the amphoteric behavior of MgO.

According to the Lewis theory of acids and basics, glass formers such as SiO_2 , B_2O_3 , P_2O_5 , BeF_2 , and GeS_2 are classified as acidic because they are electron-pair acceptors in glass reactions, and the glass modifiers Na_2O , K_2O , CaO , SrO , and BaO are basic because they are electron-pair donors; the intermediates compounds Al_2O_3 , Fe_2O_3 , BeO , MgO , and ZnO [7] are classified as amphoteric [8].

The basicity of oxide glasses increases as the amount of alkaline metals increases in the glass composition [9]. Therefore, by increasing the amount of MgO in the glass composition, the basicity will follow the same tendency, and it is expected that the compound feature will change from basic to acid. Yagi et al. [10] showed experimentally that the electronic polarisability of oxygen (α_o) for $\text{Al}_2\text{O}_3\text{--Na}_2\text{O--3SiO}_2$ increases progressively with additions of Al_2O_3 up to a limited concentration, but further additions result in a decrease of the polarisability. In other words, Al_2O_3 acts as a basic oxide at lower concentrations of Al_2O_3 , but as an acid oxide at higher concentrations [10]. The change of α_o indicates that alumina behaves as amphoteric oxide in this system [10]. Similarly we propose that the same effect occurs when MgO is added to the phosphate glass, and the trend of T_c is correlated to the acidic/basicity changes. A similar result was observed for tellurium oxide glasses doped with Er_2O_3 [11], which is also amphoteric.

Therefore for $x < 0.3$, MgO is a basic oxide. Table 2 shows that for $x < 0.3$ only crystalline phases based on metaphosphate containing either Mg or Ba are formed after devitrification. For $x > 0.3$, MgO is acting as acidic oxide, and crystalline phases based on orthophosphate and pyrophosphate containing both Mg and Ba are formed after devitrification. The crystalline phases $\text{Mg}_3(\text{PO}_4)_2$ and $\text{Ba}_3(\text{PO}_4)_2$ were not detected. The acidic feature of MgO in the glass leads to the formation of crystalline phases containing P, Mg, Ba, and O after devitrification. It was also observed that for $x > 0.3$, crystalline phases containing PO_4 , P_2O_7 , and P_4O_{13} are formed, i.e., the O/P ratio is increasing. For $x < 0.3$ only the $(\text{PO}_3)_2$ group is formed according to the XRD data shown in Table 2. Therefore it is expected that similar results could be obtained if MgO in the base glass is replaced by other amphoteric oxides, such as BeO , ZnO , Al_2O_3 , SnO_2 , and Sb_2O_3 forming new oxide crystalline phases.

Fig. 5 shows the ternary phase diagram for $\text{BaO--MgO--P}_2\text{O}_5$ [12], and the compositions investigated in the present work are represented by dots. When the composition moves out from the region

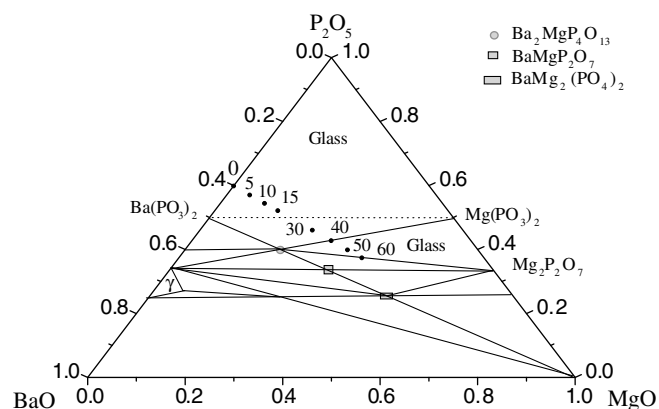


Fig. 5. Phase diagram of the ternary system $\text{BaO--MgO--P}_2\text{O}_5$ [10] and the compositions studied in the present work.

in the phase diagram where only glasses are predicted, the number of crystalline phases tends to increase. However the two crystalline phases $\gamma\text{Ba}(\text{PO}_3)_2$ and $\text{Ba}_2\text{MgP}_4\text{O}_{13}$ are only noticed in the devitrified glass that contains 30 mol% of MgO, and according to the DTA data, that is the most thermally stable glass composition against crystallization. The coordination number of Ba^{2+} in the $\text{Ba}(\text{PO}_3)_2$ phase is 8 [13], and the coordination number of Mg^{2+} in the $\text{Ba}_2\text{MgP}_4\text{O}_{13}$ phase is 6 [14]. The $\text{Ba}_2\text{MgP}_4\text{O}_{13}$ is also observed for devitrified glasses containing larger amounts of MgO, and these glasses are not as thermally stable as the ones where both crystalline phases $\gamma\text{Ba}(\text{PO}_3)_2$ and $\text{Ba}_2\text{MgP}_4\text{O}_{13}$ coexist. Therefore, changes in the intermediate range structure are involved in the glass stability.

5. Conclusions

The barium magnesium phosphate glass $0.3\text{MgO} \cdot (0.7(60\text{P}_2\text{O}_5 \cdot 40\text{BaO}) \text{ mol}\%)$ is the most stable composition against crystallization determined in the present work. The increase of MgO content in barium metaphosphate glasses causes the increase of the glass transition temperature and the increase of the maximum crystallization temperature (T_c) for x in the range of $x = 0$ – 0.3 . For larger amounts of MgO ($0.4 \leq x \leq 0.6$) T_c decreases. It is our assumption that this effect is related to changes in the glass structure caused by the variation of the number of non-bridging oxygen, and in case this tendency is related with the previously reported ‘unusual trend in the variation of physical properties’, we could attribute this behavior to a transition in the Mg–O coordination number from 6 to 4 or to changes in the short- and intermediate range. Based on the crystalline phases found in the devitrified glasses, we propose that besides the $(\text{PO}_3)^{1-}$ group, other groups

such as $(\text{PO}_4)^{3-}$, $(\text{P}_2\text{O}_7)^{4-}$, and $(\text{P}_4\text{O}_{13})^{6-}$ could be formed increasing the O/P ratio. However, further evidences are required, such as spectroscopy measurements to confirm this assumption. For $x = 0.3$ there is the coexistence of $\gamma\text{Ba}(\text{PO}_3)_2$ and $\text{Ba}_2\text{MgP}_4\text{O}_{13}$ phases for devitrified glasses. The trend of the T_c is explained based on the assumptions of changes in the Mg^{2+} coordination number and the amphoteric features of MgO.

Acknowledgements

The authors are in debt with Mr. Reinaldo Aparecido da Costa (Center of Nuclear Fuel, IPEN) for the DTA analyses, and Mr. Rene Ramos de Oliveira for the XRD analyses. Fapesp is acknowledged for the Grant 05/53241-9.

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