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Thermal (DSC) characterization of xPbO–(1–x)P_2O_5 glass system

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Abstract

The lead phosphate (LP), xPbO–$(1-x)P_2O_5$ glasses, divided into three compositional regions, $x = 0.3$–0.5 (region I), $x = 0.55$–0.6 (region II), and $x = 0.66$–0.75 (region III) were prepared by single-step melt-quenching process with the melt-temperature increasing from 550 to 750 °C. The DSC studies on the glasses in the compositional region, which are hygroscopic, revealed two endotherm peaks. The first and weak endotherm around 130 °C has been attributed to a thermal event in which dehydration of glasses takes place. The second and stronger endotherm has been attributed to the glass transition (T_g) phenomenon. The onset of the glass transition temperature was found to increase from about 212 °C for the glass sample with $x = 0.3$ to about 345 °C for the glass with $x = 0.6$ in the compositional region II where both crystalline and glass phase co-exist. The observed splitting in the endotherms of glasses in the region II co-relates well with the mixed phase. The gradual and linear increase in the average T_g value is consistent with the increase in the melt-temperatures of the glasses and correlates well with increase in the mol% of the modifier PbO in the glasses.

Keywords: Lead phosphate glasses; Differential scanning calorimetry; Thermograms; Glass transition

1. Introduction

A glassy solid does not posses as unique structural property as that of a crystal for its complete identification. However, thermal (Differential Scanning Calorimetry, DSC) characterization provides valuable, indirect information [1,2] about the structural changes that take place in a glass system with composition. The lead phosphate (LP), xPbO–$(1-x)P_2O_5$, glasses are attractive from the point of view of optical applications as they provide ultraviolet transparency [3]. However, the LP glasses are not known to be chemically stable and their glass forming region is limited to $x = 0.55$ only according to the recent optical study [4]. In order that these LP glasses are employed for any useful optical application, their thermal characterization is essential since the glass transition phenomenon and hence the occurrence of amorphous phase can be studied from DSC measurements. When the glass transition of a glass-system is situated as a function of the composition, the change in glass transition temperature (T_g) values indicates definite changes in the glass network. This paper presents the details of measurement of T_g as a function of the composition (x) employing DSC technique and hence the information on the structural changes in the LP vitreous system.

2. Experimental

The LP glasses, xPbO–$(1-x)P_2O_5$, were prepared by a single-step melt-quenching process with AR grade PbO, ADP($NH_4H_2PO_4$) as the starting chemicals [4]. The x value was varied from 0.3 to 0.75 which is observed compositional limit for obtaining the quenched LP sample. The range of x has been divided into three compositional regions with the samples of $x = 0.3$, 0.35, 0.4, 0.45, and 0.5 designated as 1LP, 2LP, 3LP, 4LP, and 5LP glasses falling under the region I, $x = 0.55$ and 0.6 designated as 6LP and 7LP falling under region II and $x = 0.66$ and 0.75 samples designated as 8LP and 9LP falling under the compositional region III. The glasses 1LP–6LP were transparent while the glasses 7LP–9LP were opaque and were found to contain both crystalline and amorphous phases as revealed by our X-ray diffraction and IR study [4].

The DSC thermograms for all the glasses were recorded on DuPont 9900 DSC instrument in the temperature range 50–400 °C with a heating rate of 10 °C/min.

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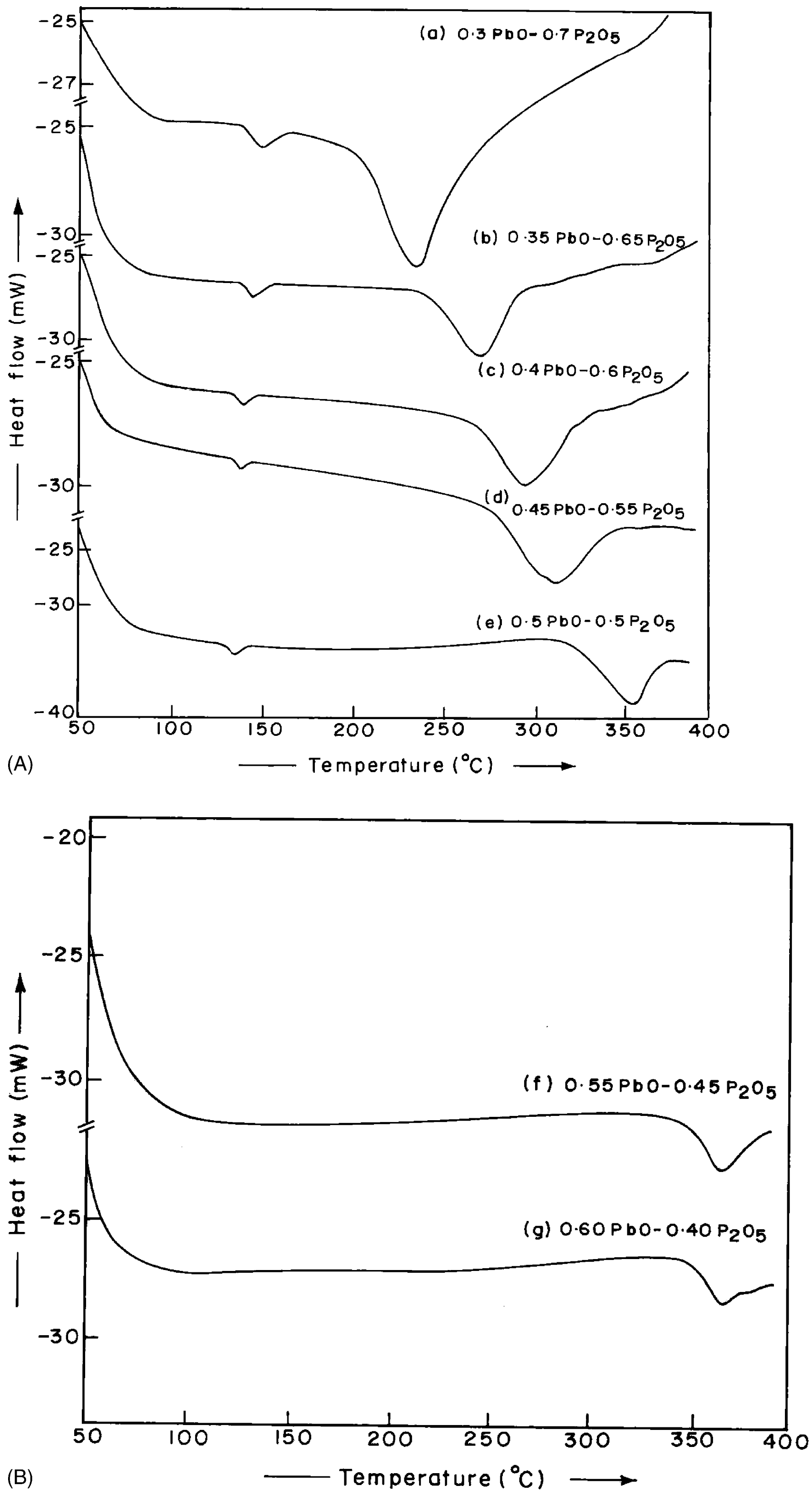

Fig. 1. Differential Scanning Calorimetry (DSC) thermograms of different samples of xPbO–$(1 - x)$P$_2$O$_5$ (LP) vitreous system arranged sequentially from top in the order of increasing PbO (mol%) (x) content. (A) Compositional region I; 1LP glass with $x = 0.3$, 2LP glass with $x = 0.35$, 3LP glass with $x = 0.4$, 4LP glass with $x = 0.45$, 5LP glass with $x = 0.5$; (B) Compositional region II; 6LP glass with $x = 0.55$, 7LP glass with $x = 0.6$; (C) compositional region III, 8LP glass with $x = 0.66$, 9LP glass with $x = 0.75$.

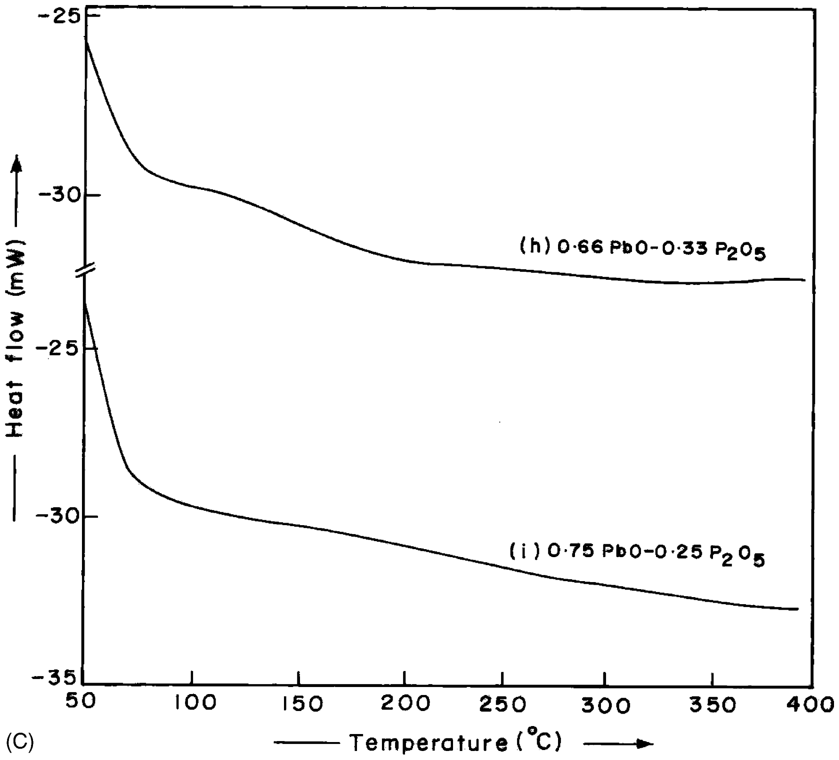

Fig. 1. (*Continued*).

3. Results and discussion

The DSC thermograms of LP samples in the compositional region I are shown by the traces (a), (b), (c), (d), and (e) corresponding to 1LP, 2LP, 3LP, 4LP, and 5LP glasses, respectively, in Fig. 1A. The two DSC traces recorded for 6LP and 7LP glasses belonging to compositional region II are shown in Fig. 1B as traces (f) and (g), respectively, in Fig. 1C, the traces (h) and (i) belong to 8LP and 9LP glasses, respectively, in the compositional region III.

The observed ranges of T_g values for different LP samples are presented in Table 1. The variation of T_g (onset) temperature values with the composition (x) of LP glass system is shown in Fig. 2. It is seen from this figure that T_g almost linearly increases with the PbO content (x) or composition.

Table 1
Variation of glass transition temperature (T_g) with composition (x) in LP vitreous system

Composition region	x	Glass sample	Range of T_g (°C)	Onset value of T_g (°C) second endotherm
I	0.3	1LP	212–265	212
	0.35	2LP	250–265	250
	0.4	3LP	285–320	285
	0.45	4LP	300–333	300
	0.5	5LP	345–373	345
II	0.55	6LP	350–382	350
	0.6	7LP	365–382	365
III	0.66	8LP	–	–
	0.75	9LP	–	–

In Fig. 1A, in addition to the strong endotherms at temperatures above 212 °C, weak endotherms at about 130 ± 2 °C are observed continuously till $x = 0.5$ (5LP glass). The area under these weak endotherms shows a gradual decrease. Since all LP glasses in the compositional region are hygroscopic with the hygroscopicity decreasing with increasing PbO (x) content, the weak endotherms are attributed to the process of dehydration of the LP glasses.

The decreasing area under these peaks obviously represents the decreasing quantity of heat energy required to expel the water (H_2O) from this glassy solid. In this context, it is significant to note that these weak endotherms are totally absent for 6LP, 7LP, 8LP, and 9LP glasses as seen from the DSC traces (f), (g), (h), and (i) in Fig. 1B and C. This means that thermal event corresponding to dehydration does not occur at all these low P_2O_5 glasses indicating that hygroscopicity is limited to the compositional region I.

The onset value of temperature (T_g) of second endotherm in Fig. 1A and B attributed to the glass transition phenomenon increases linearly as seen from Fig. 2 and Table 1. In a glass system, increase in T_g indicates increase in bond strength and cross links [1] which in turn increase the stability and chemical durability of the glasses. Therefore, the increase of T_g from about 212 ± 2 °C for 1LP glass to about 345 ± 2 °C for 5LP glass in the compositional region I suggests that the LP glass network is strengthened and stable LP glass is formed by increase in PbO content.

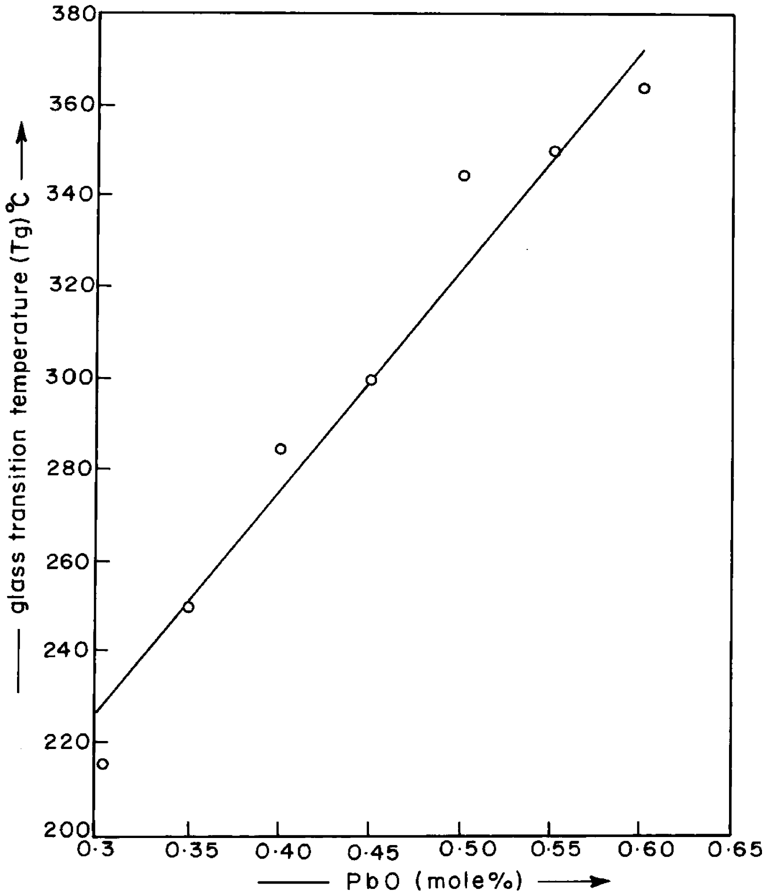

Fig. 2. Variation of T_g with the composition (x) of LP glasses.

In Fig. 1B, for 6LP glass with $x = 0.55$, the T_g is about 350 ± 2 °C which is high. The XRD results indicate that for this composition in LP glasses, devitrification begins. For $x = 0.575$ (DSC trace not shown) glass, the transparency is still retained. But for $x = 0.6$ (7LP) glass, where T_g is highest (~365 °C) covering smallest area (DSC trace (g) in Fig. 1B), the endotherm shows weak but clear splitting at 382 ± 2 °C. This is a clear indication of phase separation, i.e. coexistence of crystalline and amorphous phase.

The compositional dependence of T_g represented by the linear variation in Fig. 2 limited to $x = 0.6$ (7LP glass) indicates the continuance of glass phase even after setting in of the devitrification of in LP system around $x = 0.525$. While the opaqueness of the LP samples with $x > 0.575$ could be due to various factors including the network fragmentation, disruption in phosphate chains, increase in non-bridging oxygens (NBOs) and possibly higher degree of polymerization tendency [5] observed in pyro-phosphate ($x = 0.66$, 8LP) and ortho-phosphate ($x = 0.75$, 9LP) quenched systems, the most important observed fact that T_g exists even upto $x = 0.6$ suggests that homogeneous and transparent glass formation is extendable upto $x = 0.6$. Although it could not be achieved in the present work, such transparent LP glasses prepared by a special process have been reported [6]. In Fig. 1B, the observed gradual decrease in the area under the T_g trace is attributed to decrease in the proportion of glass phase.

In these LP glasses of compositional region III, no thermal event could be recorded (Fig. 1C) below 400 °C indicating that it could occur above 400 °C. For these glasses ($x > 0.6$), T_g is expected to be higher and could not be recorded because of instrumental limitations.

4. Conclusions

The compositional dependence of T_g of LP glasses revealed by DSC technique could be attributed to variations in bond strength, cross-link density and closeness of packing in the glasses. This is promoted by gradual decrease in hygroscopicity of the LP glasses. However, for LP glasses with $x \geq 0.55$ is attributed to the glass phase present alongwith the crystalline phase.

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