

THERMAL STUDY OF $A_2O-(MoO_3)_2-P_2O_5$ ($A=Li, Na$) GLASSES

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Abstract

Alkali phosphomolybdate glasses have been prepared by quenching melted mixtures of P_2O_5 , MoO_3 and A_2O ($A=Li, Na$). The composition dependence of the transition temperature of glasses belonging to ternary $A_2O-(MoO_3)_2-P_2O_5$ ($A=Li, Na$) systems is studied for several series of glasses corresponding to either a fixed A_2O rate or a constant Mo/P ratio. The interpretation of the results is based on the presence of different types of molybdenum and phosphorous structural groups and P–O–M ($M=P, Mo$) linkages in glasses.

Keywords: glass transition temperature, phosphomolybdate glasses

Introduction

Materials of mixed electronic-ionic conduction are a class of solids interesting from both practical and basic points of view. Due to their potential applications in various domains of modern technology, glasses containing transition-metal oxides have been subjected to intensive investigations [1–6]. In our recent papers [7–9], we have pointed out that, by an appropriate choice of composition of glass constituents in the $A_2O-(MoO_3)_2-P_2O_5$ ($A=Li, Na$) system, it is possible to prepare a whole range of electrical conductors: from pure ionic, through mixed electronic-ionic to almost purely electronic. In literature most papers on the mixed electronic-ionic conductors have concentrated on systems in which one of the mobile species (electronic or ionic) dominated [10]. Relatively rare are the papers describing systems in which the concentrations of both components are comparable. The electronic conduction process in these glasses proceeds via a charge exchange among the transition metal Mo^{6+} and Mo^{5+} ions acting as centers for electron hopping. The presence of a glass modifier Li_2O and Na_2O is responsible for the ionic part of electrical conduction (via Li^+ or Na^+ ions). The $A_2O-(MoO_3)_2-P_2O_5$ ($A=Li, Na$) systems under study, have been insufficiently characterized up to date, mainly due to their complexity and a wide range of composition which can result in amorphous solids. In particular, little is known about thermal stability.

In this paper we report the results of our thermal studies of various glassy compositions and the determination of correlations between the glassy structure and thermal properties.

Experiments

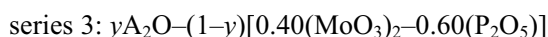
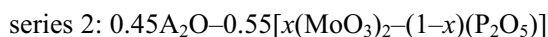
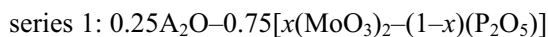
Glasses of $A_2O-(MoO_3)_2-P_2O_5$ ($A=Li, Na$) ternary systems were obtained by the classical quenching technique, the details of which are described elsewhere [7]. They were prepared by mixing and grinding together appropriate amounts of A_2CO_3 (Merck, 99.5%), $NH_4H_2PO_4$ (Merck, 99.5%) and MoO_3 (Merck, 99.9%) in an agate mortar before transferring to a platinum crucible. The mixtures were heated in an electric furnace first at 650 K for 2 h to remove the volatile products, then melted at 1100–1200 K for a few hours with frequent stirring to ensure homogeneity. The melt was then poured on a stainless steel plate preheated at 450 K to avoid shattering of the quenched samples due to thermal stress. Finally, the vitreous samples were annealed for 6 h at 550 K to relieve residual internal stress and slowly cooled to room temperature.

Selected samples were characterized by means of X-ray diffraction ($\lambda_{CuK\alpha} = 1.54051 \text{ \AA}$) analysis, using a Seifert XRD 3000 diffractometer, differential thermal analysis (DTA), using a Seiko DTA thermal analyser with a heating rate of $10^\circ\text{C min}^{-1}$ and is accurate to $\pm 5^\circ\text{C}$. XRD analysis have shown that the samples under study consisted of amorphous phase. A structureless spectrum should be obtained for an amorphous sample. DTA scans permitted to find the temperature of glass transition temperature (T_g), recrystallisation temperature (T_c) and melting temperature (T_f).

Results and discussion

The compositions investigated are shown on the Gibbs triangle in Fig. 1 in terms of the corresponding oxide component. X-ray analysis of samples obtained by quenching revealed the presence of a wide glassy range in the systems $A_2O-(MoO_3)_2-P_2O_5$ ($A=Li, Na$). All diagrams are characterized by the coloured vitreous samples. The green colour of these glasses is assigned to the presence of Mo^{5+} ions in the glass matrix owing to the $Mo^{6+} \rightarrow Mo^{5+}$ reduction due to the loss of oxygen from the melts. This hypothesis was confirmed by electron paramagnetic resonance (EPR) analysis [7, 11]. The domain of the $Li_2O-(MoO_3)_2-P_2O_5$ glasses is not so large as that of sodium glasses, owing to the presence of higher amounts of Mo^{5+} as will be shown later.

The vitreous nature of different compositions along three series of materials with the following compositions:



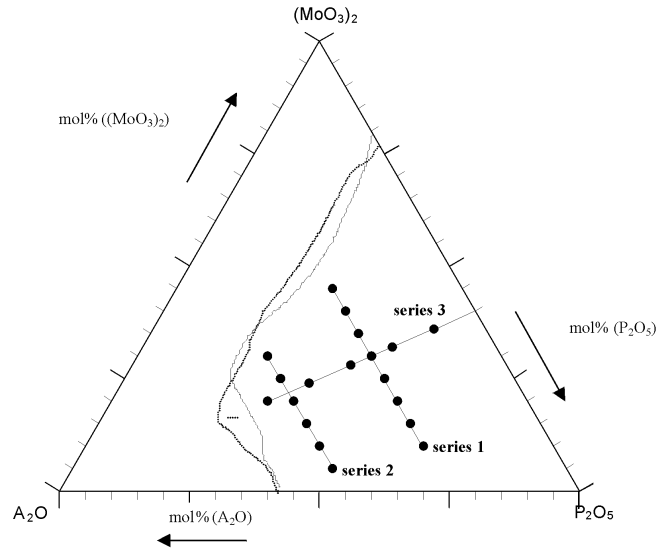


Fig. 1 Glassy compositions studied inside the $A_2O-(MoO_3)_2-P_2O_5$ ($A=Li, Na$) systems (Li – full line; Na – dashed line)

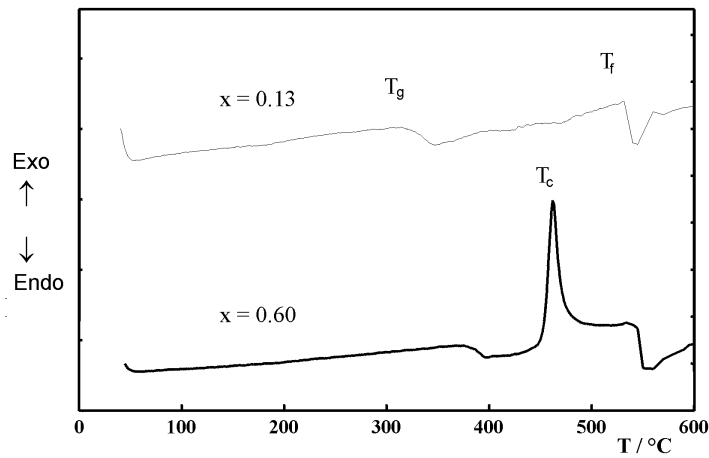


Fig. 2 DTA patterns for two $0.25Li_2O-0.75[x(MoO_3)_2-(1-x)(P_2O_5)]$ glasses

has been confirmed by the thermal differential analysis as shown, for example, for two lithium glasses (Fig. 2). It has been seen that the melting temperature, T_p , as well as the crystallization temperature, T_c and the glass transition temperature, T_g depend strongly on composition. It is also noted that DTA diagrams are better resolved for molybdenum- and/or alkaline-rich glasses. In the glass with $x=0.60$ (series 1), the

Table 1 Glass transition temperature (T_g), crystallisation temperature (T_c) and optical basicity (Λ) of the glasses studied

Glasses	x, y	Mo/P	T_g/K			T_c/K			Λ	
			Li	Na	Li	Na	Li	Na		
Series 1: $0.25 A_2O-0.75[x(MoO_3)_2-(1-x)(P_2O_5)]$	0.13	0.15	603	593	—	—	—	0.432	0.431	
	0.20	0.25	607	608	—	—	—	0.433	0.432	
	0.27	0.37	618	613	—	—	—	0.434	0.433	
	0.33	0.50	631	624	—	—	—	0.435	0.434	
	0.40	0.67	663	658	—	—	—	0.436	0.435	
	0.47	0.89	657	649	—	—	—	0.437	0.436	
Series 2: $0.45 A_2O-0.55[x(MoO_3)_2-(1-x)(P_2O_5)]$	0.53	1.13	645	640	739	736	—	0.438	0.437	
	0.60	1.50	633	634	733	732	—	0.439	0.438	
	0.09	0.10	617	580	702	660	—	0.482	0.480	
	0.18	0.22	621	587	708	673	—	0.483	0.481	
	0.27	0.37	628	610	716	695	—	0.484	0.482	
	0.36	0.56	637	632	—	—	—	0.484	0.482	
Series 3: $yA_2O-(1-y)[0.40(MoO_3)_2-0.60(P_2O_5)]$	0.45	0.82	633	627	—	—	—	0.485	0.483	
	0.55	1.22	613	610	—	—	—	0.486	0.484	
	0.10	0.67	703	694	—	—	—	0.411	0.410	
	0.20	0.67	685	670	—	—	—	0.427	0.426	
	0.25	0.67	657	658	—	—	—	0.436	0.435	
	0.30	0.67	665	656	—	—	—	0.447	0.445	
	0.40	0.67	653	641	—	—	—	0.471	0.469	
	0.50	0.67	628	625	714	710	—	0.501	0.499	
	0.60	0.67	—	590	—	677	—	—	0.538	

glass transition of $T_g \approx 360^\circ\text{C}$ and a crystallisation onset of $T_c \approx 460^\circ\text{C}$ are observed. The difference between T_g and T_c , i.e. $\Delta T = T_c - T_g$, in this glass is 100°C , indicating that the thermal stability against crystallisation is considerably high. In the glass with $x=0.13$ (series 1), a glass transition of $T_g \approx 320^\circ\text{C}$, is observed, but no crystallisation peak is detected. A similar DTA pattern showing no clear crystallisation peak was obtained for the P_2O_5 -richer glasses in the ternary $\text{A}_2\text{O}-(\text{MoO}_3)_2-\text{P}_2\text{O}_5$ ($A=\text{Li}, \text{Na}$) systems. Indeed, the thermally stable glasses, in which crystallisation peaks were not observed in the DTA curves taken at a heating rate of $10^\circ\text{C min}^{-1}$, are mostly obtained at compositions $0.13 \leq x \leq 0.50$ (series 1), $0.30 \leq x \leq 0.50$ (series 2) and $0 \leq y \leq 0.40$ (series 3).

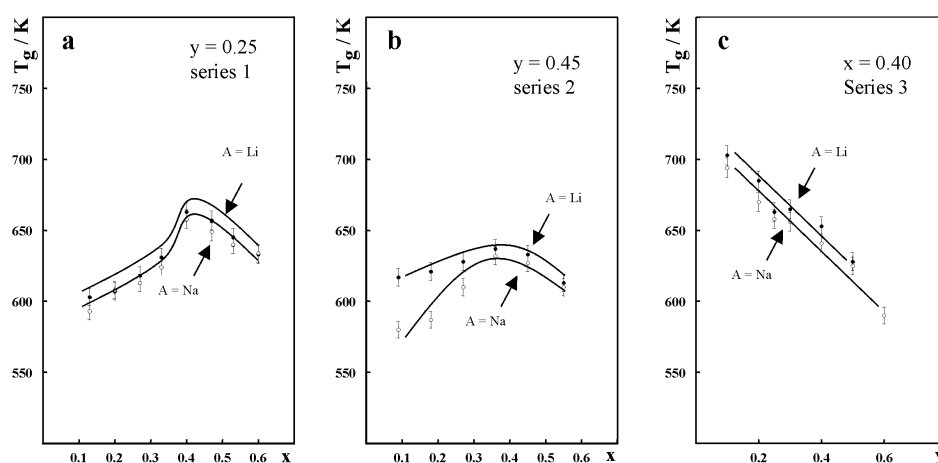


Fig. 3 Composition dependence of T_g in the $y\text{A}_2\text{O}-(1-y)[x(\text{MoO}_3)_2-(1-x)(\text{P}_2\text{O}_5)]$ system: a – series 1, b – series 2, c – series 3 (according to Fig. 1 and Table 1). The line is drawn as a guide for the eye

The T_g for all the three series of lithium and sodium glasses are given in Table 1. It shows also the crystallisation temperature (T_c) for some glasses.

The composition dependence of T_g is given in Figs 3a–b for the first two series and in Fig. 3c for series 3. As can be seen a similar trend is observed for lithium and for corresponding sodium glasses. Considering the first two series of lithium and sodium glasses, a flat T_g maximum appears for a value of x close to $x \approx 0.40$ for series 1 and 2 (Figs 3a–b). Inside the glass range, the maximum corresponds, consequently, to the value of Mo/P ratio close to 0.60.

T_g temperature is well known to be a structural sensitive parameter depending on the bond strength, degree of cross-link density and closeness of packing [12]. Thus, the glass transition temperature is increasing function of these variables. In the other hand, previous studies have shown that the structure of glasses obtained may be considered as made of several types of molybdenum and phosphorous structural groups, metaphosphate ($\text{MoO}_2(\text{PO}_3)_2$), pyrophosphate ($(\text{MoO}_2)_2\text{P}_2\text{O}_7$), orthophosphate

(MoOPO₄) and P₂O₅ groupings, the ratio of which varies with composition [7, 13]. Furthermore, in the P₂O₅-rich domain, the replacement of ruptured P=O bonds by P–O–P and P–O–Mo linkages should occur and increases the cross-link density of the glass network. Comparing structures of the molybdenum meta-MoO₂(PO₃)₂, pyro-(MoO₂)₂P₂O₇ and ortho-phosphate-MoOPO₄, it is seen that the cross-linking density is the highest in MoOPO₄ where the Mo atom has a valence of 5. So we expect that the variation of T_g temperature will depend relatively on Mo⁵⁺ content. Thus, in the glassy range studied the origin of a maximum of T_g for $x \approx 0.40$ is probably structural. As a matter of fact, according to Bridge and Patel [14, 15], the percentages of MoOPO₄ and MoO₂(PO₃)₂ groupings, which mainly involve P–O–Mo linkages, in MoO₃–P₂O₅ glasses are maxima for Mo/P ≈ 0.50 . According to Selveraj and Rao [16], the structure of the molybdophosphate glasses can be looked upon as generated from corner shared tetrahedral [POO_{3/2}] and octahedral [MoO_{6/2}] units. Since every [POO_{3/2}] tetrahedron provides three corners for oxygen sharing and a molecule of P₂O₅ generates two such tetrahedra, equimolar proportions of MoO₃ and P₂O₅ (Mo/P=0.50, i.e. $x \approx 0.33$) can be connected in such a way that [MoO_{6/2}] units are all surrounded by [POO_{3/2}] units and vice-versa, and such a glass will only contain Mo–O–P linkages [16]. Recently [8, 9], an investigation of these glasses by electron paramagnetic resonance (EPR) spectroscopy has allowed us to evaluate for each material Mo⁵⁺ and Mo⁶⁺ ion percentages. The spectra obtained for sodium glasses are similar to those of lithium, but the intensity of EPR signal is weaker for the sodium sample than for the corresponding lithium sample, resulting in a smaller Mo⁵⁺ percentage for the sodium glass, in agreement with its less deep coloration [8, 9]. The variation of Mo⁵⁺/Mo_{tot} and Mo⁵⁺/Mo⁶⁺ ratios as a function of x for series 1 and 2 is characterised by the presence of maxima for $x \approx 0.40$. The origin of these maxima is structural and was attributed to the presence of a maximum of units of the MoOPO₄ type which involve mostly P–O–Mo linkages.

With respect to the above considerations, the T_g increase, in the first two series, with increasing MoO₃ in P₂O₅-rich glasses can be attributed to a larger cross-link density. On the other hand, the mean bond strength in MoO₃–P₂O₅ glasses decreases with an increase in the MoO₃ content as the covalence of the M–O bonds decreases from $M=P$ to $M=Mo$ [17]. It appears consequently that the T_g maxima in both series 1 and 2 result from two opposite influences: the increasing cross-link density and the decreasing mean bond strength with increasing MoO₃ rate.

Furthermore, the introduction of A₂O ($A=Li, Na$) basic oxide into the binary phosphomolybdate glass, inside series 3 (Fig. 3c), results in a decrease of the mean bond strength and a T_g decrease, whatever the alkaline oxide. As a matter of fact, it is possible that the mean bond strength in a ternary A₂O–MoO₃–P₂O₅ glass containing an alkaline oxide is lower than in the binary MoO₃–P₂O₅ with the same MoO₃/P₂O₅ ratio.

The composition dependence of the optical basicity (Λ) calculated for the glasses investigated confirms these assumptions (Table 1). The theoretical optical basicities, Λ , for A₂O–(MoO₃)₂–P₂O₅ ($A=Li, Na$) glasses were calculated using the following equation, which is based on the approach proposed by Duffy and Ingram [18, 19]:

$$\Lambda = x(A_2O) \Lambda(A_2O) + y(MoO_3) \Lambda(MoO_3) + z(P_2O_5) \Lambda(P_2O_5)$$

where $x(A_2O)$, $y(MoO_3)$ and $z(P_2O_5)$ are equivalent fractions based on the amount of oxygen each oxide contributes to the overall stoichiometry and $\Lambda(A_2O)$, $\Lambda(MoO_3)$ and $\Lambda(P_2O_5)$ are basicities assigned to the individual oxides ($\Lambda(Li_2O)=1.061$, $\Lambda(Na_2O)=1.042$, $\Lambda(MoO_3)=0.411$, $\Lambda(P_2O_5)=0.388$). In effect, calculation of optical basicity by means of such a relation provides an easy and convenient method for obtaining a measure of the average electron density of the oxide (–II) atoms in an oxide medium. Within both series 1 and 2, which offer a constant A_2O rate, the Λ variation is very small. The replacement of P by Mo involves only a weak increase of Λ , due to the difference between the electronegativities of P^{5+} and Mo^{6+} cations [17]. Indeed, for the same alkaline element, Λ increases when the electronegativity of the antagonist element decreases, i.e. when the antagonist element tends to reduce the covalent character of its bond with oxygen. On the other hand, a significant increase in Λ is, of course, observed when A_2O content increases in series 3 (Table 1). As can be noted, the results obtained for the sodium are very close to those obtained with the corresponding lithium glasses. So, the composition dependence of T_g or Λ for glasses belonging to the $A_2O-(MoO_3)_2-P_2O_5$ ($A=Li, Na$) systems do not depend practically on the nature, lithium or sodium, of the alkali oxide.

Conclusions

Alkali phosphomolybdate glasses belonging to ternary $A_2O-MoO_3-P_2O_5$ ($A=Li, Na$) systems have been studied with DTA analysis. The composition dependence of the transition temperature T_g has been investigated along three series of glasses presenting either a fixed A_2O rate or a constant Mo/P ratio:

$$\text{series 1: } 0.25A_2O-0.75[x(MoO_3)_2-(1-x)(P_2O_5)]$$

$$\text{series 2: } 0.45A_2O-0.55[x(MoO_3)_2-(1-x)(P_2O_5)]$$

$$\text{series 3: } yA_2O-(1-y)[0.40(MoO_3)_2-0.60(P_2O_5)]$$

Results show that the T_g data can be understood in terms of the structural groupings, cross-link density, and a bond strength of the glass network. T_g does not depend, practically, on the nature of alkali oxide. The origin of maxima observed inside both series 1 and 2 is attributed to the presence of a maximum of units of the $MoOPO_4$ type which involves high cross-link density. The composition dependence of T_g is confirmed by those of the optical basicity (Λ) and EPR investigation.

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