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Thermal and electrical properties of $Ag_2O-M_2O_3-P_2O_5$ glasses ($0.65 \leqslant Ag_2O/P_2O_5 \leqslant 1.5$; M = Al, B; $M_2O_3/P_2O_5 \leqslant 0.36$) [1]

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Abstract

The effect of addition of small quantities of Al_2O_3 and B_2O_3 to $Ag_2O-P_2O_5$ glasses with a composition close to that of $AgPO_3$ glass has been studied. Very small amounts drastically reduce the tendency to form $AgPO_3$ crystals. The glass transformation temperature, T_g and electrical conductivities σ are strongly affected: an increase of T_g up to 150°C and a one order of magnitude increase of σ have been recorded with respect to the binary $Ag_2O-P_2O_5$ glasses.

On the basis of the T_g versus composition curves, structural hypotheses have been developed. The experimental data suggest a network former role for B_2O_3 and a network modifier role for Al_2O_3.

INTRODUCTION

Glasses of the system $Ag_2O-P_2O_5$ are known to have relatively high values of electrical conductivity [1,2]. In this paper, the effect of substitution of trivalent element oxides M_2O_3 (M = B, Al) to P_2O_5 in the range $0.65 \leqslant Ag_2O/P_2O_5 \leqslant 1.5$ on glass electrical conductivity and transformation temperature has been studied.

EXPERIMENTAL

The following series of glasses were prepared by melting Ag_3PO_4, B_2O_3, Al_2O_3, $NH_4H_2PO_4$ analytical grade reagents in a platinum crucible in the temperature range 1000-1200°C for 4 h.

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(I) $(1+x)Ag_2O \cdot yM_2O_3 \cdot (1-y)P_2O_5$ where $y = 0, 0.1$; $0 \leqslant x \leqslant 0.4$ and M = Al, B.

(II) $Ag_2O \cdot xM_2O_3 \cdot (1.5-x)P_2O_5$ where $0 \leqslant x \leqslant 0.4$ and M = Al, B.
In the case of Al_2O_3, the x values for series II were never higher than 0.2. The melts were cast between brass discs.

Differential thermal analysis (DTA) was performed with a Netzsch model 404M on about 150 mg of powdered samples with particle diameter d ($250\ \mu m \leqslant d \leqslant 315\ \mu m$) at a heating rate of 10°C min^{-1}.

Powdered Al_2O_3 was used as reference material. DTA curves display a step at the glass transition temperature. The peak temperature on the DTA derivative curve was assumed as the transition temperature, as indicated in ref. 3.

Electrical conductivity σ was determined by measuring the complex impedances in the range 0.5–60 kHz, and by applying the usual impedance analysis [4,5]. A Solartron 1250 frequency response analyser and a Solartron 1286 electrochemical interface, both controlled by a Hewlett–Packard 86B desktop computer, were used to analyse small annealed glass discs brushed with a silver conducting paint.

RESULTS

The DTA curves for the series I and II glasses are shown in Fig. 1. The step at the glass transition temperature is occasionally followed by an exothermic peak due to devitrification. The curves for Ag_2O–P_2O_5 glasses are reported in Fig. 1 and their transition, peak and liquidus temperature (T_g, T_p and T_l) values are listed in Table 1 together with those of the Hruby parameter $K_{gl} = (T_p - T_g)/(T_l - T_p)$ proposed for comparison [6] of the tendency of glasses of different composition to devitrify, which should be lower the higher K_{gl}. Table 1 suggests that the tendency decreases as x increases. In the $(1+x)Ag_2O \cdot P_2O_5$ series one can speculate that the most simple devitrification mechanism should involve structural reorganisation of polyphosphate chains and diffusion of the mobile Ag^+ ions in order to adjust the $AgPO_3$ stoichiometry. In this context the results of Table 1 can be ascribed to the greater composition and structural changes necessary as the Ag_2O content is increased. Interestingly many DTA curves for the B_2O_3 and Al_2O_3 substituted glasses (Fig. 1) show no trace of devitrification. In particular (see Fig. 1a–c) it appears that very small substitution of the trivalent element oxides to P_2O_5 drastically reduces the tendency of $AgPO_3$ crystals to form. The T_g values as a function of composition (Fig. 2) show that when the M_2O_3/P_2O_5 ratio is constant, T_g decreases as the Ag_2O content increases. The presence of M_2O_3 makes the T_g value increase with respect to the binary system values; the T_g value gets higher with progressing ratio M_2O_3/P_2O_5. Al_2O_3 addition increases the T_g more than B_2O_3. An increase to 150°C was found for the Al_2O_3 glass with

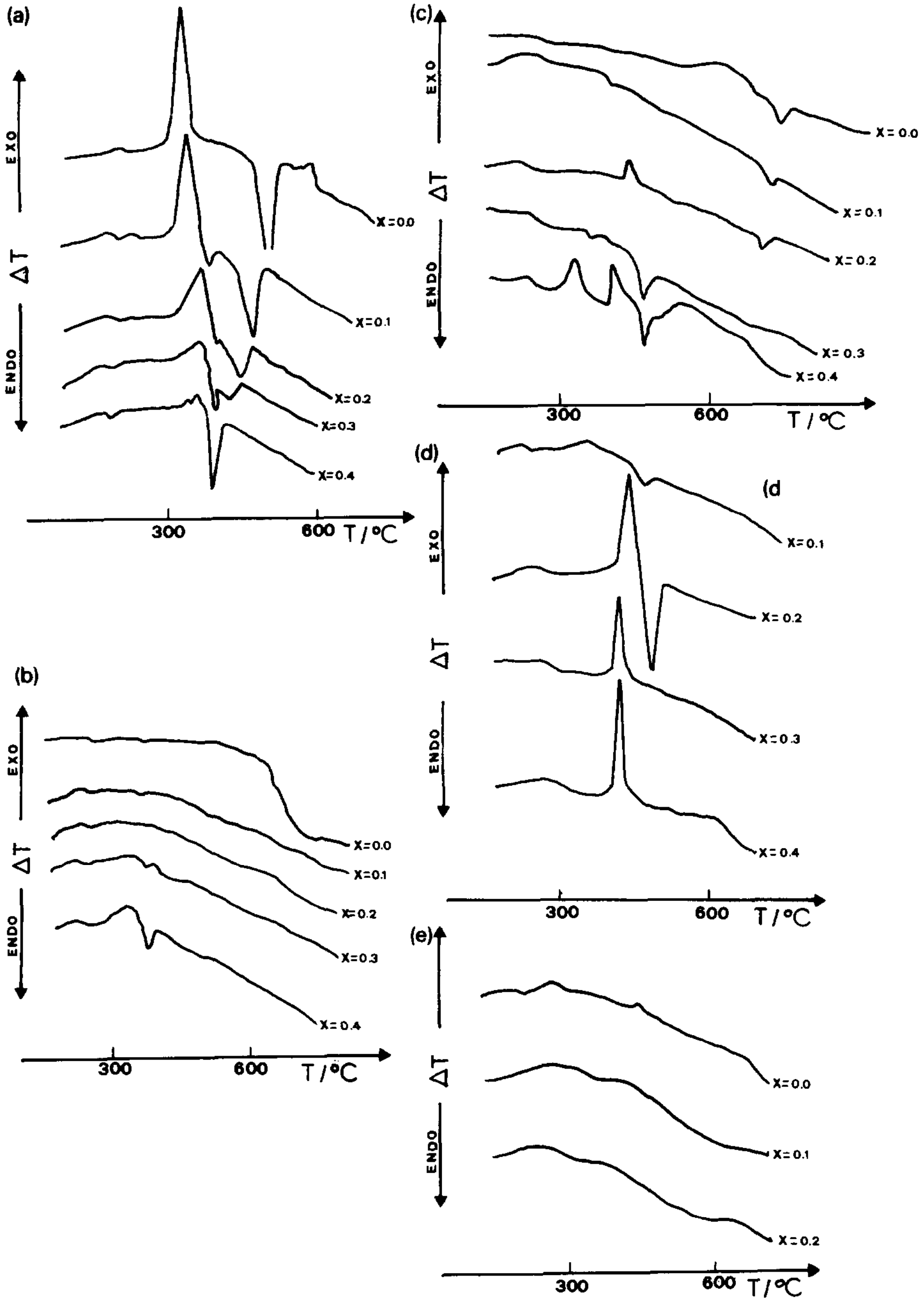

Fig. 1. DTA curves: (a) Ag_2O–P_2O_5 glasses; (b) series I B_2O_3 substituted glasses; (c) series I Al_2O_3 substituted glasses; (d) series II B_2O_3 substituted glasses; (e) series II Al_2O_3 substituted glasses.

$Al_2O_3/P_2O_5 = 0.15$. Since demixtion and crystallisation may take place above the T_g, these substitutions (especially Al_2O_3) have the advantage of increasing glass stability.

TABLE 1

Glass transition T_g, peak T_p, and liquidus T_l, temperatures [a] (taken from the DTA reported in Fig. 1) and Hruby parameter $K_{gl} = (T_p - T_g)/(T_l - T_p)$ of binary glasses $(1+x)Ag_2O \cdot P_2O_5$

x	T_g	T_p	T_l	K_{gl}
0	214	326	520	0.577
0.1	196	350	508	0.975
0.2	189	371	482	1.64
0.3	184	364	452	2.045
0.4	183	350–367	427	2.17–3.07

[a] Temperatures in °C.

In Fig. 3 the electrical conductivity σ values at $T = 25$°C, are reported. The effect of the M_2O_3/P_2O_5 ratio is poor with respect to that of Ag_2O/P_2O_5. However, at the same Ag_2O/P_2O_5 and M_2O_3/P_2O_5 values, Al_2O_3 and B_2O_3 both increase σ, the effect of Al_2O_3 being greater by as much as one order of magnitude.

STRUCTURAL HYPOTHESIS

A structural hypotheses can be formed from the data in Fig. 2. T_g depends on the following factors [7]: (1) the density of covalent cross-link-

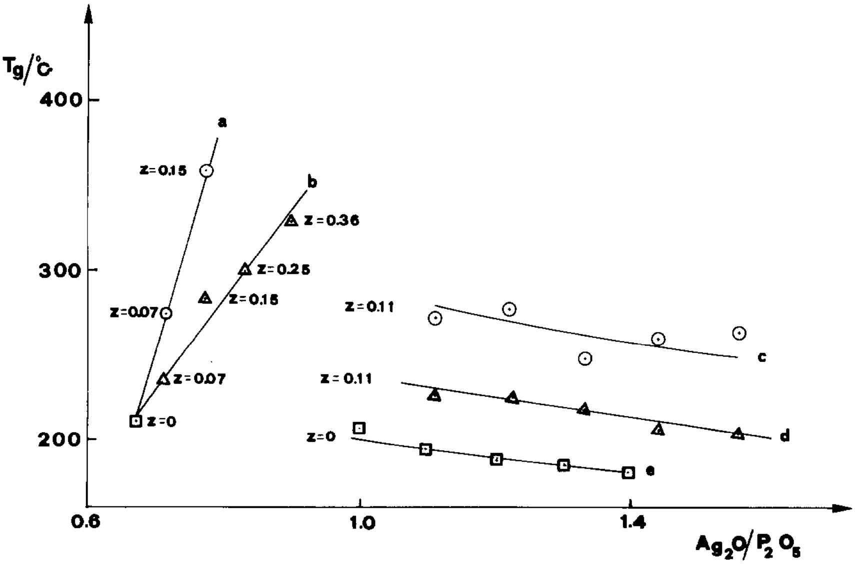

Fig. 2. T_g as a function of composition: □, $Ag_2O-P_2O_5$ glasses; △, B_2O_3 substituted glasses; ○, Al_2O_3 substituted glasses. z denotes the ratio $z = M_2O_3/P_2O_5$; curves (a) and (b) are series II glasses, (c), (d) and (e) are series I glasses.

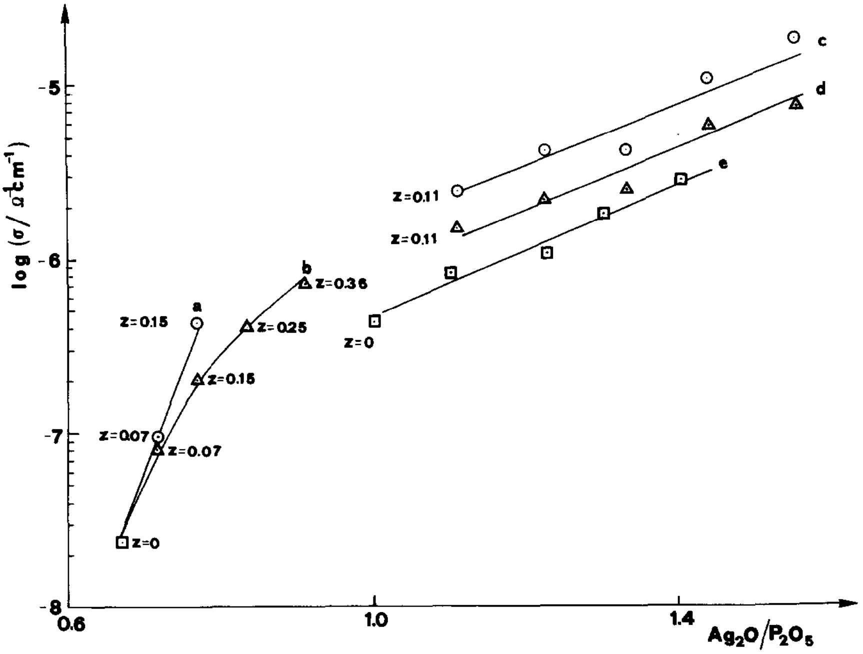

Fig. 3. σ versus composition curves. Symbols as in Fig. 2.

ing; (2) the number and strength of the cross-links between oxygen and the cation; (3) the oxygen density of the network.

The T_g decrease dependent on the Ag_2O content is easily explained. Like alkali oxides [8], Ag_2O is a modifier oxide which breaks oxygen that bridges and reduces the density of covalent cross-linking.

The T_g increase induced by B_2O_3 can be ascribed to its network-forming role. B_2O_3 enters glass structures by forming tetrahedral BO_4 groups [8] (see structure (a) in Fig. 4). The BO_4 groups need charge compensation. In phosphate glasses this can be accomplished in two ways [8,9], (1) by subtracting the network modifying oxide (Ag_2O) from its depolymerising function (structure (b) of Fig. 4), (2) by coupling with PO_4 groups (see structure (c) in Fig. 4). In both cases, the density of covalent cross-linking is increased and so is the T_g expected, as can be seen in Fig. 2.

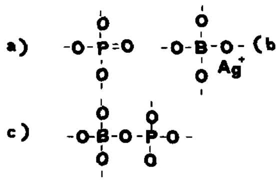

Fig. 4. Structural units.

Al_2O_3 is regarded as an intermediate oxide [8,10], i.e. one that can enter glass structures both as a network-former oxide giving rise to the same kind of structures as B_2O_3, and a network modifier oxide. In its network former role, when the Ag_2O/P_2O_5 and M_2O_3/P_2O_5 ratios are the same, the same increase of covalent cross linking as in the case of B_2O_3 substituted glasses should be expected. The higher T_g increase observed for Al_2O_3 substituted glasses thus requires another explanation. Cations of high charge in a network modifying role produce a large T_g increase [11]. Owing to the greater coordination attainable (in this role AlO_6 groups are formed) greater T_g increases can be expected, according to Ray [7], than in the case of a network-forming role. The drastic reduction of the rate of $AgPO_3$ crystal formation, (see remarks on Fig. 1) can also be simply explained as being due to the viscosity increase induced by a higher degree of polymerisation (in the case of the B_2O_3 containing glasses), or the interstitial presence of the large charge bearing Al^{3+} cation.

CONCLUSIONS

Addition of Al_2O_3 and B_2O_3 to the Ag_2O–P_2O_5 glasses decreases the tendency to form $AgPO_3$ crystals and increases their T_g and σ values. This is especially true for Al_2O_3 glasses. The experimental data are consistent with a glass-forming role on the part of B_2O_3 and a network-modifying role on the part of Al_2O_3.

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