

VITREOUS PHASES OF THE $\text{Ag}_2\text{O}:\text{B}_2\text{O}_3:\text{P}_2\text{O}_5$ SYSTEM

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Most optimized vitreous electrolytes are obtained by doping an oxide glass with a salt (MX); the resulting substance has an increased ionic conductivity, but a reduced thermal stability. On the other hand, this paper shows that it is possible to obtain vitreous electrolytes with enhanced electrical and thermal performances by mixing two glass formers. This phenomenon may be called the "mixed anion effect". The $\text{Ag}_2\text{O}:\text{B}_2\text{O}_3:\text{P}_2\text{O}_5$ system is shown to offer a very interesting example of such a phenomenon.

Optimized vitreous electrolytes based on oxide glass formers have been studied for about ten years [1]. It is now well known that the ionic conductivity increases when a salt of the mobile metal ion is added to the glass former. This "doping" effect is the more pronounced, the higher the polarizability of the anion and the amount of salt added. However, the thermal stability (or glass transition temperature, T_g) decreases with the addition of doping salt. Another means of improving conductivity consists in substituting oxides with sulfides in the glass network [1]. A drawback of this procedure is that highly hygroscopic substances are usually obtained. We have recently begun systematic studies of vitreous electrolytes containing more than one glass former [2] in the hope of finding another way to improve their thermal and electric performances. The first results were very encouraging, and similar "mixed glass former effects" have recently been reported for more than one system [3].

In this paper we present a detailed study of the homogeneous vitreous phases of the $\text{Ag}_2\text{O}:\text{B}_2\text{O}_3:\text{P}_2\text{O}_5$ system, which includes the identification of crystalline compounds which occur outside the "glass-forming region". Furthermore, this paper completes information available in the literature on the binary subsystems $\text{Ag}_2\text{O}:\text{B}_2\text{O}_3$ [4], $\text{Ag}_2\text{O}:\text{P}_2\text{O}_5$ [5] and $\text{B}_2\text{O}_3:\text{P}_2\text{O}_5$ [6, 7].

Experimental

All starting materials used (i.e. $\text{NH}_4\text{H}_2\text{PO}_4$, AgNO_3 and B_2O_3) were of certified reagent grade. Finely mixed powders were melted in air until gas evolution stopped.

The melt was kept at temperatures in the range 900–1300° and were occasionally stirred for ~ 30' before being poured in to metal molds at room temperature (rt). The absence of sharp reflections in the X-ray diffraction spectrum was the criterion used to define a vitreous phase. Information about the regions of subliquidus immiscibility was given by the change from transparent to opaque glasses when entering these regions. Furthermore, electron microscope microprobe analyses were made on many transparent samples which did not reveal suboptical inhomogeneities. Crystalline phases were identified by means of X-ray powder diffraction methods. Furthermore, the incipient nucleation of Ag_3PO_4 crystals was shown to exert dramatic effects upon the ^{31}P NMR spectra during magic angle spinning (MAS) experiments..

Differential scanning calorimetry (Dupont 1090, DSC mod 910) was used to identify T_g . Finally, electrical data were collected with a Solartron frequency response analyzer (mod. 1174) and with a Wayne Kerr bridge mod B331.

Results and discussion

The glass-formation region of the $\text{Ag}_2\text{O}:\text{B}_2\text{O}_3:\text{P}_2\text{O}_5$ system was determined by studying ten sets of samples, each one having a fixed value for the $[\text{B}_2\text{O}_3]/[\text{P}_2\text{O}_5]$ ratio. With the quenching procedure described above, homogeneous and transparent glasses are formed in the region indicated by C in Figs 1 and 2.

Opaque samples are formed in region B. In this region, X-ray diffractometry shows that many samples contain crystalline Ag_3PO_4 , which forms easily in B_2O_3 -rich glasses. A quantitative determination of the Ag_3PO_4 content was made in ^{31}P NMR MAS experiments. The phosphorus atoms in the crystalline orthophosphate do not have the relatively wide distribution of isotropic chemical shifts which characterizes phosphorus in the glass matrix. The very narrow NMR-MAS signal due to crystalline orthophosphate was observed only in region B. Details of the ^{31}P NMR investigation of phosphate glasses will be given elsewhere.

In samples with nominal compositions belonging to region A, we observed deposition of metallic silver, due to the decomposition of Ag_2O . Samples are also opaque in region D, one of the causes being the formation of BPO_4 crystals, as proved by X-ray diffractometry. In the phosphorus-rich side of region D, the boundary between homogeneous glasses and composite materials (heavy broken lines in Figs 1 and 2) is ill-defined, due to sublimation of P_2O_5 . In addition, the melting temperature of the BPO_4 -containing samples was often above the explored temperature range.

Figure 1 summarizes the thermal data for the homogeneous glasses of the $\text{Ag}_2\text{O}:\text{B}_2\text{O}_3:\text{P}_2\text{O}_5$ system. The curves in region C connect compositions having the same glass transition temperature, indicated in °C in the figure. Notice the rapid increase of T_g when B_2O_3 is added to phosphorus-rich glasses. The highest T_g values (480°) were obtained for compositions close to $\text{Ag}_2\text{O}:2\text{B}_2\text{O}_3:2\text{P}_2\text{O}_5$. This glass transition temperature should be compared with the values ~ 400° and ~ 220°, which are the highest T_g 's for pure borate and phosphate glasses, respectively.

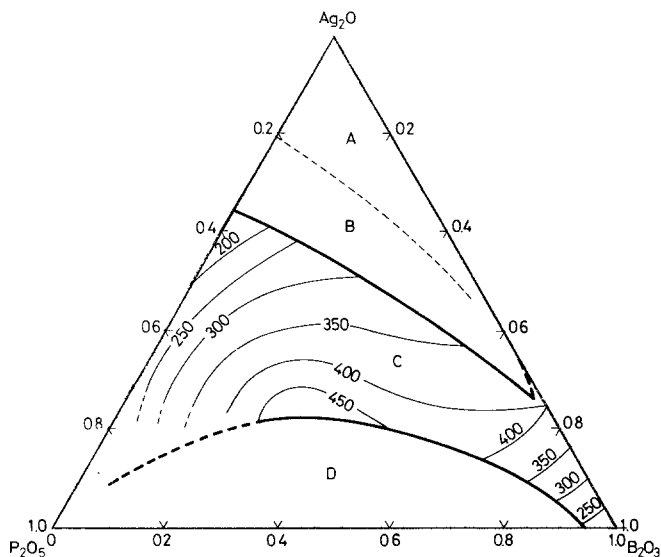


Fig. 1 Region of formation of homogeneous glasses (c) with iso-Tg lines. Temperatures are in °C

Figure 2 reports the isoconductivity curves at room temperature. The numbers which identify these curves are the decimal logarithms of the r.t.-conductivity in $\text{ohm}^{-1} \text{cm}^{-1}$. For all samples in the C region, the transport number of Ag^+ is nearly one. As expected, the ionic conductivity increases with increasing Ag_2O content. In addition on change of the $\text{B}_2\text{O}_3/\text{P}_2\text{O}_5$ ratio, the r.t.-conductivity passes through

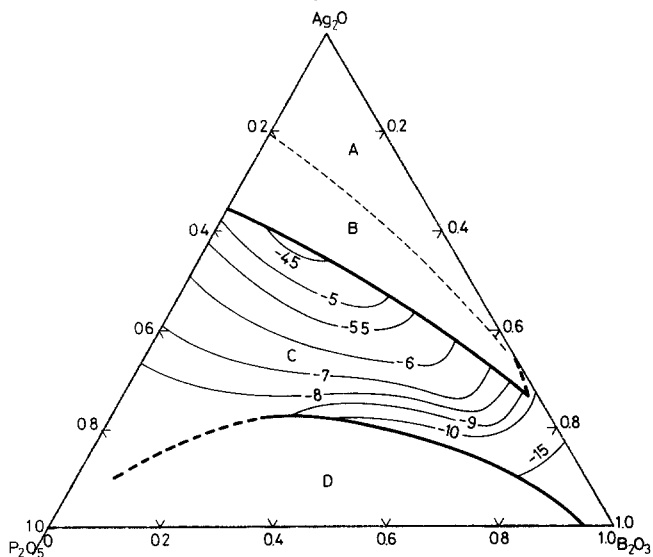


Fig. 2 Region of formation of homogeneous glasses (c) with iso-conductivity curves at rt. Numbers represent $\log \sigma_{rt} [\text{ohm}^{-1} \text{cm}^{-1}]$

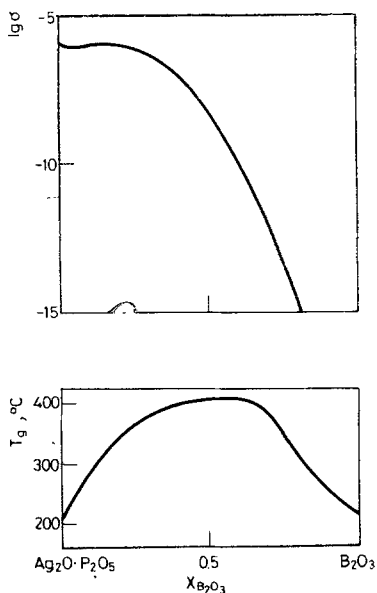


Fig. 3 Logarithm of room temperature conductivity and glass transition temperature for the $\text{Ag}_2\text{O} \cdot \text{P}_2\text{O}_5\text{-B}_2\text{O}_3$ system

a maximum, which occurs when $[B]/[P] \cong 4$. From the above results, it is apparent that the thermal stability and/or conductivity of undoped borophosphate glasses can be optimized through an appropriate choice of the B/P ratio, without changing the $\text{Ag}/(\text{B} + \text{P})$ ratio. In Fig. 3, we show in more detail the effect of the addition of boron oxide to silver metaphosphate. While the r.t.-conductivity is nearly constant for $\text{B}/\text{P} < 0.3$, T_g increases by nearly 200° in the same interval.

Conclusions

Borophosphate glasses reveal that the ionic conductivity and thermal stability of vitreous electrolytes may be increased substantially by mixing more than one glass former. The improvement of the transport properties is much more dramatic than that observed when more than one doping salt is mixed (mixed anion effect) [3]. A unified interpretation of the enhancement of conductivity by mixing is provided by the so-called weak electrolyte theory [8]. According to this theory, the partial molar entropy of Ag_2O decrease for mixing, and/or its partial molar enthalpy increases. This causes an increase in the Ag_2O activity, which determines the concentration of "mobile" Ag^+ . In our opinion, the enthalpic contributions to the free energy changes for mixing in borophosphate glasses are highly predominant. In other words, we believe that the increased thermal stability and increased Ag_2O activity are due to the formation of still unidentified borophosphate units. Early evidence for the modification of

borate structural units upon the addition of P was produced by Beekenkamp [9]. An NMR and IR investigation of borophosphate glasses is under way; it is hoped that this will provide a full characterization of the structural units in this complex glass system.

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Zusammenfassung — Optimale glasartige Elektrolyte werden durch Dopen eines Oxydglases mit einem Salz (MX) erhalten; die Produkte weisen eine erhöhte ionische Leitfähigkeit, jedoch auch eine verminderte thermische Stabilität auf. Andererseits wird gezeigt, daß glasartige Elektrolyte mit besseren elektrischen und thermischen Eigenschaften durch Mischen von zwei Glasbildnern erhalten werden können. Für dieses Phänomen wird die Bezeichnung "mixed anion effect" in Vorschlag gebracht. Es wird gezeigt, daß das System $Ag_2O:B_2O_3:P_2O_5$ ein sehr interessantes Beispiel dieses Phänomens bietet.

Резюме — Большинство стеклообразных электролитов оптимального состава получено легированием оксидного стекла солью MX. Образующиеся при этом стекла обладали повышенной ионной проводимостью, но более низкой термостабильностью. В статье показана возможность получения стеклообразных электролитов с повышенной электропроводностью и термоустойчивостью путем смешения двух исходных стекол. Это явление может быть названо "смешанным анионным эффектом". Показано, что система $Ag_2O:B_2O_3:P_2O_5$ представляет весьма интересный пример такого явления.