LITHIUM BOROPHOSPHATE VITREOUS ELECTROLYTES

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Summary

This paper investigates the ionic (Li^+) conductivity and thermal stability properties of glasses of the $Li_2O/B_2O_3/P_2O_5$ system. For the same molar ratio between lithium oxide and glass formers ($B_2O_3 + P_2O_5$), the ionic conductivities at room temperature can be substantially higher in borophosphate glasses than in pure borates or phosphates. An attempt is made to relate this technologically interesting conductivity enhancement to the coordination chemistry of borophosphate glasses.

Introduction

The ionic conductivity properties of oxide glasses based on phosphorus or boron are well known, although only partially understood. The addition of a monovalent metal oxide (M_2O) modifies the covalent network of boron or phosphorus oxide and results in substances with a conductivity which is essentially due to the metal ions. For this reason, these materials have a potential use as electrolytes in solid state electrochemical cells. Their ionic conductivity can be substantially enhanced by "doping" the glass with a salt (MX) and by substituting oxygen with sulfur. However, the dopant usually reduces the glass transition temperature, T_g, by an amount which is roughly proportional to the [MX]/[glass former] ratio [1].

An interesting possibility for optimizing the conductivity and thermal stability properties of oxide glasses was suggested by Tsuchiya and Moriya [2]. These authors showed that ionic conductivity in borophosphate glasses can be a highly non-linear function of the [B]/[B + P] ratio, and that the occurrence of a conductivity maximum is not accompanied by a decrease of T_g.

More recently, we have reported an investigation of conductivity and electrochemical behavior in the $AgI/Ag_2O/B_2O_3/P_2O_5$ system [3] where similar "mixed network effects" were found. The evidence is growing [4]

that such effects are a general feature of network glasses. This has prompted us to begin a systematic study of these effects with the aim of defining their phenomenology.

In this paper we present conductivity and glass transition data for glasses of the $Li_2O/B_2O_3/P_2O_5$ system. Although the potential for technological exploitation prompted the appearance of numerous papers dealing with lithium-containing borates [5, 6] and phosphates [6, 7], we found the data concerning borophosphates to be incomplete. A comment is in order concerning the choice of the system coordinates. We will compare properties of glasses with the same Li_2O fraction and different values of $Y = [B]/[B + P]$. In fact, it is known that the ionic conductivity in glasses of both the M_2O/B_2O_3 and the M_2O/P_2O_5 systems increases with the metal oxide fraction, which is a coordinate used by most authors. In the following, we will maintain the notation introduced in previous papers [8, 9] where, instead of the metal oxide fraction, we used an equivalent coordinate defined by $n = [B + P]/[M]$.

Experimental

Finely-mixed powders of reagent-grade starting materials ($NH_4H_2PO_4$, $LiNO_3$ and B_2O_3) were melted in air until gas evolution stopped. The melt was kept for about 30 min in air at temperatures in the range 900 - 1300 °C and occasionally stirred. It was then poured into metal molds kept at room temperature (R.T.). The glass formation region is defined as the composition range where transparent solids are obtained which do not show any sharp reflections in their X-ray diffraction spectra. Differential Scanning Calorimetry (Dupont 1090, DSC model 910) was used to identify T_g. Electrical data were collected using a Solartron Frequency Response Analyzer model 1174 and a Wayne–Kerr model B331 bridge on smooth and platinum-plated, disk-shaped samples. Powder X-ray diffraction spectra were taken with a Philips PW-1001 diffractometer.

Results and discussion

Figure 1 portrays the glass formation region of the $Li_2O–B_2O_3–P_2O_5$ system. The vitreous substances we obtained are indicated with squares. The cross-hatched area has been investigated by Levasseur et al. [6] while the nominal compositions quoted by Tsuchiya and Moriya [2] lie on the two dashed horizontal lines. For Li_2O-rich compositions (upper region of Fig. 1), X-ray diffraction peaks were often found which have been assigned to crystalline Li_3PO_4. The formation of crystalline BPO_4 takes place in the lower region. The meaning of the dotted line is discussed below.

The conductivity data at room temperature (R.T.) are reported, on a logarithmic scale and as a function of Y, in Fig. 2, while the corresponding
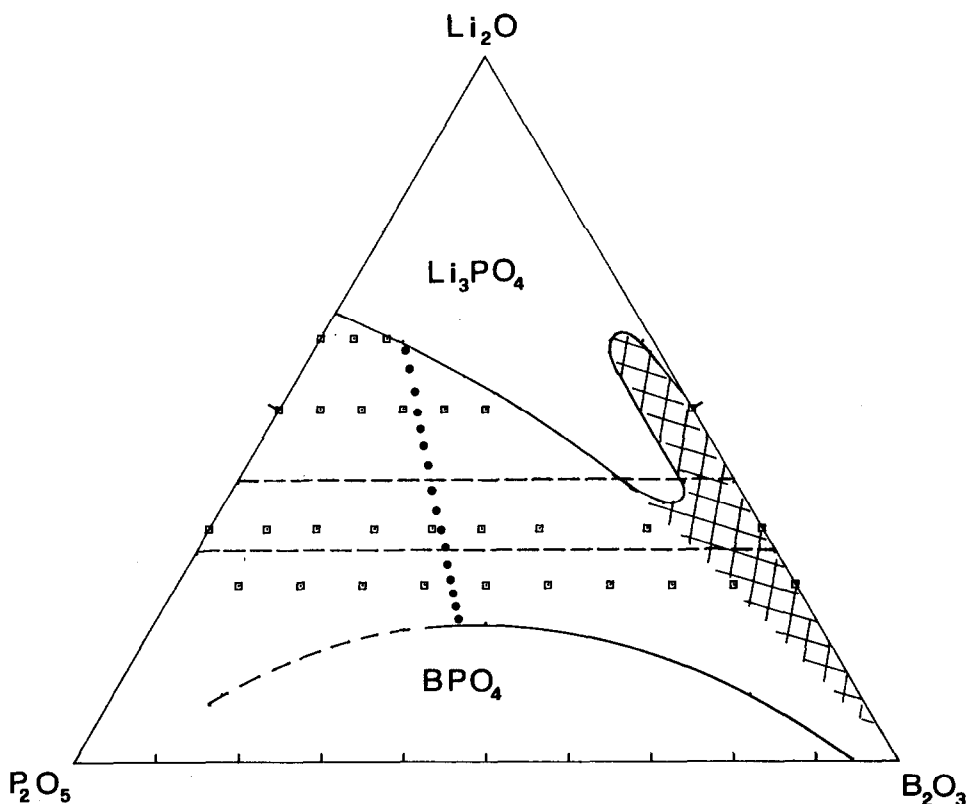
Fig. 1. Glass formation region of the $Li_2O-B_2O_3-P_2O_5$ system (see text).

T_g values are plotted in Fig. 3. Attention is drawn to the fact that a very large enhancement of conductivity occurs near $Y = 0.5$, so long as these compositions belong to the glass formation region. It is worth mentioning that the phenomenon is apparently very different in silver borophosphates where well defined conductivity maxima are observed for $n > 2$, and are definitely displaced towards the boron rich side [3]. On the other hand, the behavior of T_g is essentially the same for Li^+ and Ag^+ borophosphates; T_g increases by 100 - 200 °C when we begin to substitute P with B, and near $Y = 0.5$ reaches either a plateau or an absolute maximum.

A qualitative but simple model which explains the T_g behavior in both lithium and silver borophosphate glasses hypothesizes that the most stable structures consist of a network of BPO_4 tetrahedra in which the tetrahedral orthophosphate ions are dispersed. Accordingly, the maxima of T_g as a function of Y occur for compositions lying on the dotted line that connects the BPO_4 and the Li_3PO_4 points in Fig. 1. The arrows in Figs. 2 and 3 indicate these critical compositions for the various n-values. The maxima of the R.T. conductivity as a function of Y may arise from competition between two different mechanisms of conductivity enhancement. On the one hand,
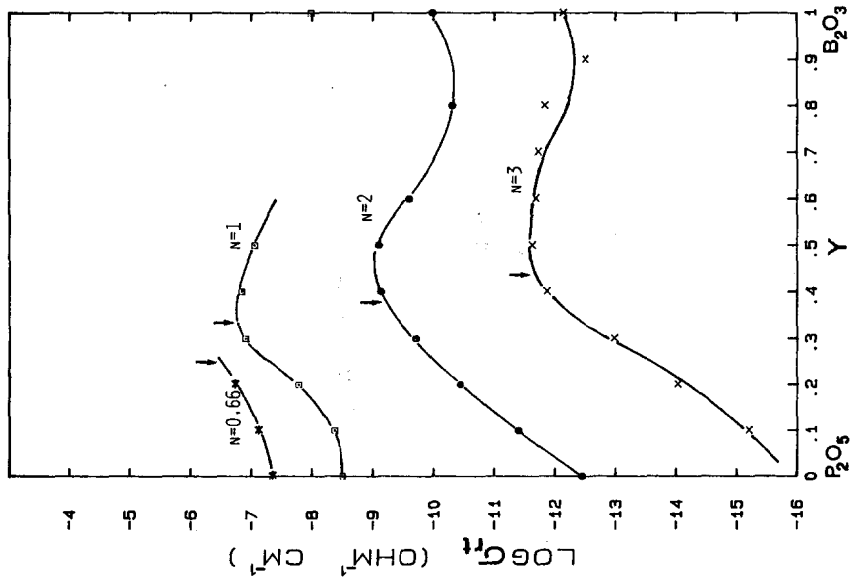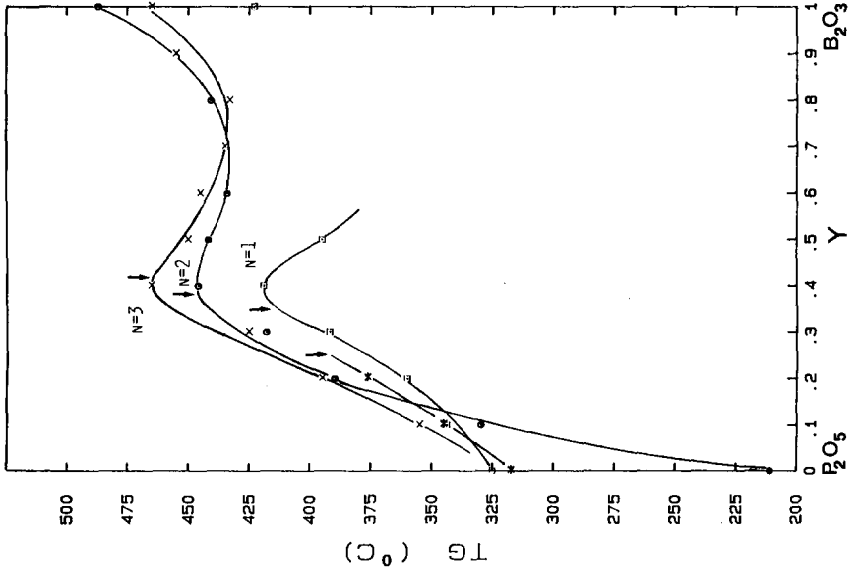
Fig. 2. Conductivities at 22 °C (R.T.) as a function of Y for n = 3, n = 2, n = 1 and n = 0.66.

Fig. 3. Glass transition temperatures for the Li₂O–B₂O₃–P₂O₅ system.

the large orthophosphate ions act as a doping salt; on the other hand, a doping salt can coexist only with a negatively charged covalent network and we expect the cations "bonded" to BO_4^- tetrahedra to be more mobile than those to metaphosphate or pyrophosphate groups. If this is the case, the conductivity changes as a function of the [B]/[P] ratio depend on the equilibrium population of a few types of structural units, which may nevertheless explain the apparently complicated behavior of conductivity in silver borophosphate.

Acknowledgement

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