

$(\text{Ag}_2\text{O})_x(\text{Li}_2\text{O})_{1-x} \cdot 2\text{B}_2\text{O}_3$ MIXED CATION GLASSES

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Summary

An analysis of the ^{11}B NMR spectra in the $(\text{Ag}_2\text{O})_x(\text{Li}_2\text{O})_{1-x} \cdot 2\text{B}_2\text{O}_3$ glasses shows that the glass network consists of an equal number of BO_3 and BO_4 units and that it does not undergo major changes when a cation is totally or partially substituted by another. The ^7Li NMR spectra reveal the existence of cation pairs and suggest that Li-Li pairs are more stable than Li-Ag pairs. The ^{11}B spin-lattice relaxation times at 117 K display a kind of mixed alkali behavior. These findings suggest that a relationship exists between the increased resistivity of the mixed glasses and the spectra of the low-lying excitations.

Introduction

Vitreous compounds often display ionic resistivity, ρ , substantially lower than that of their crystalline counterparts. In addition, when one cation is substituted by another in a glass, ρ and other physical properties have a highly non-linear dependence upon the composition parameter. These phenomena, known as mixed alkali (MA) effects, appear to be a landmark of ionic transport in highly disordered systems [1]. Here, we will discuss the relationship between structure and ionic diffusion in borate glasses and will present an investigation of MA effects in $(\text{Ag}_2\text{O})_x(\text{Li}_2\text{O})_{1-x} \cdot 2\text{B}_2\text{O}_3$ glasses.

Results and discussion

The glasses made from B_2O_3 , a metal halide (MX) and M_2O appear particularly suitable for technological exploitation because their stability range extends well above room temperature and they are good ionic conductors of Ag^+ and Li^+ [2, 3]. Some ^{11}B NMR results for the $\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass are given in Fig. 1. The spectra show that, for molar ratios $[\text{M}_2\text{O}]/$

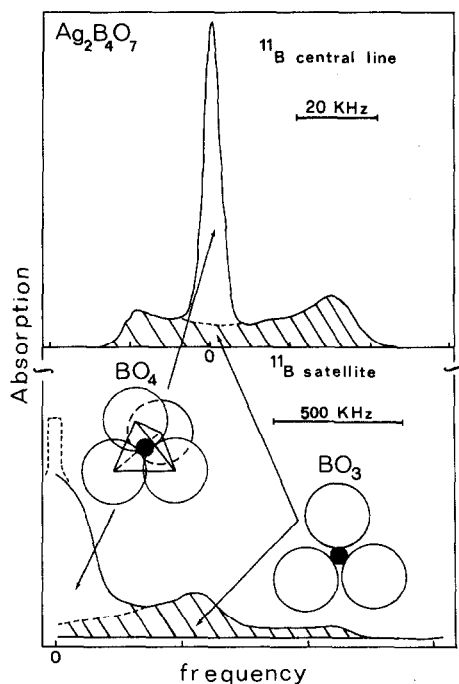


Fig. 1. ^{11}B central line (upper figure) and ^{11}B downfield satellite (lower figure) after subtraction of the central line contribution (dashed line).

$[\text{B}_2\text{O}_3] < 0.5$, each M_2O molecule approximately causes the conversion of two three-coordinated boron units (BO_3) to four-coordinated units (BO_4). Furthermore, the ^{11}B satellite spectrum (lower portion of Fig. 1) gives no evidence of oxygens bonded to a single boron (non-bridging oxygens). We conclude that M^+ ions are coordinated to negatively charged BO_4 units. Addition of metal halides further decreases the strength of the M^+-BO_4 bond which is believed to be the most relevant microscopic parameter for ionic diffusion in the borates.

Information about Li^+ distribution is contained in the ^7Li (3/2 spin) NMR spectra. At 295 K these spectra consist of satellite transitions ($\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$) spread over a ~ 200 kHz interval, and a central transition ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) which is a few kHz wide. The width and shape of the satellite spectra depend upon the interaction of the ^7Li nucleus with the electric field gradients at its position. At high Li content ($X < 0.2$) some sharp features appear in the satellite spectra which may be due to the formation of "ordered regions" which are not detected by X-rays. The second moment, M_2 , of the ^7Li central line is due to $^7\text{Li}-^{11}\text{B}$ and $^7\text{Li}-^7\text{Li}$ magnetic dipolar interactions. If the Li^+ was uniformly distributed, one would expect that M_2 behaves according to the dashed line of Fig. 2. Instead, when Ag^+ substitutes Li^+ , M_2 changes from 1.99 gauss² (at $X = 0$) to 1.38 gauss² (at $X = 0.8$). These find-

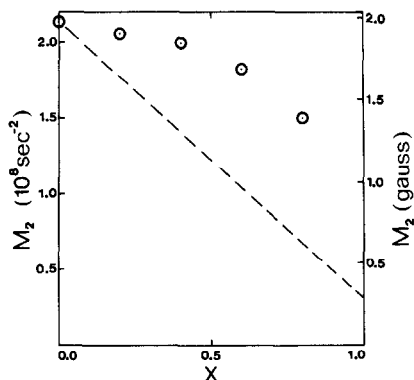


Fig. 2. Second moment of ${}^7\text{Li}$ central line as a function of X . The dashed line gives the M_2 behavior expected for a uniform distribution of lithium ions.

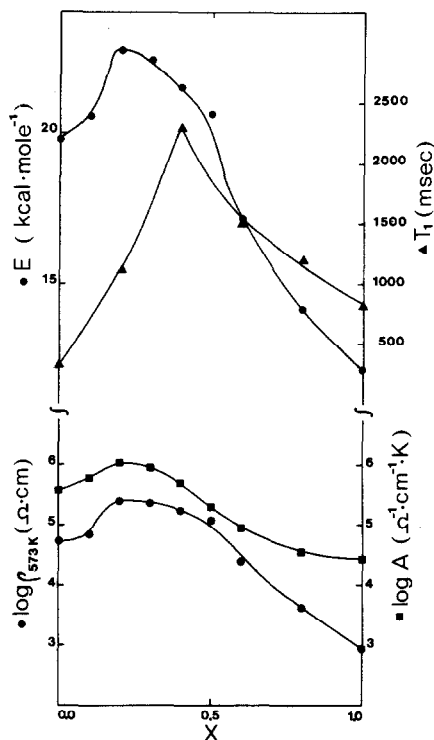


Fig. 3. The upper portion gives the activation energies (\bullet) and the ${}^{11}\text{B}$ relaxation times at 117 K (\blacktriangle) as a function of X . The lower part gives, on a logarithmic scale, the resistivities at 573 K (\bullet) and the conductivity prefactors (\blacksquare).

ings can be related to the existence in the borate glasses of cation pairs [4], and indicate that Li^+-Li^+ pairs are more stable than Ag^+-Li^+ pairs. With increasing X , the glass transition temperature (T_g) and the density (d) go monotonically from the values for $X = 1$ ($T_g = 682$ K, $d = 4.03$ g cm^{-3}) to those for $X = 0$ ($T_g = 735$ K, $d = 2.21$ g cm^{-3}).

The ionic conductivities have an Arrhenian behavior

$$\sigma T = A \exp\left(-\frac{E}{RT}\right)$$

from room temperature up to T_g and display a typical MA effect as a function of X (see Fig. 3). A combined analysis of ^{11}B and ^7Li spin-lattice relaxation times, T_1 's, shows that Li^+ ions are not immobile in the Ag^+ -rich glasses. This finding is confirmed by cation exchange experiments in molten nitrates. Thus, contrary to other glasses [5], the MA effect is not due to a nearly complete immobilization of the "guest" ion. The ^{11}B T_1 data at low temperature (117 K) shed some light on the nature of the interaction responsible for MA effects in the borates. As shown in Fig. 3, the ^{11}B T_1 goes through a maximum as a function of X . Since the boron relaxation near 100 K is due to "disorder modes" [6] (*i.e.*, a deformation motion of the borate units), the T_1 data suggest that the glass network is more rigid in the mixed glasses than in $\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glasses. This fact also confirms that a relationship exists between low temperature glasslike "anomalies" and the phenomenon of ion transport at elevated temperatures [7].

We suggest that both enhanced conductivity and MA effects in glasses, as well as in β -aluminas [1], are due to an interaction between the potentially mobile ion and the low lying excitations typical of disordered systems.

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