

## LIX (X=Br, F) SALT DOPING EFFECT IN LITHIUM BOROPHOSPHATE GLASSES

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Received 20 July 1987

In an attempt to enhance the conductivity of lithium conducting glasses, the "mixed former effect" and the halide salt doping effect have been combined. Thus, borophosphate glasses  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$  doped with LIX (X=Br, F) have been characterized by the measurements of  $T_g$  and the electrical conductivity. The variation of the electrical conductivity versus salt doping is interpreted with a regular thermodynamic solution model, in which the base glass  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$  is the solvent and the salt LIX the solute.

### 1. Introduction

Several studies were carried out recently on Li glassy conductors in order to set up all solid state batteries. These conductors are generally constituted by a vitreous network former, mainly  $\text{P}_2\text{O}_5$  or  $\text{B}_2\text{O}_3$ , and a modifier as  $\text{Li}_2\text{O}$  which is responsible of the  $\text{Li}^+$  conductivity.

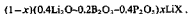
In order to improve the conductivity of these glasses, several authors [1-4] propose a doping by lithium halides  $\text{LiX}$  (X=F, Cl, Br, I). On the other hand, Tsuchiya and Meriya [5] have shown that simultaneous use of the two network formers  $\text{P}_2\text{O}_5$  and  $\text{B}_2\text{O}_3$  also improves the conductivity. In the ternary system an increase of two orders of magnitude was observed in comparison to those of the binary systems  $\text{P}_2\text{O}_5-\text{Li}_2\text{O}$  and  $\text{B}_2\text{O}_3-\text{Li}_2\text{O}$ . We call this phenomenon the "mixed former effect".

In a previous work [6] we have already discussed the mixed network former in the  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$  system and the salt doping effect by adding LiCl.

The present study completes the previous work, using LiF and LiBr as salt dopants. Because of synthesis difficulties the use of LiI as salt dopant cannot be achieved.

### 2. Sample preparation

The general formula corresponds to



The basic glass  $(0.4\text{Li}_2\text{O}-0.2\text{B}_2\text{O}_3-0.4\text{P}_2\text{O}_5)$  was prepared by fusion in air of  $\text{Li}_2\text{CO}_3$  (Prolabo-Rectapur),  $\text{B}_2\text{O}_3$  (Merck, high purity for analysis),  $\text{P}_2\text{O}_5$  (Prolabo-RP Normapur) or  $(\text{NH}_4)_2\text{HPO}_4$  (Prolabo-Rectapur) anhydrous powders in a platinum crucible heated by the Joule effect ( $T \approx 950^\circ\text{C}$ ), then quenched at room temperature. Anhydrous LiBr (Merck) or LiF (Merck) were subsequently mixed in appropriate proportions with the basic glass in powdered form. The mixture was heated to  $900^\circ\text{C}$  under vacuum in sealed quartz tubes. The melts were quenched in air.

The glass obtained was then annealed for 3 to 5 h at a temperature of  $50^\circ\text{C}$  less than its glass transition temperature  $T_g$  in order to relieve internal strains.

### 3. Glass characteristics

#### 3.1. X-ray diffraction

The absence of X-ray diffraction indicates an absence of crystallization. Crystalline phases appear for  $x \geq 0.35$  in the case of LiF and for  $x \geq 0.40$  in the case of LiBr.

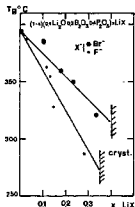


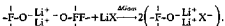
Fig. 1. Glass transition temperature ( $T_g$ ) as a function of  $x_{LiX}$ .

### 3.2. Chemical analysis

Glass compositions were controlled by chemical analysis. B, P and Li contents were measured by plasma emission spectroscopy, Br content by silver potentiometry and F content with a specific electrode.

### 3.3. Glass transition temperature ( $T_g$ )

$T_g$  were measured by differential scanning calorimetry (DSC). Fig. 1 gives  $T_g$  as a function of LiX content. A considerable decrease in  $T_g$  is observed, suggesting that the macromolecular skeleton of the doped glass is less rigid than that of the basic glass. This indicates that LiX can only be dissolved if non-bridging oxygens exist, as illustrated by the following reaction:



## 4. Electrical measurements

Electrical conductivity measurements were made by impedance spectroscopy in the 5 to  $13 \times 10^6$  Hz frequency range from room temperature to 200°C. On both sides of the cylindrical samples, gold electrodes were deposited by rf sputtering.

For all glasses in the range of temperature considered, the results show that the electrical conductivity varies according to an Arrhenius relationship:

$$\sigma = \sigma_0 \exp(-E_a/RT). \quad (1)$$

The conduction activation energy  $E_a$  was deduced for each glass composition.

## 5. Results and discussion

Variations of the electrical conductivity and activation energy with LiX content are interpreted with the weak electrolyte approach [7] and a regular solution model [6,8].

The weak electrolyte approach supposes the following assumptions:

(i) The mobility  $\mu$  of charge carriers  $\text{Li}^+$  is independent of  $x$  for a given temperature

$$\mu = \frac{F}{2nRT} \lambda^2 \nu_0 \exp(-E_m/RT), \quad (2)$$

where  $n$  is the number of dimensions in which the  $\text{Li}^+$  can move (glasses are isotropic, so  $n=3$ );  $\lambda$  is the average jump distance,  $\nu_0$  the  $\text{Li}^+$  vibration frequency and  $E_m$  is the energy required for  $\text{Li}^+$  migration.

Assuming constant mobility at constant temperature implies a low variation of  $\lambda$ ,  $\nu_0$  and  $E_m$ . Recently this assumption was experimentally demonstrated [9] by ion Hall effect measurements in  $\text{AgPO}_3\text{-AgI}$  glasses.

(ii) The mobile  $\text{Li}^+$  ions come from dissociation of  $\text{Li}_2\text{O}$  or LiX. But quickly the charge carriers originating from the halide become more numerous than those from the basic glass,

$$\text{LiX} \rightleftharpoons \text{Li}^+ + \text{X}^-, \quad K_1 = \frac{\gamma_+ [\text{Li}^+] \gamma_- [\text{X}^-]}{a_{\text{LiX}}}, \quad (3)$$

where the activity coefficients  $\gamma_+$  and  $\gamma_-$  are considered constant with the LiX content.

The equilibrium constant  $K_1$  may be expressed as a function of the thermodynamic quantities of dissolution (for a chosen reference state):

$$\begin{aligned} K_1 &= \exp(-\Delta G_{\text{diss}}^0/RT) \\ &= \exp(-\Delta H_{\text{diss}}^0/RT) \exp(\Delta S_{\text{diss}}^0/R). \end{aligned} \quad (4)$$

The electroneutrality condition  $[Li^+] = [X^-]$  leads to

$$[Li^+] = (K_1 a_{LiX})^{1/2} \quad (5)$$

To calculate the dependence of  $a_{LiX}$  on the LiX molar fraction  $x$ , we suppose that the glass is a regular solution of LiX (the solute) in the basic glass  $Li_2O-B_2O_3-P_2O_5$  (the solvent).

The free energy of mixing  $\Delta G_m$  can thus be written as

$$\Delta G_m = \alpha x(1-x) + RT[x \log x + (1-x) \log(1-x)] \quad (6)$$

$\alpha$  is a term representing the rearrangement of the bonds after mixing.

The Gibbs-Duhem equation gives

$$\Delta G_{LiX} = \Delta G_m + (1-x) \delta \Delta G_m / \delta x, \quad (7)$$

then

$$a_{LiX} = \exp(\Delta G_{LiX}/RT) = x \exp[\alpha(1-x)^2/RT] \quad (8)$$

Combining (2), (4), (5) and (8) and grouping the

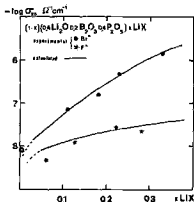


Fig. 2. Room temperature conductivity ( $\sigma_{25}$ ) as a function of  $x_{LiX}$ .

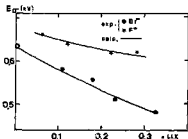


Fig. 3. Activation energy for conduction as a function of  $x_{LiX}$ .

constant terms in  $K$ , the conductivity may be written as

$$\sigma = Kx^{1/2} \exp\left(\frac{-E_m - \frac{1}{2}\Delta H_{\text{mix}}^0 + \frac{1}{2}\alpha(1-x)^2}{RT}\right) \quad (9)$$

The activation energy  $E_a$  is

$$E_a = E_m + \frac{1}{2}\Delta H_{\text{mix}}^0 - \frac{1}{2}\alpha(1-x)^2, \quad (10)$$

where  $E_m + \frac{1}{2}\Delta H_{\text{mix}}^0 = \text{constant}$ .

Figs. 2 and 3 show the experimental values of the electrical conductivity and activation energy against the LiX content. Solid curves represent the theoretical variations  $\sigma=f(x)$  and  $E_a=f(x)$  according to (9) and (10).

In the cases, where  $\alpha = -35$  kJ/mole for LiBr and  $\alpha = -13$  kJ/mole for LiF, the theoretical curves are in good agreement with the experimental points.

These values of  $\alpha$  correspond to the order of magnitude of the mixing enthalpies of molten salts with a common cation and different anions.

#### Acknowledgement

The present research was carried out with the financial support of the Groupement Scientifique (C.N.R.S.) Stockage Electrochimique de l'Energie. ACMR is working under a Brazilian C.N.P.q. grant.

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