

LITHIUM CONDUCTING GLASSES: THE $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{TeO}_2$ SYSTEM

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New Li vitreous conductors have been synthesized using simultaneously B_2O_3 and TeO_2 as glass forming networks. Tg measurements and electrical conductivity are presented for different $\text{B}_2\text{O}_3/\text{TeO}_2$ ratio. Results show a "mixed former effect" on the electrical conductivity: at room temperature $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{TeO}_2$ is more conducting (≈ 2 orders of magnitude higher) than the binary systems $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ and $\text{Li}_2\text{O} \cdot \text{TeO}_2$.

1. Introduction

In order to build up all-solid state batteries, several studies are undertaken nowadays on glassy electrolytes conducting by lithium. In the case of oxide glasses, it has been shown that the simultaneous use of two former networks leads to a significant enhancement of the conductivity. Such effect is called the "mixed former effect". For example, a gain of one or two orders of magnitude is observed by adding B_2O_3 to SiO_2 or P_2O_5 in Li^+ , Na^+ , or Ag^+ glassy conductors [1-5]. It is well known that B_2O_3 is among the best glass formers. The disponibility of the p orbitals in borium allows the change of its hybridation state and its coordination index. This latter was observed by NMR for $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot \text{BO}_3$ system [6]. On the other hand, a few studies were performed on TeO_2 based glassy electrolytes. The first lithium tellurite, in the vitreous state, was obtained by Brady [7,8] and studied for structural considerations. More recently the $\text{Li}_4\text{Te}_2\text{O}_4$ glass was synthesized by Sunandana and Kumaraswani [9] in order to study their electrical properties.

The present work deals with the mixed former effect on the $\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{TeO}_2$ glass system.

2. Experimental

In order to compare glasses with the same number of cationic network former, we have chosen to write

TeO_2 as $\frac{1}{2}\text{Te}_2\text{O}_4$. The general formula of studied glasses is



2.1. Samples preparation

Glasses are obtained by melting calculated quantities of Li_2CO_3 (Prolabo, Rectapur), TeO_2 (Janssen) and B_2O_3 (Merck) in a platinum crucible. Mixtures were melted for 30 min between 700 and 900°C according to the composition and then quenched in a cylindrical mould in air at room temperature. For samples with high B_2O_3 content the melts were poured into a polished brass plate and the formed drop is immediately flattened by another plate. In order to relieve internal strains, the samples were annealed during 24 h at a temperature 50° lower than the glass transition temperature (T_g). However, samples remain very brittle.

2.2. Characterization

Chemical analysis (by plasma emission spectroscopy) show less than 1% difference between nominal and effective compositions. The amorphous state is controlled by X-ray diffraction: for the binary system $y\text{Li}_2\text{O}(1-y)\text{Te}_2\text{O}_4$ glassy samples are obtained in a short glass forming region defined by $0.30 \leq y \leq 0.40$; for the ternary system $0.4\text{Li}_2\text{O} \cdot$

Table 1
Electrical characteristics and glass transition temperature for the glass system $y\text{Li}_2\text{O} \cdot (1-y)\text{Te}_2\text{O}_5$

x	E_a (eV)	$\sigma_{\text{ion-c}}$ ($\Omega^{-1}\text{cm}^{-1}$)	$\log \sigma_0$	T_g ($^{\circ}\text{C}$)
0.30	1.13	1.48×10^{-12}	3.45	267
0.33	1.12	2.95×10^{-12}	3.58	263
0.37	1.15	1.58×10^{-11}	4.82	260
0.40	1.07	5.75×10^{-11}	3.39	257

$0.6(x\text{B}_2\text{O}_3(1-x)\text{Te}_2\text{O}_5)$ all the samples are amorphous.

The glass transition temperature was measured by differential scanning calorimetry (DSC) with a heating rate equal to $10^{\circ}/\text{min}$. Table 1 gives T_g for the binary $\text{Li}_2\text{O} \cdot \text{Te}_2\text{O}_5$. A slight decrease of T_g is observed when Li_2O content increases. For the ternary system fig. 1 gives the T_g variation versus x . T_g increases continuously with the B_2O_3 content, giving a small variation up to $x=0.5$. At this point, T_g rises steeply with the increase of x .

2.3. Electrical measurements

Gold electrodes are deposited by rf sputtering on both faces of the samples. Electrical measurements

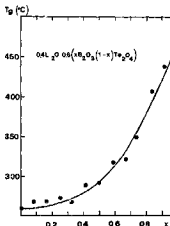


Fig. 1. Glass transition temperature (T_g) in the system $0.4\text{Li}_2\text{O} \cdot 0.6(x\text{B}_2\text{O}_3(1-x)\text{Te}_2\text{O}_5)$.

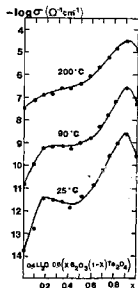


Fig. 2. Variation of the conductivity as a function of x , in the glass system $0.4\text{Li}_2\text{O} \cdot 0.6(x\text{B}_2\text{O}_3(1-x)\text{Te}_2\text{O}_5)$ (at 25°C ; extrapolated data).

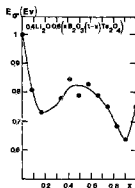


Fig. 3. Activation energy for conduction as a function of x , in the glass system $0.4\text{Li}_2\text{O} \cdot 0.6(x\text{B}_2\text{O}_3(1-x)\text{Te}_2\text{O}_5)$.

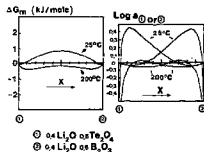


Fig. 4. Theoretical free mixing energy ΔG_m , and activity as a function of x under the assumption of a regular solution model.

were performed using the impedance spectroscopy technique in the 5 Hz– 13×10^5 Hz frequency range. For all the samples, the Arrhenius plots are linear in the whole investigated temperature domain.

3. Results and discussion

For the binary system $y\text{Li}_2\text{O} (1-y)\text{Te}_2\text{O}_4$, table 1 shows a linear increase of the conductivity versus Li_2O content, while the activation energy exhibits small variation.

For the ternary system the isothermic variations of $\ln \sigma$ (conductivity versus x) show (fig. 2) two maxima for $x=0.17$ and $x=0.91$. We notice that these maxima are close to the limit compositions of the system. A minimum occurs at $x=0.5$. The maxima are less pronounced when the temperature increases and they practically vanish at 200°C .

Fig. 3 shows that the conductivity maxima are related to two minima of the activation energy. Thermodynamic consideration may explain qualitatively the occurrence of these two extrema. The $0.4\text{Li}_2\text{O} \cdot 0.6(x\text{B}_2\text{O}_3 + (1-x)\text{Te}_2\text{O}_4)$ glass may be considered as resulting from the mixtures of the two limit compositions $x(0.4\text{Li}_2\text{O} \cdot 0.6\text{B}_2\text{O}_3)$ and $(1-x)(0.4\text{Li}_2\text{O} \cdot 0.6\text{Te}_2\text{O}_4)$. The investigated glasses tend to demixing because of the mixing enthalpy ΔH_m , as shown

by Kone [4] in the $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ system and by Hervig and Navrotsky [10] in the $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ system. This demixing does not take place for kinetic reasons. This involves an increase of the free mixing energy ΔG_m and of the partial free energies and, therefore, the increase of the thermodynamic activity of both glasses: $0.4\text{Li}_2\text{O} \cdot 0.6\text{B}_2\text{O}_3$ and $0.4\text{Li}_2\text{O} \cdot 0.6\text{Te}_2\text{O}_4$. Fig. 4 shows for different temperatures the theoretical activity and the ΔG_m variations with x , assuming a regular solution model

$$\Delta G_m = \alpha x(1-x) + RT[x \ln x + (1-x) \ln (1-x)]$$

with $\alpha = 10$ kJ/mole. We can consider that the Li_2O activity increases in each component. According to the weak electrolyte mode [11], the enhancement of the conductivity at the limit compositions, is due to these Li_2O activity variations.

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