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Influence of the fluorine-oxygen substitution on the ionic conductivity properties of lithium tellurite glasses

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Abstract.

A large range of glassy compositions has been found inside the ternary $\text{LiF-Li}_2\text{O-TeO}_2$ system. The influence of the fluorine-oxygen substitution on the ionic conduction properties of $(50-x)\text{LiO}_{0.5}-(x)\text{LiF}-(50)\text{TeO}_2$ ($0 \leq x < 50$) glasses has been investigated. These results have been correlated with the data relative to ion distribution and microstructure obtained by NMR and TEM. A maximum of conductivity associated with a minimum of activation energy is observed for $\text{F/Te} \approx 0.5$. The composition dependence of conductivity with rising x can be explained by a progressive decrease of the F-F associations around the Te^{4+} ions and a simultaneous increase of the Li-F associations. The clustering of the Li^+ and F^- ions produces small domains which hinder the Li^+ ions diffusion in these glasses.

1-Introduction.

The formation of stable glasses in a large range of compositions inside the $\text{Li}_2\text{O-TeO}_2$ and LiF-TeO_2 systems [1-4] has been reported. Ionic conductivity and NMR investigations of these binary glasses have shown that transport is mainly due to motion of the Li^+ ions. The electrical properties have been explained on the basis of two different distributions of the Li^+ ions : one in which the Li^+ ions are dispersed in the $\text{Li}_2\text{O-TeO}_2$ glasses and another in which the Li^+ and F^- ions are associated in the network of the LiF-TeO_2 glasses.

This article deals with the transport properties variation as a function of the fluorine-oxygen substitution for the $(50-x)\text{LiO}_{0.5}-(x)\text{LiF}-(50)\text{TeO}_2$ ($0 \leq x < 50$) glasses which have the same lithium

content. To elucidate the conduction mechanisms, NMR and TEM investigations of these glasses have been simultaneously undertaken.

2-Experimental.

The glasses have been synthesized from mixtures of TeO_2 , Li_2CO_3 and LiF in open crucibles of alumina following the method described elsewhere [3]. Electrical measurements were carried out by the complex impedance method using a Solartron 1170 frequency response analyser. ^7Li and ^{19}F NMR spectra were recorded with a SXP 4/100 Bruker spectrometer. The frequencies used for lithium and fluorine were respectively 35 and 84.7 MHz. Transmission electron micrographs were obtained on a Jeol 4000 EX electron microscope, working at 400 Kv. and equipped with a $\pm 25^\circ$ goniometer stage.

3-Results.

The glass domain is shown in Fig.1. Chemical compositions ($\text{LiO}_{0.5}$: LiF : TeO_2 %mol.) of studied glasses, deduced from chemical analysis of lithium, fluorine and tellurium (Analysis Central Service of CNRS) are respectively : A(50:0:50), B(40:10:50), C(27:23:50), D(15:35:50) and E(0:47:53).

Fig.1 -Vitreous domain in the Li_2O - LiF - TeO_2 system.

3-2-Ionic conductivity.

In the investigated temperature range (20–250°C), the variation of conductivity with temperature follows an Arrhenius law. $\sigma_{200^\circ\text{C}}$ and $\Delta E_{\sigma T}$ are shown in Fig.2 as a function of the F/Te ratio. $\sigma_{200^\circ\text{C}}$ increases slightly for $F/Te \lesssim 0.5$, while it decreases quickly for $F/Te \gtrsim 0.5$. Simultaneously, $\Delta E_{\sigma T}$ decreases in the first F/Te range and increases in the second one.

Fig.2 (a)-Variation of $\log \sigma T$ vs. $10^3/T$ for some glasses.

(b)-Variation of $\sigma_{200^\circ\text{C}}$ and $\Delta E_{\sigma T}$ as a function of the F/Te ratio (the solid and dashed lines are drawn to guide the eye).

3-3- ^7Li and ^{19}F NMR spectroscopy.

The ^7Li and ^{19}F NMR spectra are given in Fig.3 for the A, C and E samples. Second moment of ^7Li NMR spectra increases progressively with rising F/Te ratio. On the contrary, second moment of ^{19}F is practically constant for $F/Te \lesssim 0.8$ but increases above this value. For comparison, experimental $S_2(^7\text{Li})$ and $S_2(^{19}\text{F})$ values of binary LiF- TeO_2 glasses, experimental values of crystalline LiF and calculated values corresponding to pair, row and planar arrangements of the Li^+ and F^- ions with the crystalline LiF geometry are included in Fig.3.

Fig.3 - ^7Li NMR (a) and ^{19}F NMR (c) spectra of some glasses. Variation of $S_2(^7\text{Li})$ (b) and $S_2(^{19}\text{F})$ (d) as a function of the F/Te ratio. (closed circles and squares represent respectively values relative to $(50-x)\text{LiO}_{0.5} - (x)\text{LiF} - (50)\text{TeO}_2$ and binary $\text{LiF} - \text{TeO}_2$ glasses).

3-4-Transmission electron microscopy.

Micrographs corresponding to the A, C and E samples are shown in Fig.4. In the A sample, an amorphous matrix is observed only while in the C and E samples, LiF and $\alpha\text{-TeO}_2$ domains have been identified inside the amorphous matrix. In spite of the lack of cluster detection by X-ray diffraction, these domains are clearly observed in the C sample, far from the glass domain boundary.

4-Discussion.

Electrical study of the $(50-x)\text{LiO}_{0.5} - (x)\text{LiF} - (50)\text{TeO}_2$ glasses has shown that the variation of $\sigma_{200^\circ\text{C}}$ with rising F/Te ratio is not linear but involves a maximum for $\text{F/Te} \approx 0.5$. That conductivity variation can be explained by the relative distribution of the Li^+ and F^- ions as a function of the F/Te ratio determined by NMR spectroscopy.

Fig.4 - TEM micrographs corresponding to the A, C and E samples.

For the low fluorine contents, $S_2(^7\text{Li})$ is small while $S_2(^{19}\text{F})$ is very high. It results in weak Li-Li and Li-F and strong F-F interactions, indicating that the Li-F aggregations as row or planar arrangement are not developed in these glasses. On the contrary, the F-F associations around the Te^{+4} ions would be significant and the Li^+ ions dispersed in an oxygen environment. That dispersion is even higher in the ternary $(50-x)\text{LiO}_{0.5}-(x)\text{LiF}-(50)\text{TeO}_2$ glasses than in the binary $\text{LiF}-\text{TeO}_2$ ones. The replacement of oxygen by fluorine in the ternary glasses results consequently in a weakening of the Li-O bond within the glass network and a larger mobility of carriers. So, one observes a decrease of ΔE_g and a small conductivity increase when the F/Te ratio rises in the $\text{F/Te} \lesssim 0.5$ glass domain.

In the glasses involving F/Te contents $\gtrsim 0.5$, the Li-F associations become strong, in agreement with the existence of LiF clusters detected by TEM analysis. It results in a sharp decrease of conductivity.

These results can be interpreted by the "cluster by pass" model. According to this model [5], conductivity should be due to motions of the Li^+ ions into the connective tissue of glass. For $\text{F/Te} \lesssim 0.5$, the formed clusters are not many enough to block the Li^+ ions diffusion pathways. On the contrary, for $\text{F/Te} \gtrsim 0.5$, these pathways are partially blocked by the presence of $\alpha\text{-TeO}_2$ and LiF clusters.

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References.

- [1]-W.VOGEL, H.BURGER, B.MULLER, G.ZERGE, W.MULLER and K.FORKEL, Silikat-technik, 25 (1974) 205.
- [2]-T.YOKO, K.KAMYA, T.TANAKA, H.YAMADA and S.SAKKA, Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi, 973 (1989) 298.
- [3]-J.M.ROJO, J.SANZ, J.M.REAU and B.TANGUY, J.Non-Cryst. Solids, 116 (1990) 167.
- [4]-A.C.MARTINS-RODRIGUES and M.J.DUCLOT, Solid State Ionics, 28-30 (1988) 729.
- [5]-M.D.INGRAM, M.A.MACKENZIE, W.MULLER and M.TORGE, Solid State Ionics 28-30 (1988) 677.