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New solid electrolytes with high ionic conductivity

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Abstract : Li glasses $B_2O_3-xLi_2O-yLiX$, where X is a halogen, $x \leq 0.85$, and $y \leq 0.85$ and ternary fluorides with cations of high polarizability and structure derived from the CaF_2 type were studied. The main technique used for studying glasses were x-ray and neutron diffraction; complex impedance measurements; NMR studies on ^{19}F , 7Li , and ^{11}B ; and IR and Raman spectroscopies. The conductivities of $\leq 10^{-3} (\Omega\text{-cm})^{-1}$ at 150° obtained with glasses are related to the short-range ordering in these glasses. The best ternary fluoride is $PbSnF_4$, which has a conductivity of $\sim 10^{-1} (\Omega\text{-cm})^{-1}$ at 150° and an activation energy of 0.14 eV at $>80^\circ$. The presence of cation lone pairs strongly increases the mobility of the F^- ions.

1) Emphasis is given to materials with strong Li^+ ion-conductivity because of the high voltage and mass capacity expected in lithium batteries.

It has been shown recently that the solid solutions $Li_{4+x}B_7O_{12+x/2}Cl$ and $Li_{4+x}B_7O_{12+x/2}Br$ ($0 \leq x \leq 1$) with the boracite type structure have a very high ionic conductivity (of the order of $10^{-2} \Omega^{-1}cm^{-1}$ at $300^\circ C$). The lower the lithium content of these materials, the higher the conductivity - due to the increasing number of available vacancies [1].

This study has been extended to ternary glassy materials of composition $B_2O_3 - xLi_2O - yLiCl$ obtained by melting at $900^\circ C$ and then quenching the liquid melt. Such glasses should be much more convenient for use in batteries as thin layers than boracite type ceramics, which are difficult to sinter. The existence range is given in fig. 1. The composition limits are approximately $0 \leq x \leq 0.85$ and $0 \leq y \leq 0.85$ [2,3].

It has been shown that for a given x or y value the conductivity increases when the LiCl or Li_2O concentration rises. Fig. 2 and 3 show that for small chloride or oxide content this increase is very steep, but then it slackens progressively [4]. A corresponding decrease is observed in the activation energies, which are calculated from the Arrhenius law diagrams. Above $350^\circ C$ Li_2O and LiCl-rich materials are better ionic conductors than sodium β -alumina and they are much easier to handle.

The variation of σ and ΔE with x may be explained by the investigations of B.E. WARREN and J. BISCOE [5,6] on LiCl-free lithium borate glasses of composition $B_2O_3 - xLi_2O$. For small x values boron coordination changes from 3 to 4, involving a contraction of the glassy matrix : the weakening of the Li - O bonding

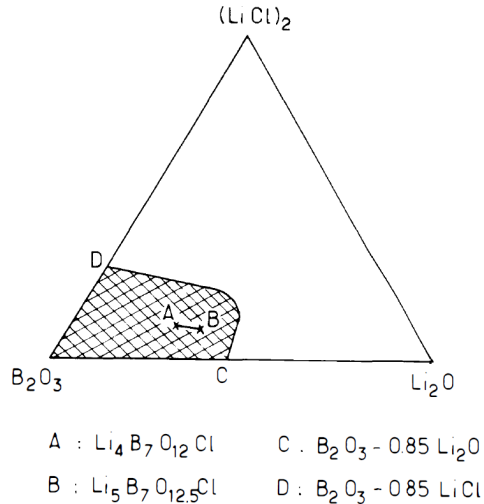


Fig. 1 : Existence range of the glassy materials in the system $B_2O_3-xLi_2O-yLiCl$

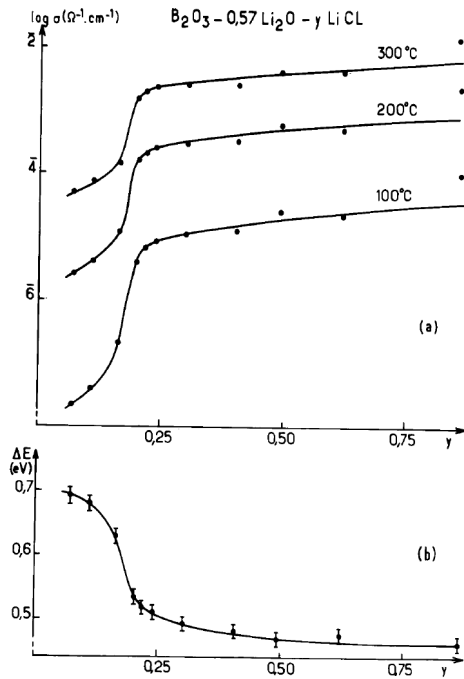


Fig. 2 : Variation of the conductivity and the activation energy of $\text{B}_2\text{O}_3 - 0.57\text{Li}_2\text{O} - y\text{LiCl}$ vs lithium chloride concentration at various temperatures

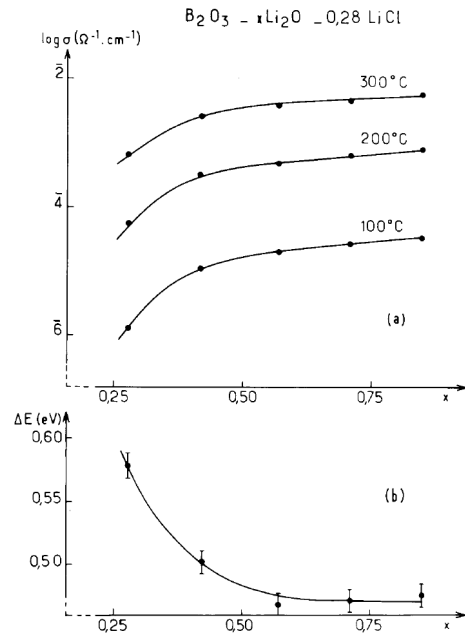


Fig. 3 : Variation of the conductivity and the activation energy of $\text{B}_2\text{O}_3 - x\text{Li}_2\text{O} - 0.28\text{LiCl}$ vs lithium oxide concentration at various temperatures

raises the mobility of the Li^+ ions. For higher x values the mobile ions are slowed-down by trapping due to non-bridging oxygen atoms : an excess of Li_2O breaks the sequences of the boron coordination polyhedra which for low x -values share oxygen-corners. Such an interpretation is confirmed by a ^{11}B NMR study [7]. IR and Raman spectroscopy illustrates also these structural modifications on the base of KONIJNENDIJK [8] and BRIL [9] assignments relative to pure alkali borate glasses [10].

LiCl additions lead to Li^+ and Cl^- ions "diluted" in the vitreous lattice. As a consequence the number of Li^+ carriers increases, bringing about a higher conductivity. When y becomes too high, Li^+ and Cl^- tend to associate, creating progressively microclusters of LiCl (fig. 4). At this stage the conductivity stops increasing [4].

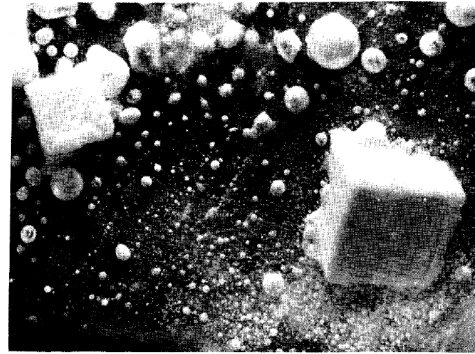


Fig. 4 : Microcrystallites of LiCl in a vitreous matrix of $\text{B}_2\text{O}_3 - x\text{Li}_2\text{O} - y\text{LiCl}$

The IR and Raman spectra are practically not modified by the LiCl additions, which supposes that the Li^+ and Cl^- do not interact with the boron-oxygen matrix [10] (fig. 5).

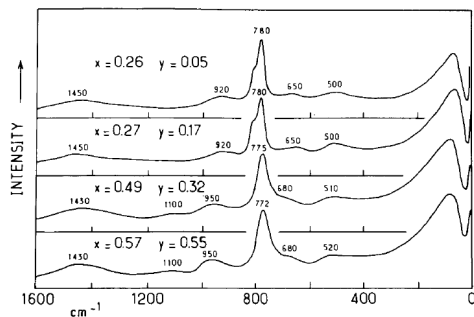


Fig. 5 : Raman spectrum of some $\text{B}_2\text{O}_3-x\text{Li}_2\text{O}-y\text{LiCl}$ glasses

^7Li NMR studies on the glasses show that at low temperature the movement of Li^+ ions is frozen in. A thin signal due to mobile ions appears only progressively at rising temperature on the expense of the rigid lattice signal. The temperature where all present Li^+ ions are involved in the conduction varies of course with composition. The inadequacy of a B.P.P. model indicates that there are probably several mobility mechanisms [3].

An ESR investigation after X-ray radiation gives rise for $0.18 < x < 0.30$ and $0.05 < y < 0.18$ to a signal characteristic of a Cl_2^- pair (ν_k center) (fig. 6). Such a center supposes that the Cl^- ions have a certain degree of freedom in the lattice, but are close enough to associate. When y increases it disappears because of the LiCl microcrystallite formation [11]. A BOHC center similar to those observed in LiCl-free alkali borate glasses also appears when x is high enough.

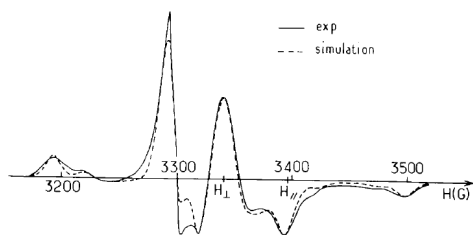


Fig. 6 : ESR spectrum of a Cl_2^- center (exper. and recal.)

Halogenoborate glasses with various halogens have been compared ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). Their existence range decreases with rising size of the halogen. It appears that the larger the X-ions, the higher the conductivity. Fig. 7 allows a compare σ vs y at 300°C for $\text{B}_2\text{O}_3 - 0.56\text{Li}_2\text{O} - y\text{LiX}$ glasses. This phenomenon may be the consequence either of a dilatation of the boron-oxygen matrix or of the higher polarizability of the halogen, both effects being able to increase the Li^+ ion mobility [12].

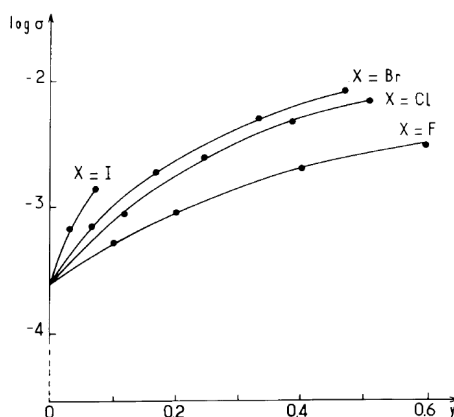


Fig. 7 : Variation of the logarithm of the conductivity at 300°C as a function of the LiX concentration in $\text{B}_2\text{O}_3-0.56\text{Li}_2\text{O}-y\text{LiX}$ glasses when X is fluorine, chlorine, bromine or iodine.

2) Investigations have also been performed on fast F^- ion conductors, such materials being better ionic conductors at the same temperature than the homologous oxides, where the O^{2-} is more strongly bound to the cationic sublattice. Emphasis is given to fluorite type materials, since in MF_2 compounds with this structure, half of the normal fluorine sites are available and also because of the ease with which F^- ions may occupy interstitial positions.

One could expect that the presence of extra fluorine atoms in the lattice would decrease the energy difference between normal and interstitial sites. This is confirmed by the complex impedance measurements on the $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$ solid solution ($0 < x < 0.50$), which is characterized by a conductivity maximum for $x \approx 0.25$ (fig. 8) [13]. This corresponds to a minimum of the activation energy (fig. 9). The conductivity is much higher and the activation energy much lower for the same F^- substitution rate in $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$ than in $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$ ($0 \leq x \leq 0.38$) (fig. 9): the higher polarizability of the Pb^{2+} and Bi^{3+} ions increase the mobility of the F^- ions.

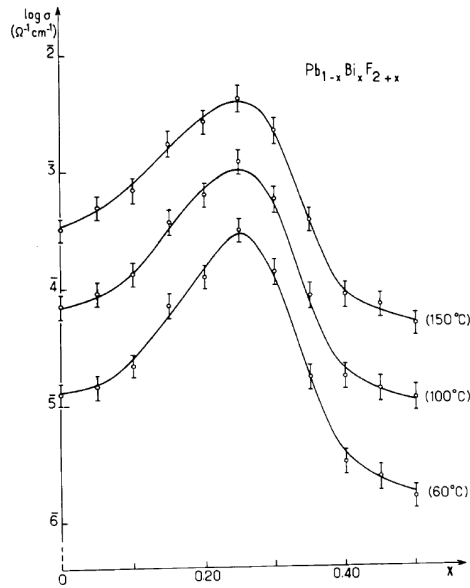


Fig. 8 : Conductivity isotherms of the $Pb_{1-x}Bi_xF_{2+x}$ solid solution as a function of x

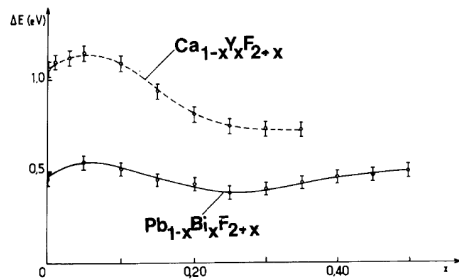


Fig. 9 : Variation of the activation energy for $Pb_{1-x}Bi_xF_{2+x}$ and $Ca_{1-x}Y_xF_{2+x}$

A neutron diffraction study on $Pb_{1-x}Bi_xF_{2+x}$ for $0.05 \leq x \leq 0.50$ shows that $x \approx 0.25$ corresponds to high disordering with many vacancies in the normal F_I sublattice sites and a large number of interstitial F_{II} atoms (fig. 10) [14]. When $x > 0.25$ the V_{F_I} vacancies in the F_I sublattice tend to associate with two F_{II} anions. New ordering appears, at first locally, and then in parallel long range files. Fig. 11

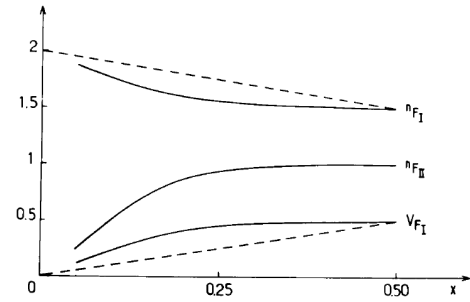


Fig.10 : Decrease with x of the number of F_I fluorine atoms in the normal sublattice and increase of the number of V_{F_I} vacancies and total interstitial F_{II} atoms for $Pb_{1-x}Bi_xF_{2+x}$. The dotted lines correspond to a formal substitution model $Pb^{2+} + F_I^- = Bi^{3+} + V_{F_I} + 2F_{II}^-$

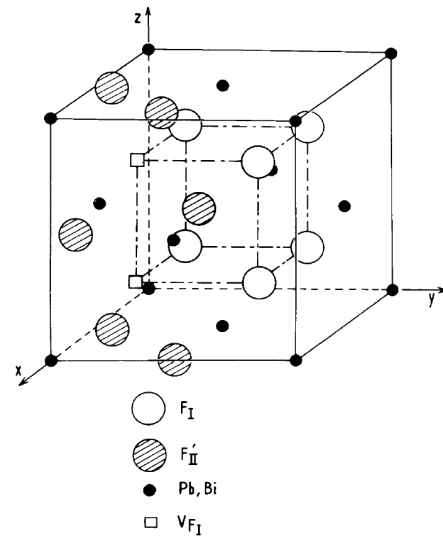


Fig.11 : Structure corresponding to the limit composition $Pb_{0.5}Bi_{0.5}F_{2.5}$

shows the new structural type which forms at $x = 0.50$: it gives rise to a superlattice with doubling of the a and b parameters. This ordering phenomenon explains the slight increase of the activation energy when $x > 0.25$: the F^- ions are blocked by a mobility barrier.

A similar conductivity behavior is observed for the fluorite type $Pb_{1-x}Th_xF_{2+2x}$ solid solution but the minimum of activation energy occurs at $x \approx 0.125$ (fig. 12). Therefore, the maximum of structural disordering seems again to correspond to an anion/cation ratio of 2.25 [15]. The minimum in activation energy is smaller for the lead-thorium compound than for the lead-bismuth material (0.32 eV instead of 0.39 eV), this may be due to the very high polarizability of thorium.

Relatively low activation energies have been found also for other fluorides of the fluorite type with a definite composition : $KBiF_4$

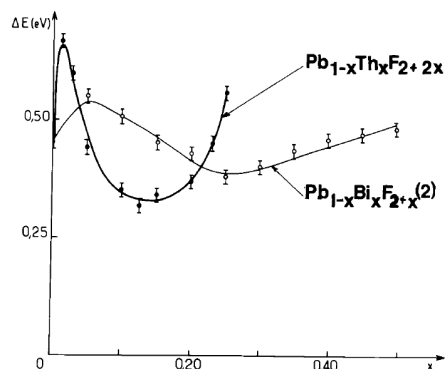


Fig. 12 : Comparison of the variation of the activation energies of both $Pb_{1-x}Th_xF_{2+2x}$ and $Pb_{1-x}Bi_xF_{2+x}$ solid solutions

$RbBiF_4$, $TlBiF_4$ [16]. The lone pair electron of Bi^{3+} seem obviously to favor the F^- mobility. A preliminary neutron diffraction study shows a strong tendency of the F^- ions to migrate into low energy interstitial positions in the vicinity of bismuth.

The best F^- ion conductor among the fluorite type structures is, so far, $PbSnF_4$, whose stable β -variety has at $100^\circ C$ a conductivity close to $10^{-1} \Omega^{-1}cm^{-1}$ with an activation energy of 0.14 eV. β - $PbSnF_4$ has an existence range between 80 and $355^\circ C$ [17]4. The lone pair of tin + II is probably responsible of such an outstanding behavior. A NMR study indicates the existence in both α and β low temperature phases of at least two conduction mechanisms, the fastest corresponding probably to migrations between normal F^- positions and the slowest between normal and interstitial sites [18].

Fig. 13 gives an overall view of the electrical performances of the best fluorine conductors which are reported here [19].

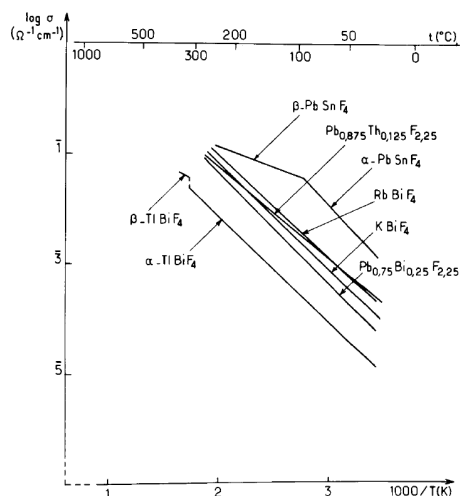


Fig. 13 : Variation of the logarithm of the conductivity vs temperature of some new fluorine-ion conductors

Some of our materials may be used as solid electrolytes in secondary batteries. Other applications are also possible, for instance, the detection of O_2 or CO_2 by a galvanic cell. Fig. 14 gives for example the response curve of the galvanic cell : $Bi/\beta-PbF_2/Bi$ under oxygen partial pressure with a 200 mV voltage. BiF_3 is formed at the Bi anode. Space charges appear

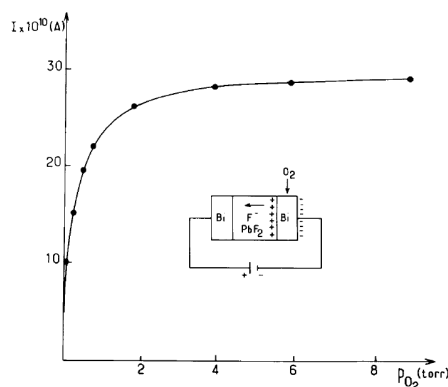


Fig. 14 : Response curve of $Bi|\beta-PbF_2|Bi$ galvanic cell under a 200 mV voltage as a function of oxygen partial pressure

at the Bi cathode due to the flux of electrons coming from the anode. They may be neutralized by oxygen. Formation of cathodic PbO allows the continuation of the electrolytic process [15].

These investigations show how important is the role of the chemist so far as there exists a need of fast ionic conductors working at a temperature as low as possible. But his predictions should be strongly facilitated by a good knowledge of the structural features and the bonding characteristics of the already known materials.

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