Fast Ionic Conduction of Fluorides with the Fluorite-Type Structure

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The authors have studied the $Ca_{1-x}Y_xF_{2+x}$ ($0 < x \leqslant 0.38$), $Pb_{1-x}Bi_xF_{2+x}$ ($0 < x \leqslant 0.50$), $Pb_{1-x}Th_xF_{2+2x}$ ($0 < x \leqslant 0.25$), $MBiF_4$ (M = K, Rb, Tl), and $PbSnF_4$ phases, which are outstanding conductors of the F^- ions. They give some quantitative information about the influence of various structural criteria on the electric properties of these materials.

The study of the F^- ion conductivity in a number of fluorides has permitted the definition of several criteria characteristic of high mobility (*1*):

—low entropy of fusion;

—vacancies in the anionic sublattice due to nonstoichiometry;

—high cation polarizability; and

—presence of cations having different oxidation states.

This article deals especially with the transport properties of fluorides with the CaF_2-type structure. In this structure there exists a central vacancy suitable for F^- ion diffusion. In addition, by a suitable choice of cations it can easily meet the above criteria. We will mention particularly here studies concerning some fluorides which have been investigated recently in collaboration with other workers: the solid solutions $Ca_{1-x}Y_xF_{2+x}$ (*2*), $Pb_{1-x}Bi_xF_{2+x}$ (*3*), and $Pb_{1-x}Th_xF_{2+2x}$ (*4*) as well as the phases $MBiF_4$ (M = K, Rb, Tl) (*5*) and $PbSnF_4$ (*6*).

Preparation and Experimental Techniques

The starting materials MF (M = K, Rb, Tl) and MF_2 (M = Ca, Pb, Sn) are ultrapure (Alfa). The trifluorides MF_3 (M = Y, Bi) and the tetrafluoride ThF_4 have been prepared in the laboratory from the corresponding oxides by reaction with a fluorinating gas (*7*). The various compounds studied have been prepared in sealed gold tubes and have a cylindrical form. These samples are sintered in sealed gold or platinum tubes at slightly lower temperatures than the melting or decomposition temperatures.

The gold electrodes are then deposited by evaporation under vacuum. The ionic conductivity measurements were made by the complex impedance method at frequencies between 20 Hz and 200 kHz (*8*). In the temperature range considered, the conductivity is expressed by the equation $\sigma = nq\mu_0 \exp(-\Delta E/kT)$, where n is the number of charge carriers of charge q and mobility $\mu = \mu_0 \exp(-\Delta E/kT)$, ΔE being the activation energy relative to the mobility.

Correlations between Electrical Properties and Structure

(i) Solid Solutions $Pb_{1-x}Bi_xF_2$ and $Pb_{1-x}Th_xF_{2+2x}$

The structure of the solid solutions $Pb_{1-x}Bi_xF_{2+x}$ $(0 < x \leqslant 0.50)$ and $Pb_{1-x}Th_xF_{2+2x}$ $(0 < x \leqslant 0.25)$ derives from the CaF_2 type.

The variation of $\log \sigma$ vs composition for these solid solutions is given in Fig. 1 (3, 4). A conductivity maximum has been observed for the solid solutions of bismuth and thorium at $x = 0.25$ and $x = 0.125$, respectively. These values correspond to the same

number of extra fluorines introduced in the matrix of β-PbF_2.

A neutron diffraction study by Cheetham et al. (9, 10) on the homologous solid solutions $Ca_{1-x}Y_xF_{2+x}$ $(0 < x \leqslant 0.38)$ had shown that the replacement of Ca^{2+} by Y^{3+} corresponds to the following substitutional model:

$$Ca^{2+} + F_I^- \rightarrow Y^{3+} + 2F_{II}^- + V_F,$$

with F_I^- = fluorine in a normal position of the fluorine sublattice of CaF_2, F_{II}^- = fluorine in an interstitial position, and V_F = vacancy in a normal position of the fluorine sublattice.
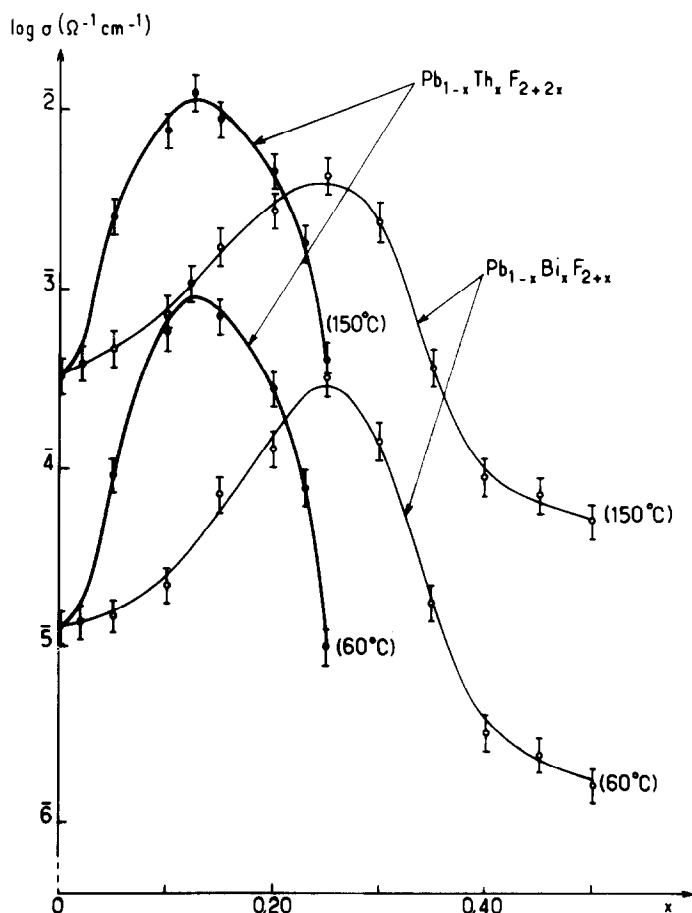

FIG. 1. Conductivity variation isotherms for $Pb_{1-x}Bi_xF_{2+x}$ $(0 < x \leqslant 0.50)$ and $Pb_{1-x}Th_xF_{2+2x}$ $(0 < x \leqslant 0.25)$.

The observed vacancy content was maximum for $x = 0.25$. This result could be related to the conductivity maximum and the activation energy minimum observed for this composition (2). Such findings can also be expected for the phases $Pb_{1-x}Bi_xF_{2+x}$ which also show a conductivity maximum for $x = 0.25$.

The conductivity maximum observed for $Pb_{1-x}Th_xF_{2+2x}$ corresponds exactly to the same number of extra fluoride ions, that is, to a substitution $x = 0.125$. If the structural changes were analogous to those observed in $Ca_{1-x}Y_xF_{2+x}$, the replacement of Pb^{2+} by Th^{4+} would correspond to the following substitutional model:

$$Pb^{2+} + 2F_I^- \rightarrow Th^{4+} + 4F_{II}^- + 2V_F.$$

A neutron diffraction study of the phases $Pb_{1-x}Bi_xF_{2+x}$ and $Pb_{1-x}Th_xF_{2+2x}$ would verify this hypothesis.

(ii) $MBiF_4$-Type Compounds ($M = K, Rb, Tl$)

The structure of the phases $KBiF_4$ and $RbBiF_4$ belongs to the fluorite type. On the other hand, $TlBiF_4$ has two allotropic forms: the low-temperature variety α characterized by an X-ray pattern similar to that of α-PbF_2, and the high-temperature variety β which is of the fluorite type. The reversible transition $\alpha \rightleftarrows \beta$ takes place at $310 \pm 10°C$.

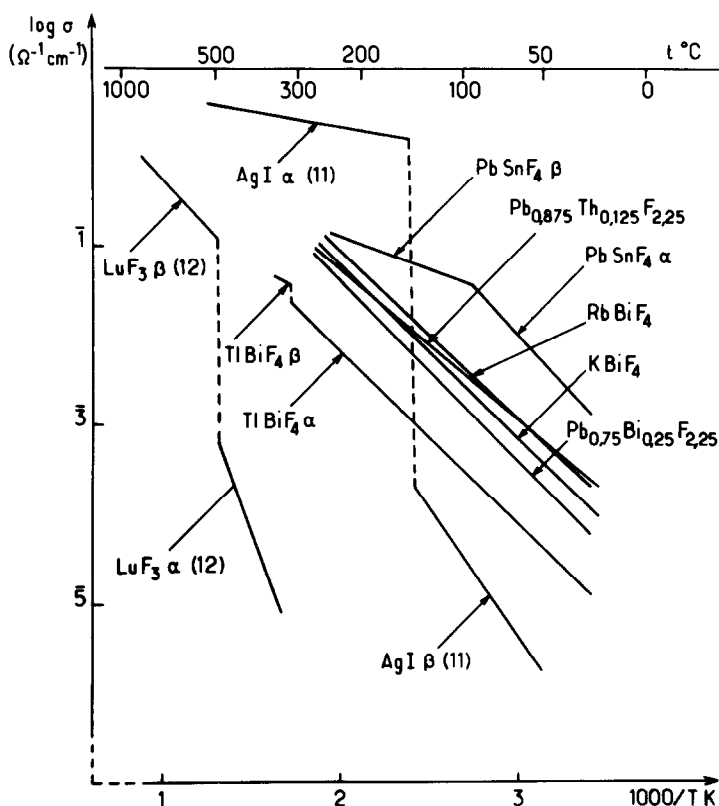The conductivity as a function of temperature for the $MBiF_4$ phases is compared in Fig. 2 to those of

FIG. 2. Variation of log σ as a function of reciprocal temperature for $KBiF_4$, $RbBiF_4$, α- and β-$TlBiF_4$, α- and β-$PbSnF_4$, $Pb_{0.75}Bi_{0.25}F_{2.25}$, $Pb_{0.875}Th_{0.125}F_{2.25}$, α- and β-AgI, and α- and β-LuF_3.

$Pb_{0.75}Bi_{0.25}F_{2.25}$ and $Pb_{0.875}Th_{0.125}F_{2.25}$ (5). Their performances are very similar.

At 310°C $TlBiF_4$ shows a discontinuity. In other words, at the $\alpha \rightleftarrows \beta$ transition point, a structural rearrangement and an electrical transition appear simultaneously. An analogous behavior has also been observed for AgI (11) and LuF_3 (12) (Fig. 2). It could correspond either to an entropy increase or to the formation of a crystallographically more "open" phase. Both hypotheses are favorable to an increased mobility. It seems that in this case the second hypothesis is more likely to occur (13).

(iii) The Lead Tin Fluoride $PbSnF_4$[1]

Three allotropic forms have been shown to exist by DTA and powder X-ray diffraction. The reversible transformations $\alpha \rightleftarrows \beta \rightleftarrows \gamma$ take place at about 80 and 355°C, respectively. The high-temperature γ-phase is of the fluorite type. The structures of the α- and β-phases, whose powder patterns can be indexed using orthorhombic and tetragonal unit cells, respectively, can be derived also from the fluorite structure.

We give in Fig 2 the conductivity variation as a function of temperature (6). A change of slope is observed at $t \approx 90°C$, which is near the $\alpha \rightleftarrows \beta$ transition temperature. There exists at this temperature, as was the case for $TlBiF_4$, both an electrical and a structural transition. However, in comparison to AgI (11), LuF_3 (12), and $TlBiF_4$, $PbSnF_4$ does not show a discontinuity in its conductivity at the transition point. This observation seems to confirm that the structures of α- and β-$PbSnF_4$ are very similar. As was the case with other fluorides, $PbSnF_4$ shows high electrical performances. The $PbSnF_4$ phase is at the moment the best-known anionic conductor.

Table I gives the conductivities at 20 and 150°C, as well as the corresponding activation energies.

[1] This work was carried out in collaboration with L. Cot, S. Vilminot, and G. Perez, Laboratoire de Chimie Minérale Appliquée, ENSCM de Montpellier.

TABLE I

CONDUCTIVITIES AT 20 AND 150°C AND ACTIVATION ENERGIES FOR $Pb_{0.75}Bi_{0.25}F_{2.25}$, $Pb_{0.875}Th_{0.125}F_{2.25}$, $KBiF_4$, $RbBiF_4$, α-$TlBiF_4$, AND α- AND β-$PbSnF_4$

	$\sigma_{20°C}$ $(\Omega^{-1} cm^{-1})$	$\sigma_{150°C}$ $(\Omega^{-1} cm^{-1})$	ΔE (eV)
$Pb_{0.75}Bi_{0.25}F_{2.25}$	6×10^{-5}	8×10^{-3}	0.39
$Pb_{0.875}Th_{0.125}F_{2.25}$	2×10^{-4}	2.5×10^{-2}	0.32
$KBiF_4$	10^{-4}	2×10^{-2}	0.38
$RbBiF_4$	2×10^{-4}	3×10^{-2}	0.37
α-$TlBiF_4$	10^{-5}	10^{-3}	0.38
α-$PbSnF_4$	10^{-3}		0.42
β-$PbSnF_4$		8×10^{-2}	0.14

Applications

These fluoride electrolytes are of great interest from the point of view of applications, and patents have been obtained (14–16). They can be used as ceramics or as thin films in galvanic cells, as specific electrodes for fluoride ions, or as gas detectors (1, 17–19). A secondary battery $Au|Pb_{0.75}Bi_{0.25}F_{2.25}|Au$ has been made giving a voltage of 1.25 V.

Figure 3 gives the response of the thin-film galvanic cell $Bi|\beta$-$PbF_2|Bi$ as a function of the oxygen partial pressure. This method of detection, which is both sensitive and inexpensive, is an original way of gas detection (20).

Thin-film electrochemical generators using β-PbF_2 have been made. Such rechargeable cells can be used as energy sources in the field of microelectronics (21).
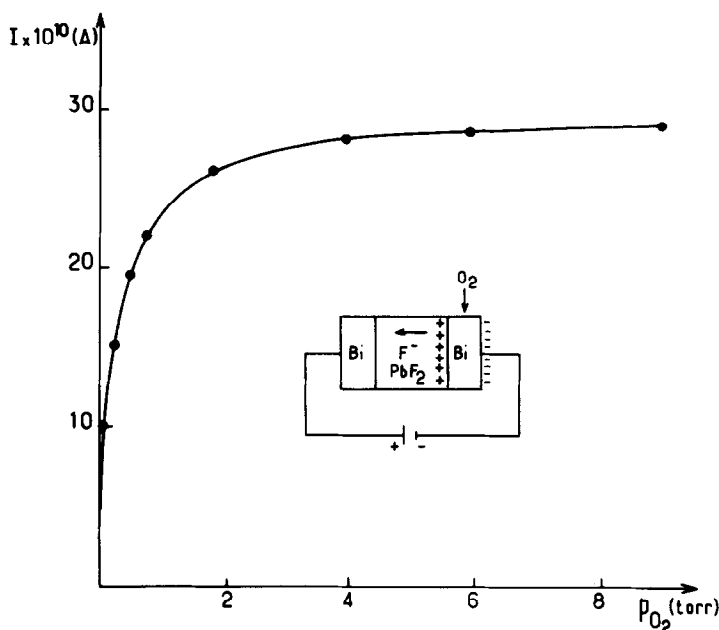
Acknowledgments

FIG. 3. Response curve of the galvanic cell Bi|β-PbF₂|Bi as a function of the oxygen partial pressure.

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