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ANIONIC CONDUCTIVITY OF SOME BISMUTH FLUORIDES WITH FLUORITE-TYPE STRUCTURE

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SUMMARY

The transport properties of fluorite-type $Na_{1-x}Bi_xF_{1+2x}$ $(0.60 \leqslant x \leqslant 0.70)$, $K_{1-x}Bi_xF_{2+x}$ $(0.50 \leqslant x \leqslant 0.70)$, $Rb_{1-x}Bi_xF_{1+2x}$ $(0.50 \leqslant x \leqslant 0.60)$ and $Pb_{1-x}Bi_xF_{2+x}$ $(0 \leqslant x \leqslant 0.50)$ solid solutions have been studied. They are all anionic superconductors. Some of them could be used as electrolytes in solid galvanic cells.

INTRODUCTION

As is well known, electrolytic oxides with CaF_2-type structure whose conduction is due to O^{2-} ions have good perfomances only at high temperature ($t > 600^oC$) [1,2]. On the contrary, isostructural fluorides have a significant anionic conduction at relatively low temperatures. This property is obviously a consequence of the greater mobility of the F^- ions, as a result of smaller electric charge and less covalent bonding. Furthermore fluorides are excellent electronic insulators, an essential property for using them as electrolytes in electrochemical batteries [3].

The factors responsible for high ionic conductivity in solid electrolytes have been determined in several exhaustive studies [3,4]. In particular, a study of F^- ion conductivity in a large number of fluorides has permitted the definition of some criteria for high mobility in fluorides [5] :

-vacancies in the anionic sublattice due to non-stoichiometry. For instance, the fluorite, tysonite and YF_3-type structures can lead to non-stoichiometric MF_{2+x} or MF_{3-x} phases in which deviations from stoichiometry make available new vacancies for ionic conduction ,

- high cationic polarizability. For a series of homologous fluorides with similar structure, the larger the polarizability of the cation, the higher the ionic conductivity ,
- low coordination number of the mobile species. As for cationic conductors [6], fast ionic conduction is favored in fluorides for carriers with low coordination numbers ,
- low melting point and low entropy of melting.

A quasi-liquid state of the mobile species within the mobile sublattice of a material will appear at lower temperature the lower the melting point. A good example is given by fluorite-type CaF_2 and β-PbF_2, whose melting temperatures are much below that of zirconia or thoria, but where anionic conductivity is also much higher at the same temperature.

From all these considerations we have investigated fluorides with fluorite-type structure, since, in MF_2 compounds with this structure, the cationic octohedral sites are only half occupied, which makes the other half avaiblable for interstitial fluorides [7]. Furthermore, since the Bi^{3+} ion has a high polarizability, we have investigated the MF-BiF_3 (M = Na, K, Rb) and PbF_2-BiF_3 systems and studied the transport properties of $M_{1-x}Bi_xF_{1+2x}$ and $Pb_{1-x}Bi_xF_{2+x}$ solid solutions with fluorite-type structures.

SAMPLE PREPARATION AND CRYSTAL CHEMICAL ANALYSIS

The $M_{1-x}Bi_xF_{1+2x}$ (M = Na, K, Rb) and $Pb_{1-x}Bi_xF_{2+x}$ have been obtained by synthesis from binary fluorides BiF_3 and MF (or PbF_2). Due to their sensitivity to moisture, starting materials in suitable proportions are mixed in the dry atmosphere of a glove box, then they are introduced into gold tubes and heated under vaccum at 150°C. The tubes are sealed in a dry argon atmosphere. The reactions are carried out over 15 hours at temperatures varying from 430°C up to 500°C according to the starting materials.

X-ray diffraction analysis of the phases obtained by quenching from working temperature shows the existence in each system of a solid solution with a structure of the fluorite-type :

$Na_{1-x}Bi_xF_{1+2x}$	$0.60 \leqslant x \leqslant 0.70$	(430°C)
$K_{1-x}Bi_xF_{1+2x}$	$0.50 \leqslant x \leqslant 0.70$	(450°C)
$Rb_{1-x}Bi_xF_{1+2x}$	$0.50 \leqslant x \leqslant 0.60$	(450°C)
$Pb_{1-x}Bi_xF_{2+x}$	$0 \leqslant x \leqslant 0.50$	(500°C)

No faint lines resulting from a possible superstructure could be detected in the Guinier-Hägg spectra. Consequently the solid solutions seem to be disordered. However, a neutron diffraction study of $Pb_{1-x}Bi_xF_{2+x}$ has shown that the $Pb_{0.50}Bi_{0.50}F_{2.50}$ limiting composition is ordered [8].

The variation of the lattice parameters in $M_{1-x}Bi_xF_{1+2x}$ solid solutions is shown in Fig. 1. Such an evolution is not surprising because the size of Bi^{3+}, which is smaller than Rb^+ or K^+, approximates to that of Na^+. With the substitution of the cations by Bi^{3+}, there simultaneously occurs an insertion of two F^- ions into interstitial positions : this latter effect is more sensitive in sodium phases, involving a lattice dilatation.

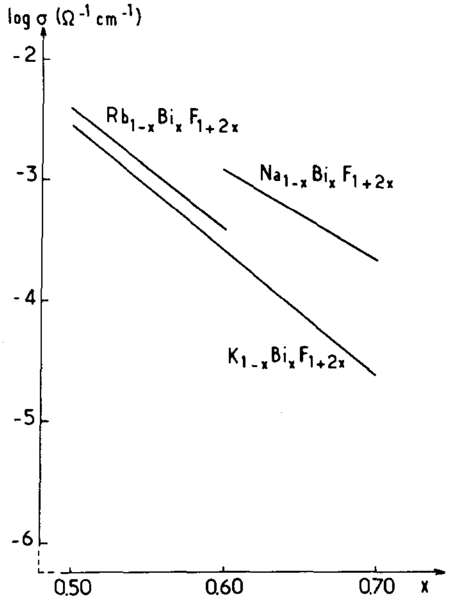


Fig. 1. Variation of the lattice parameters of the $M_{1-x}Bi_xF_{1+2x}$ phases with composition.

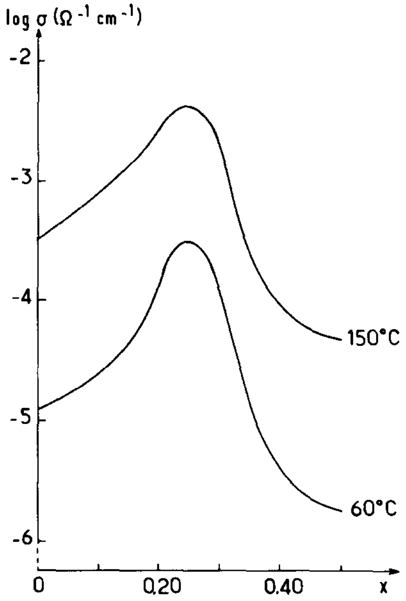


Fig. 2. Variation of the specific mass of the $Na_{1-x}Bi_xF_{1+2x}$ system with composition.

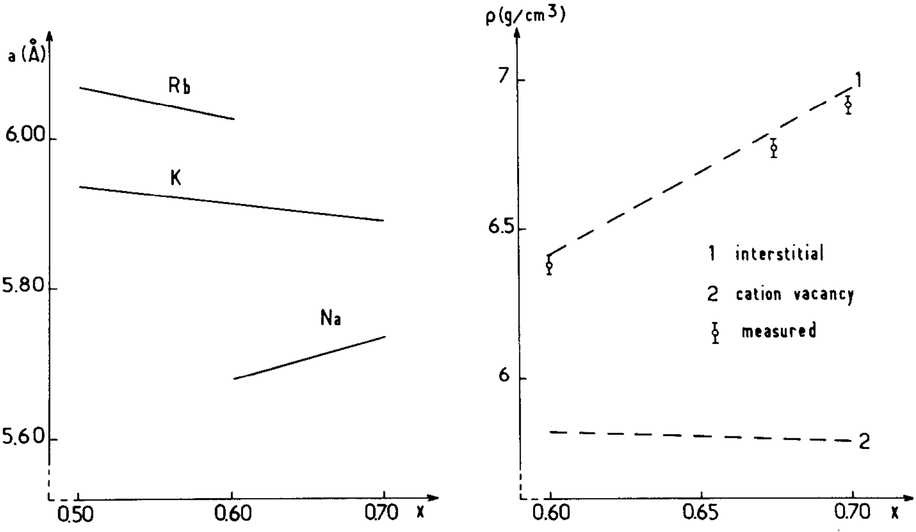
A similar variation of the parameter is observed with increasing x in $Pb_{1-x}Bi_xF_{2+x}$ ($a_{cub.}$ = 5.939 ± 0.002 Å for x = 0; $a_{cub.}$ = 5.894 ± 0.002 Å for x = 0.50).

Anionic insertion in interstitial sites has been confirmed by specific mass measurements on the $Na_{1-x}Bi_xF_{1+2x}$ solid solution (Fig. 2).

CONDUCTIVITY MEASUREMENTS

Samples are used as pellets, heated first under vacuum at 100°C, then sintered at suitable temperature for 15 hours in gold sealed tubes under dry nitrogen. Their compactness is close to 90 %. Gold electrodes are deposited by vacuum evaporation. Electrical properties have been studied with A.C. between 10^{-2} and 10^4 Hz by the complex impedance method [9]. Measurements have been carried out between 20 and 250°C for several cycles of temperature.

Fig. 3 gives the variation of log σ as a function of x for $M_{1-x}Bi_xF_{1+2x}$ (M = Na, K, Rb) and $Pb_{1-x}Bi_xF_{2+x}$ solid solutions. When x increases, decreasing conductivity is observed, independent of the nature of M, for $M_{1-x}Bi_xF_{1+2x}$.



(a) (b)

Fig. 3. Conductivity variation isotherms for $M_{1-x}Bi_xF_{1+2x}$(a) at 100°C and $Pb_{1-x}Bi_xF_{2+x}$ (b) at 60°C and 150°C.

On the contrary, a maximum of conductivity is observed for x = 0.25 in $Pb_{1-x}Bi_xF_{2+x}$. A minimum of activation energy is associated with the conductivity maximum. A neutron diffraction study of $Pb_{1-x}Bi_xF_{2+x}$ shows that a disordering maximum appears for the $Pb_{0.75}Bi_{0.25}F_{2.25}$ composition which contains an important number of normal site vacancies and interstitial fluorine ions [8] .

In the same way, $K_{0.50}Bi_{0.50}F_2$ and $Rb_{0.50}Bi_{0.50}F_2$ which have the best electrical performances in $K_{1-x}Bi_xF_{1+2x}$ and $Rb_{1-x}Bi_xF_{1+2x}$ solid solutions, are characterized by a disordering maximum [10] .

Table I gives the values of the conductivity at 50°C and 100°C and the activation energy for the limiting compositions of $M_{1-x}Bi_xF_{1+2x}$ and $Pb_{0.75}Bi_{0.25}F_{2.25}$. $Na_{0.40}Bi_{0.60}F_{2.20}$, $K_{0.5}Bi_{0.5}F_2$, $Rb_{0.5}Bi_{0.5}F_2$ and $Pb_{0.75}Bi_{0.25}F_{2.25}$ have high electrical performances; these bismuth compounds are among the best conductors of F^- ions.

TABLE I

Conductivities at 50°C and 100°C and activation energies for some investigated solid solutions

	σ (50°C) $\Omega^{-1}.cm^{-1}$	σ (100°C) $\Omega^{-1}.cm^{-1}$	ΔE(eV)
$Pb_{0.75}Bi_{0.25}F_{2.25}$	3.10^{-4}	2.10^{-3}	0.39
$Rb_{0.50}Bi_{0.50}F_2$	10^{-3}	5.10^{-3}	0.37
$K_{0.50}Bi_{0.50}F_2$	7.10^{-4}	4.10^{-3}	0.38
$Na_{0.40}Bi_{0.60}F_{2.20}$	$1.5.10^{-4}$	10^{-3}	0.46
$Rb_{0.40}Bi_{0.60}F_{2.20}$	10^{-4}	7.10^{-3}	0.44
$K_{0.30}Bi_{0.70}F_{2.40}$	3.10^{-6}	4.10^{-5}	0.48
$Na_{0.30}Bi_{0.70}F_{2.40}$	10^{-5}	2.10^{-4}	0.62

CONCLUSIONS

Due to the good performances of the investigated materials, which are also excellent electronic insulators, their use as electrolytes in electrochemical batteries may be considered. Encouraging results have been obtained in particular for $K_{0.50}Bi_{0.50}F_2$ [11] . These successful preliminary attempts will induce us to investigate galvanic cells associating various solid electrolytes with graphite fluorometallate salts. The feasibility of such batteries has been demonstrated [12] .

REFERENCES

1 J.W. Patterson, E.C. Bugrew and R.A. Rapp, J. Electrochem. Soc., 114 (1967) 752.

2 A. Hammou, Ch. Deportes and G. Robert, J. Chem. Phys., 7-8 (1971) 1162.

3 M. Pouchard and P. Hagenmuller, Solid Electrolytes; Solid Electrolytes as a material problem, chap. 12, (edited by P. Hagenmuller and W. Van Gool), Academic Press, 1978.

4 R.D. Armstrong, R.S. Bulmer and T. Dickinson, J. Solid State Chem., 8 (1973) 219.

5 J.M. Réau and J. Portier, Solid Electrolytes; Fluorine ion conductors, chap. 19, (edited by P. Hagenmuller and W. Van Gool), Academic Press, 1978.

6 R.D. Armstrong, R.S. Bulmer and T. Dickinson, Fast Ion Transport in Solid, Colloq., p. 269, (Edited by W. Van Gool), Belgirate, Italy, 1972.

7 A.K. Cheetham, B.E.F. Fender and M.J. Cooper, J. Phys. Chem., Solid State Phys., 4 (1971) 3107.

8 C. Lucat, J. Portier, J.M. Réau, P. Hagenmuller and J.L. Soubeyrous, J. Solid State Chem., 32 (1980) 279.

9 J.F. Bauerle, J. Phys. Chem., 30 (1969) 2657.

10 J.L. Soubeyroux, J.M. Réau, S. Matar, G. Villeneuve and P. Hagenmuller, Solid State Ionics, in press.

11 J. Grannec, C. Lucat and J. Portier, Private communication.

12 J. Grannec, C. Lucat, E.M. McCarron. J. Portier, N. Bartlett and P. Hagenmuller, J. Electrochem. Soc., in press.