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STRUCTURAL AND ELECTRICAL STUDIES OF THE PbF_2-BiOF SYSTEM

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ABSTRACT

An investigation of the PbF_2-BiOF system at 600°C has allowed isolation of a $Pb_{1-x}Bi_xO_xF_{2-x}$ solid solution ($0< x \leqslant 0.80$). For $x \leqslant 0.66$ the structure is of fluorite type and for $0.66< x \leqslant 0.80$ it undergoes a fluorite derived rhombohedral distortion. The transport properties of $Pb_{1-x}Bi_xO_xF_{2-x}$ are for $x \geqslant 0.50$ as good as those of the best fluorides.

INTRODUCTION

Many solid solutions with fluorite type structure have been recently investigated in order to find solid electrolytes with high fluoride ion conduction [1,2]. The purpose was the synthesis of materials with favourable conductivities for new electrochemical devices. The best properties were obtained when the host matrix was β-PbF_2 where Pb^{2+} has a strong polarizability [2].

The influence of cationic impurities in the matrix on the electrical properties of β-PbF_2 has been investigated [3 to 9]. A minimum of conductivity associated with a maximum of activation energy appears in solid solutions of lead difluoride for a very small value of x $|x \simeq 0.01$ for $Pb_{1-x}M'_xF_{2+x}$ (M' = Sb, Bi), $x \simeq 0.005$ for $Pb_{1-x}M''_xF_{2+2x}$ (M" = Zr, Th)$|$ [9]. In the same way it was reasonable to predict that oxygen ion impurities may modify the electrical properties of β-PbF_2. In fact the conductivity decreases as the amount of O^{2-} increases in BiO_xF_{3-2x} ($0.09< x \leqslant 0.10$) solid solution, which has a tysonite type structure [10]. Therefore it appeared important to us to determine the influence of the

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replacement in β-PbF_2 of F^- by O^{2-} anions on its electrical properties. Consequently we have carried out a study of ionic conduction of the PbF_2-BiOF system where there was likely to be a structural type deriving from fluorite over a wide composition range.

EXPERIMENTAL

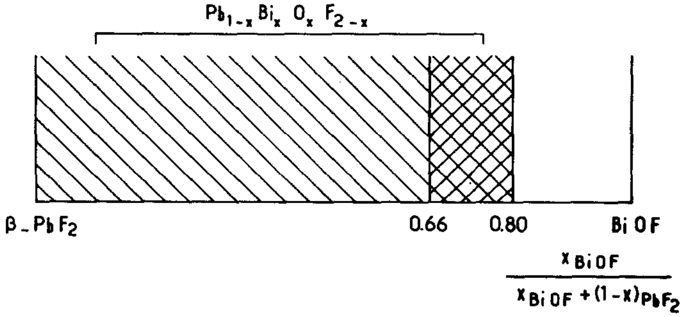
The starting lead fluoride was α-PbF_2 of purity 99.9 %. BiOF was prepared by synthesis from BiF_3 and Bi_2O_3 in equimolar proportions. The homogenized mixture was introduced into a gold tube and heated under vacuum at 200°C for 2 hours to remove residual moisture. The container was then sealed under a dry argon atmosphere. Reaction was allowed to occur over 12 hours at 600°C. BiOF thus obtained has the X-ray pattern previously identified by B. AURIVILLIUS [11,12].

The various compositions of the PbF_2-BiOF system have been studied under the same experimental conditions as BiOF. The reactions are complete after 12 hours heating at 600°C.

Radiocristallographic study

Phase identifications were made from X-ray diffraction patterns on a Philips diffractometer using CuKα radiation. Unit-cell dimensions are obtained by computer minimization of the differences between calculated and observed d_{hkl} values. X-ray diffractograms are scanned at 1°/mn using silicon as internal standard.

Radiocristallographic analysis of the phases obtained by quenching from 600°C shows the presence in the PbF_2-BiOF system of (fig. 1) :



- a disordered cubic solid solution of composition $Pb_{1-x}Bi_xO_xF_{2-x}$ $(0 < x \leqslant 0.66)$. The structure is of the fluorite type.
- for $0.66 < x \leqslant 0.80$ the solid solution shows a progressive deformation of the fluorite cell with increasing x. There is a splitting of the fluorite reflections typical of a rhombohedral distortion (Table I).

TABLE I

Splitting of fluorite type reflections typical of a rhombohedral distortion for $Pb_{0.20}Bi_{0.80}O_{0.80}F_{1.20}$

$a_{hex.} = 4.060$ Å		$c_{hex.} = 20.32$ Å	
hkl cub.	**hkl hex.**	$d_{calc.}$	$d_{obs.}$
111	006	3.39	3.36
	012	3.32	3.28
002	104	2.891	2.891
220	018	2.059	2.069
	110	2.030	2.026
311	$10\underline{10}$	1.760	1.761
	116	1.741	1.748
	202	1.732	1.729
222	$00\underline{12}$	1.693	1.691

Such a deformation of the fluorite unit-cell has been reported previously in studies of fluorides [13] and oxide fluorides [14]. Fig. 2 shows the evolution of the distortion of the fluorite cell with composition for $0.66 < x \leqslant 0.80$.

- for $0.80 < x < 1$ a two phase domain appears with $Pb_{0.20}Bi_{0.80}O_{0.80}F_{1.20}$ and BiOF in equilibrium.

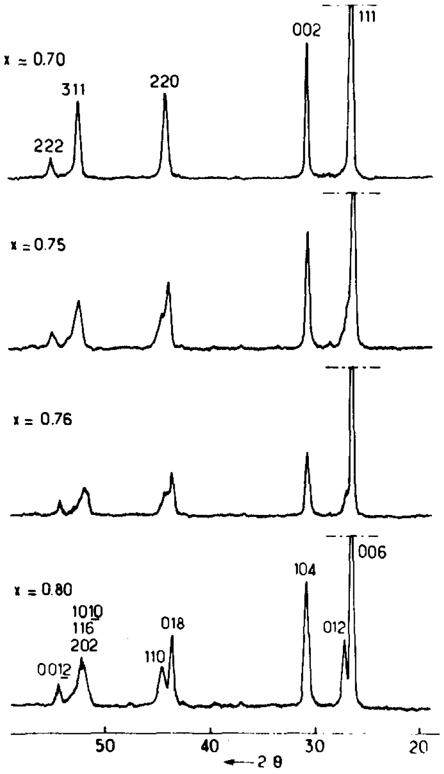


Fig. 2. Progress of the distortion of the fluorite cell with composition for $Pb_{1-x}Bi_xO_xF_{2-x}$ $(0.66 < x \leqslant 0.80)$.

The unit-cell parameter of the cubic solid solution decreases linearly with x from 5.940 ± 0.005 Å for x = 0 to 5.840 ± 0.005 Å for x = 0.66. Study of the variation of density as a function of composition shows that the replacement of Pb^{2+} by Bi^{3+} in PbF_2 occurs by a direct substitution. As a consequence, the size difference between O^{2-} and F^- being very small, the decrease of the parameter with x is only because of replacement of Pb^{2+} by Bi^{3+}.

For $0.66 < x \leqslant 0.80$ there is a decrease in unit-cell volume (Table II).

TABLE II

Unit-cell volumes of $Pb_{1-x}Bi_xO_xF_{2-x}$ for x = 0.66 and 0.80.

x = 0.66	a_{cub} = 5.840 Å	V = 199.16 $Å^3$ (Z = 4)	V/Z = 49.80 $Å^3$
x = 0.80	$a_{hex.}$= 4.060 Å $c_{hex.}$= 20.32 Å $a_{rhomb.}$=7.168Å $\alpha_{rhomb.}$= 32.9°	$V_{hex.}$=290.1$Å^3$ $Z_{hex.}$ = 6	V/Z = 48.35 $Å^3$

Electrical conductivity study

For each composition a powder sample is pressed to form a pellet which is heated for 12 hours at 600°C in a large gold tube sealed under argon. The compactness of the pellets is about 90 %. Vacuum evaporated gold is used as electrodes. The bulk resistance is measured by the complex impedance method using a " Solartron 1170" frequency response analyser [15]. The frequency range used is 5Hz - 10 kHz and measurements are carried out for several cycles of temperature between 25 and 200°C.

In fig. 3 we show the temperature dependence of the conductivity for several compositions of the $Pb_{1-x}Bi_xO_xF_{2-x}$ solid solution ($0 < x \leqslant 0.80$). In the temperature range considered σ can be expressed as $\sigma = A/T\exp.(-\Delta E/kT)$ where A is constant and ΔE the activation energy related to the diffusive motions of carriers.

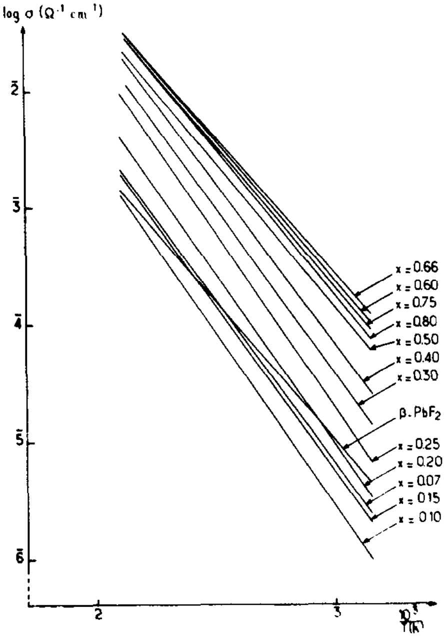


Fig. 3. Variation of log σ with reciprocal temperature for different compositions of the $Pb_{1-x}Bi_xO_xF_{2-x}$ solid solutions.

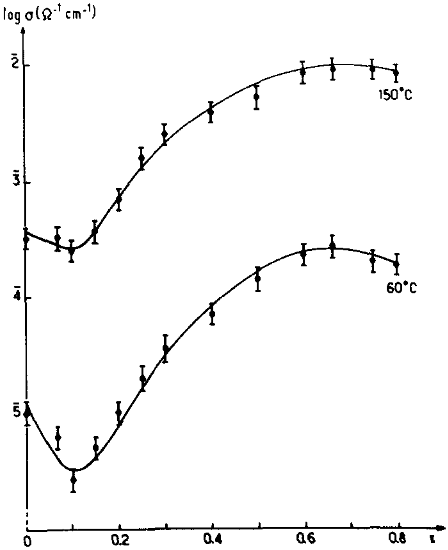


Fig. 4. Variation of log σ with x for $Pb_{1-x}Bi_xO_xF_{2-x}$ solid solutions at two temperatures.

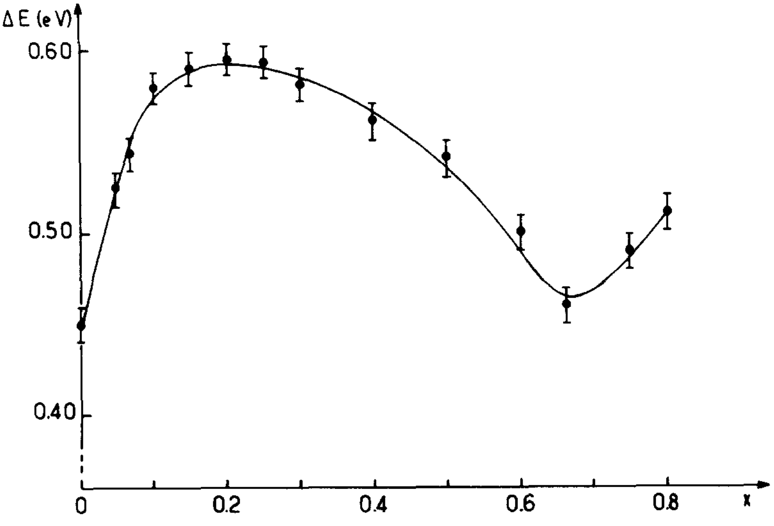


Fig. 5. Variation of activation energy with x for $Pb_{1-x}Bi_xO_xF_{2-x}$ solid solutions.

Figures 4 and 5 give isotherms of conductivity and the variation of the activation energy ΔE as a function of substitution. Three regions may be detected.

- for $0 < x \leqslant x_1$ with $x_1 \simeq 0.15 \pm 0.05$, when x increases, there is lowered conductivity associated with increasing ΔE.
- for $x_1 < x \leqslant 0.66$ on the contrary the conductivity increases with x and the activation energy decreases.
- for $0.66 < x \leqslant 0.80$ the conductivity decrease is again observed whereas activation energy increases.

DISCUSSION

Measurements of transport number have been attempted for the composition $Pb_{0.70}Bi_{0.30}O_{0.30}F_{1.70}$ of $Pb_{1-x}Bi_xO_xF_{2-x}$ solid solution. The e.m.f. method applied to $Bi|BiF_3|Pb_{0.70}Bi_{0.30}O_{0.30}F_{1.70}|Sn|SnF_2$ galvanic cell at 60°C involves no appreciable electronic conduction in this electrolyte.

On the other hand it seemed to us reasonable to suppose that, in the range of temperature studied, the O^{2-} ion transport is negligible in $Pb_{1-x}Bi_xO_xF_{2-x}$.

We have shown above that the introduction of small amounts of BiOF into β-PbF_2 gives less favourable electrical performance characterized by a minimum of conductivity associated with a maximum of activation energy for $x_1 \simeq 0.15 \pm 0.05$. Similarly a detailed study of the transport properties of the $Pb_{1-x}M'_xF_{2+x}$ (M' = Sb, Bi) and $Pb_{1-x}M''_xF_{2+2x}$ (M" = Zr, Th) solid solutions has previously shown that for very small values of x (x = 0.010 for $Pb_{1-x}M'_xF_{2+x}$, x = 0.005 for $Pb_{1-x}M''_xF_{2+2x}$) these solid solutions have a conductivity minimum corresponding to a maximum of activation energy [9]. Several hypotheses have been proposed to explain these results. The increasing ΔE shown for very small values of x could be due to the tendency for the first M^{3+} or M^{4+} cations introduced into β-PbF_2 to trap locally the residual traces of oxygen [9]. The results obtained for $x < x_1$ in $Pb_{1-x}Bi_xO_xF_{2-x}$ seem to confirm this hypothesis.

J. SCHOONMAN et al. [10] have shown that the electrical conductivity of the BiO_xF_{3-2x} solid solution $(0.09 < x \leqslant 0.10)$, in which the mobile species is fluoride, appears to decrease as x increases. This result seems to contradict the proposal that the existence of vacancies in the anion sublattice favors conduction. It appears, therefore, that in this system oxygen blocks the conduction. It is reasonable to think that the stronger Bi-O bond induces a weaker contribution of the cationic polarizability to F^- ion mobility.

It appears that, independently of the structural type, the introduction of small amounts of oxygen into the fluorides lowers electrical performance.

The existence for $Pb_{1-x}Bi_xO_xF_{2-x}$ of a minimum of conductivity for $x = x_1$ and the changes of electrical properties for $x_1 < x \leqslant 0.66$ are difficult to explain. Neutron diffraction studies carried out with ^{19}F and ^{18}O may allow the possibilities of determining their distribution over the normal F_I and interstitial F_{II} sites of the CaF_2-type lattice as a function of x. The change of σ and ΔE with x could be then understood. In fact neutron diffraction studies of the fluorite type solid solutions $Pb_{1-x}Bi_xF_{2+x}$ $(0 < x \leqslant 0.50)$ [16] and $Pb_{1-x}Th_xF_{2+2x}$ $(0 < x \leqslant 0.25)$ [17] had allowed the determination of the distribution of fluorine between normal and interstitial sites as a function of the amount of substitution. An atomic density has been shown for interstitial anions. Electrical and structural data have been correlated and two conductivity mechanisms proposed according to whether the ionic pathway is free or blocked. The best conductivities are obtained for the compositions of solid solutions which correspond to a maximum of vacancies.

The $Pb_{1-x}M'_xF_{2+x}$ and $Pb_{1-x}M''_xF_{2+2x}$ solid solutions are different from $Pb_{1-x}Bi_xO_xF_{2-x}$ which apparently has the stoichiometric fluorite formulation TX_2 (T = Pb, Bi; X = F,O) independently of x. However, it is reasonable to think that the presence of foreign cations in β-PbF_2 involves local disordering and shifting of anions from normal sites to interstitial ones with formation of vacancies. This occurs in β-PbF_2 itself, whose F_I sites are partly depopulated, as temperature increases, in favour of F_{II} sites [18].

Although we do not at present have available the structural data of $Pb_{1-x}Bi_xO_xF_{2-x}$ by neutron diffraction, we put forward a few hypotheses. Let us suppose that oxygen can be either in a F_I(normal) or in a F_{II}(interstitial) site [19]. There are three possibilities :

Hypothesis 1

Suppose that the O^{2-} anions are preferentially located in interstitial sites. Since O^{2-} is not likely to be mobile in the temperature range of our measurements, the mobility of the carrier F^- becomes weaker when x increases and conductivity decreases. This hypothesis could explain easily the variation of the electrical properties of $Pb_{1-x}Bi_xO_xF_{2-x}$ for $x < x_1$, but unfortunately cannot account for the development of conductivity for $x_1 < x < 0.66$. It contradicts also the probable presence of oxygen close to highly charged bismuth cations.

Hypothesis 2

We may also suppose that the O^{2-} anions are mostly located in normal F_I sites. It would result in shifting of fluorine atoms from F_I sites to F_{II} sites. Such an anionic distribution can account for the improvement of electrical properties for $x_1 < x \leqslant 0.66$, but does not give a clear explanation of the conductivity decrease for $x < x_1$, unless this is considered to be simply a consequence of the strong Bi-O bonds, which supposes preferential presence of oxygen in the vicinity of bismuth.

Hypothesis 3

To account for the development of the electrical properties of $Pb_{1-x}Bi_xO_xF_{2-x}$ for $0 < x \leqslant 0.66$, it is possible also to suppose that oxygen anions are located in both F_I and F_{II} sites, but that the proportion of oxygen present in F_{II} sites is greater than in F_I sites for $0 < x < x_1$, but becomes smaller for $x_1 < x < 0.66$. We could thus explain why the value of x_1, for which an activation energy maximum appears, is not clearly determined.

For $0.66 < x \leqslant 0.80$, a decrease of conductivity is observed associated with an increase of activation energy. Simultaneously the solid solution shows a growing rhombohedral distortion with increase in x. Local ordering is likely to become more important when x increases, and to lead to lower conductivities. It should be possible to identify locally wide domains containing layers of $|Bi_2O_2|^{2+}$ and F_2^{2-} as in BiOF with a tendency to a quasi-bidimensional conductivity

The study of $Pb_{1-x}Bi_xO_xF_{2-x}$ by neutron diffraction will allow a check on all these hypotheses.

The change of the transport properties with x of the $Pb_{1-x}Bi_xO_xF_{2-x}$ solid solution shows that for $x \geqslant 0.50$ conductivities are good ($\sigma_{150°C} \simeq 10^{-2}\ \Omega^{-1}cm^{-1}$), comparable to that of $Pb_{0.75}Bi_{0.25}F_{2.25}$ [1]. Furthermore the introduction of oxygen in β-PbF_2 gives the oxide fluoride a higher thermal stability. This result associated with good electrical performance makes this class of materials quite suitable for applications in all-solid batteries.

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