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Optimization of fluoride ion conduction in new fluorite-type anion excess solid solutions involving two substitutional cations

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New fluorite-type anion excess phases have been prepared within the $\text{PbF}_2\text{-M}'\text{F}_3\text{-ZrF}_4$ ($\text{M}' = \text{In, Bi}$) systems involving simultaneously trivalent and tetravalent cations. The materials showing the highest ionic conductivity are characterized by presence of column clusters of ($n=2$) size and by values of the Zr/In and Bi/Zr ratios close to 1/2. The obtained results are discussed on the base of a previously set up clustering model.

1. Introduction

The fluorite-type $\text{M}'_{1-x}\text{M}_x^{2+\alpha}\text{F}_{2+\alpha x}$ solid solutions, disordered at long range, are characterized by a short range ordering under the form of defect clusters. The F^- conduction mechanisms in these materials depend largely on the nature of the clusters which form progressively at rising substitution rate. Their determination based on various and complementary techniques such as neutron diffraction and ^{19}F NMR is supported by a clustering model [1]. Correlations between structural data and ionic conductivity properties have allowed us to show that the substitution rate x_{max} for which a maximum of conductivity associated with a minimum of activation energy can be observed is close to both x_s rate for which the number of fluoride ions (F_i)_m responsible for long range motions is the highest and to the value for which the diffusion of the mobile ions is the fastest [1]. According to this model the sum of fluoride ions representing each type of interstitial anions and the amount of vacancies in the normal sites of the fluorite-type lattice can be respectively represented by the general functions y_{int} and $y_{\square}$ which depend on three parameters, λ , m and x_s :

$$y_{\text{int}} = \frac{mx^3 + \lambda x_s^2 x}{x^2 + x_s^2},$$

$$y_{\square} = \frac{(m-\alpha)x^3 + (\lambda-\alpha)x_s^2 x}{x^2 + x_s^2}.$$

The x_s parameter has been defined; the λ [$\lambda = (\text{d}y_{\text{int}}/\text{d}x)_{x=0}$] and m [$m = (\text{d}y_{\text{int}}/\text{d}x)_{x \rightarrow \infty}$] parameters define respectively the clustering conditions for the lowest and highest values of x [1].

This model applied to various solid solutions has allowed us to determine the nature of the formed clusters. Thus the existence of the $n+1:2n:1:0$ single-file column clusters and of the $2n+2:3n:2:0$ and $2n+2:4n:2:0$ two-files ones has been established respectively for $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$, $\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$ and $\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$ [2]. The four integer numbers $n_1:n_2:n_3:n_4$ characterizing such clusters indicate that they are constituted by the association of n_1 vacancies in the normal positions ($1/4, 1/4, 1/4$) of the fluorite-type network with n_2 F' ($1/2, u, u:0.36 \leq u \leq 0.41$), n_3 F'' ($v_1, v_1, v_1:v_1 \approx 0.40$) and n_4 F''' ($v_2, v_2, v_2:v_2 \approx 0.30$) interstitial fluoride ions [1,3]. The materials of best conductivity in each of the three $\text{Pb}_{1-x}\text{M}'_x\text{F}_{2+\alpha x}$ solid solutions ($\text{M}' = \text{In, Zr, Bi}$) correspond respectively to ($0.10 \leq x_{\text{max}} \leq 0.12$) for $\text{M}' = \text{In}$, ($x_{\text{max}} \approx 0.10$) for $\text{M}' = \text{Zr}$ and ($x_{\text{max}} \approx 0.25$) for $\text{M}' = \text{Bi}$; the three are characterized

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by clusters of similar size involving $n=2$ substitutional cations [4].

In a previous paper [5] we have shown that the partial replacement in $Pb_{1-x}M'_x F_{2+x}$ ($M' = \text{In, Bi}$) of one M' ion by the other trivalent cation results in an increase of the disorder, favoring thus the enhancement of the transport properties: the materials having the highest conductivity are characterized by the formation of In^{3+} and Bi^{3+} clusters of similar size and involving $n=2$ substitutional cations and by a number of In^{3+} clusters equal to twice that of Bi^{3+} clusters [5].

We report in this paper the results of our investigations on the $\text{PbF}_2\text{-M}'\text{F}_3\text{-ZrF}_4$ ($M' = \text{In, Bi}$) systems involving simultaneously one trivalent and one tetravalent cation. The existence of a large domain of solid solutions was expected between the border limit phases, $\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$ ($0 \leq x \leq 0.27$) and $\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$ ($0 \leq x \leq 0.18$) on the one hand, $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$ ($0 \leq x \leq 0.50$) and $\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$ on the other hand. The influence of the $M'^{3+} = \text{Zr}^{4+} + \text{F}^-$ substitution on the transport properties could be so determined within each system investigated.

2. Synthesis and radiocrystallographic analysis

The ternary $\text{PbF}_2\text{-InF}_3\text{-ZrF}_4$ and $\text{PbF}_2\text{-ZrF}_4\text{-BiF}_3$ systems can be represented in equilateral ABG and AGC triangles, the A, B, C and G being respectively PbF_2 , InF_3 , BiF_3 and ZrF_4 (fig. 1). The lines parallel to the AB, AC, AG, BG and CG sides of the triangles correspond to the formal substitutions: (AB) $\text{Pb}^{2+} = \text{In}^{3+} + \text{F}^-$; (AC) $\text{Pb}^{2+} = \text{Bi}^{3+} + \text{F}^-$; (AG) $\text{Pb}^{2+} = \text{Zr}^{4+} + 2\text{F}^-$; (BG) $\text{In}^{3+} = \text{Zr}^{4+} + \text{F}^-$ and (CG) $\text{Bi}^{3+} = \text{Zr}^{4+} + \text{F}^-$.

The materials have been prepared from mixtures of PbF_2 , ZrF_4 and $M'\text{F}_3$ ($M' = \text{In, Bi}$) fluorides, in sealed gold tubes, at 550°C during 15 h. An XRD analysis of the samples obtained after quenching has revealed the existence of large domains of disordered solid solutions with the fluorite-type structure, $\text{Pb}_{1-x}\text{In}_{x(1-z)}\text{Zr}_{xz}\text{F}_{2+x(1+z)}$ and $\text{Pb}_{1-x}\text{Zr}_{x(1-z)}\text{Bi}_{xz}\text{F}_{2+x(2-z)}$ ($0 \leq z \leq 1$).

The domains have a triangular form; their bound-

Fig. 1. Domains of solid solutions with fluorite type structure in the ternary $\text{PbF}_2\text{-InF}_3\text{-ZrF}_4$ (a) and $\text{PbF}_2\text{-ZrF}_4\text{-BiF}_3$ (b) systems.

aries are respectively the AB, AG, DD' and AG, AC, D'D' lines within the $\text{PbF}_2\text{-InF}_3\text{-ZrF}_4$ and $\text{PbF}_2\text{-ZrF}_4\text{-BiF}_3$ systems, where D, D' and D'' represent respectively the compositions $\text{Pb}_{0.73}\text{In}_{0.27}\text{F}_{2.27}$, $\text{Pb}_{0.50}\text{Bi}_{0.50}\text{F}_{2.50}$ and $\text{Pb}_{0.82}\text{Zr}_{0.18}\text{F}_{2.36}$ (fig. 1).

The composition dependence of the unit cell parameter a_c for the upper limit $\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$ and $\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$ solid solutions is quite similar [6,7]. It results in an insignificant variation of a_c as a function of z for the $\text{Pb}_{1-x}\text{In}_{x(1-z)}\text{Zr}_{xz}\text{F}_{2+x(1+z)}$ compositions at given values of x . The influence of the replacement of the In^{3+} ion by the Zr^{4+} ion of smaller size is compensated by the introduction of one extra fluoride ion into an interstitial site. On the contrary

Fig. 2. Variation of a_c as a function of x for various $Pb_{1-x}Zr_x(1-x)Bi_{xz}F_{2+x(2-z)}$ compositions relative to fixed z values ($0 \leq z \leq 1$).

the replacement of the Zr^{4+} ion by the Bi^{3+} ion of larger size involves an increase of a_c with rising z for the $Pb_{1-x}Zr_x(1-x)Bi_{xz}F_{2+x(2-z)}$ compositions at constant values of x (fig. 2). This result is analogous to that observed for the $Pb_{1-x}In_x(1-x)Bi_{xz}F_{2+x}$ solid solutions [5].

3. Electrical properties

Conductivity measurements have been carried out on powder samples pressed to form pellets, sintered at $550^\circ C$ in sealed gold tubes and then quenched. The compactness of the pellets was about 90%. Vacuum evaporated gold was used as electrodes. The bulk resistance was measured by the complex impedance method using a Solartron frequency analyser. The frequency range was 10^{-2} – 10^4 Hz and the measurements were carried out for several temperature cycles between 20 and $150^\circ C$.

In the investigated temperature range, the temperature dependence of the conductivity is in agree-

ment with an Arrhenius-type law for each composition.

3.1. Variation of the electrical properties as a function of x for the $Pb_{1-x}In_x(1-x)Zr_{xz}F_{2+x(1+z)}$ and $Pb_{1-x}Zr_x(1-x)Bi_{xz}F_{2+x(2-z)}$ compositions for fixed values of z

Fig. 3a, b and fig. 4a, b give the variation of $\log \sigma_{60^\circ C}$ and the activation energy ΔE_σ as a function of x for various series of $Pb_{1-x}In_x(1-x)Zr_{xz}F_{2+x(1+z)}$ and $Pb_{1-x}Zr_x(1-x)Bi_{xz}F_{2+x(2-z)}$ materials corresponding to z equal to $1/3$, $1/2$ and $2/3$. Results previously obtained for the limit solid solutions relative to $z=0$ and $z=1$ [5,8,9] are also reported in these figures:

Whatever the values of z , a conductivity maximum associated with a minimum of activation energy appears for a particular value of the substitution rate (x_{max}).

The variation of x_{max} with z for $Pb_{1-x}Zr_x(1-x)Bi_{xz}F_{2+x(2-z)}$ shows a quasi-linear increase of x_{max} with increasing x (fig. 5a), behavior analogous with that observed for $Pb_{1-x}In_x(1-x)Bi_{xz}F_{2+x}$ [5]. On the contrary, x_{max} seems to be independent of z for $Pb_{1-x}In_x(1-x)Zr_{xz}F_{2+x(1+z)}$ (fig. 5b). As a matter of fact the quasi-constant value of x_{max} observed when z increases results simply from the very close values of x_{max} shown for $z=0$ and $z=1$.

The conductivity maxima observed for x_{max} in each boundary solid solution correspond to particular compositions involving clusters of similar size [4]. As a consequence, whatever the value of z ($0 \leq z \leq 1$), the highest electrical conductivity is observed for compositions characterized by the presence of column clusters containing two substitutional cations ($n=2$).

Fig. 6 represents the $2n+2:3n:2:0$, $2n+2:4n:2:0$ and $n+1:2n:1:0$ clusters proposed respectively for $Pb_{1-x}In_xF_{2+x}$, $Pb_{1-x}Zr_xF_{2+2x}$ and $Pb_{1-x}Bi_xF_{2+x}$.

The formation of mixed clusters containing simultaneously Zr^{4+} and Bi^{3+} substitutional cations has a low probability due to the nature difference of two-file $2n+2:4n:2:0$ clusters and one-file $n+1:2n:1:0$ ones. The formation of a disordered distribution of Zr^{4+} and Bi^{3+} ion clusters of the same size is much more likely and in agreement with the

Fig. 3(a) Variation of $\log \sigma_{60^\circ\text{C}}$ as a function of x for some series of $\text{Pb}_{1-x}\text{In}_x(1-x)\text{Zr}_{xz}\text{F}_{2+x(1+z)}$ materials relative to fixed z values ($0 \leq z \leq 1$); (b) Variation of ΔE_σ as a function of x for some series of $\text{Pb}_{1-x}\text{In}_x(1-x)\text{Zr}_{xz}\text{F}_{2+x(1+z)}$ materials relative to fixed z values ($0 \leq z \leq 1$).

linear relation previously observed between x_{max} and z . Such a hypothesis has been already proposed for the $\text{Pb}_{1-x}\text{In}_x(1-x)\text{Bi}_{xz}\text{F}_{2+x}$ compositions [5].

On the contrary the structures of two-file $2n+2:3n:2:0$ and $2n+2:4n:2:0$ column clusters are very similar, with elementary polyhedra constituted by monocapped trigonal prisms (InF_7) and square antiprisms (ZrF_8) (fig. 6). This means that, for the $\text{Pb}_{1-x}\text{In}_x(1-x)\text{Zr}_{xz}\text{F}_{2+x(1+z)}$ solid solutions involving clusters of the same size, formation of mixed clusters containing both substitutional cations and the occurrence of a disordered distribution of In^{3+} and Zr^{4+} ion clusters can be proposed. We shall con-

sider the latter hypothesis below, by analogy with the $\text{Pb}_{1-x}\text{In}_x(1-x)\text{Bi}_{xz}\text{F}_{2+x}$ and $\text{Pb}_{1-x}\text{Zr}_x(1-x)\text{Bi}_{xz}\text{F}_{2+x(2-z)}$ compositions.

3.2. Variation of electrical properties for some series of materials involving clusters of the same size

Equations representing y_{int} , $y_{\square}$, $y_{\text{F}'}'$, and $y_{\text{F}''}$ for the $\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$, $\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$ and $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$ solid solutions are given in table 1. The identification of the formal $y_{\text{F}'}'/y_{\text{F}''}$ and the experimental $n_{\text{F}'}'/n_{\text{F}''}$ ratios has allowed us to define the particular x_n values of x corresponding to the presence of clus-

Fig. 4(a) Variation of $\log \sigma_{60^\circ\text{C}}$ as a function of x for some series of $\text{Pb}_{1-x}\text{Zr}_x(1-x)\text{Bi}_{xz}\text{F}_{2+x(2-z)}$ materials relative to fixed z values ($0 \leq z \leq 1$); (b) Variation of ΔE_σ as a function of x for some series of $\text{Pb}_{1-x}\text{Zr}_x(1-x)\text{Bi}_{xz}\text{F}_{2+x(2-z)}$ materials relative to fixed z values ($0 \leq z \leq 1$).

ters of n extension [1]. x_n is related to x_s by the equation: $x_n^2 = (n-1)x_s^2$ ($n > 1$). According to model [1] x_s must be close to x_{max} , the value for which a conductivity maximum is observed.

$$(x_s)_{\text{In}} = (x_s)_{\text{Zr}} = \sqrt{2}/12 \approx 0.118,$$

$$(x_s)_{\text{Bi}} = 2\sqrt{2}/12 \approx 0.236,$$

$$0.10 \lesssim (x_{\text{max}})_{\text{In}} \lesssim 0.12,$$

$$(x_{\text{max}})_{\text{Zr}} \approx 0.10,$$

$$(x_{\text{max}})_{\text{Bi}} \approx 0.25.$$

As a consequence:

$$(x_n)_{\text{In}} = (x_n)_{\text{Zr}} = \sqrt{2(n-1)}/12,$$

$$(x_n)_{\text{Bi}} = 2\sqrt{2(n-1)}/12.$$

We shall call these values in the following x_n , x_n and $2x_n$ instead of $(x_n)_{\text{In}}$, $(x_n)_{\text{Zr}}$ and $(x_n)_{\text{Bi}}$ by reasons of simplicity.

The solid solution range with fluorite-type structure appearing in the PbF_2 - InF_3 - ZrF_4 system can be represented in the orthonormal (At , Ay) reference (fig. 7). At is the bisectrix of the (AB , AG) angle of the equilateral ABG triangle where the apexes figure PbF_2 , InF_3 and ZrF_4 (fig. 1a). In this reference the t and x parameters are bound by the linear relation: $t = x(\sqrt{3}/2)$. Compositions characterized by the formation of clusters of n dimension are located on the D_n line parallel to Ay and the border limit compositions are $\text{Pb}_{1-x_n}\text{In}_{x_n}\text{F}_{2+x_n}(\text{L}_{\text{In}})$ and $\text{Pb}_{1-x_n}\text{Zr}_{x_n}\text{F}_{2+2x_n}(\text{L}_{\text{Zr}})$. Crossing from L_{In} to L_{Zr} corresponds to following substitution process: $y\text{In}^{3+} = y\text{Zr}^{4+} + y\text{F}^-$. In other words the compositions located on the D_n line may be represented by the general formulation $\text{Pb}_{1-x_n}\text{In}_{x-y}\text{Zr}_y\text{F}_{2+x_n+y}$ ($0 \leq y \leq x_n$). The total number of clusters present in a material characterized by the parameter y is thus:

$$N = [(x_n - y)/n]_{\text{In}} + [y/n]_{\text{Zr}}.$$

Fig. 5(a) Variation of $x_{\max}$ as a function of z for the $\text{Pb}_{1-x}\text{Zr}_x(1-x)\text{Bi}_{1-x}\text{F}_{2+x(2-z)}$ compositions; (b) Variation of $x_{\max}$ as a function of z for the $\text{Pb}_{1-x}\text{In}_x(1-x)\text{Zr}_x\text{F}_{2+x(1+z)}$ compositions.

Whatever the value of y , N is constant.

The variation of $\log \sigma_{60^\circ\text{C}}$ as a function of y is given in fig. 8 for some series of materials corresponding to fixed values of the cluster extension n :

Whatever n , a conductivity maximum appears for a particular value $y_{\max}$ of y . $y_{\max}$ increases with n .

Compositions relative to various values of $y_{\max}$ and n are located on a curve called C which shows a maximum when $n=2$.

The values of $y_{\max}$ correspond to $y_{\max} \approx x_n/3$, i.e. to materials characterized by the value $r=1/2$ of the Zr/In ratio ($z=1/3$).

Fig. 6. Representation of the $2n+2:3n:2:0$ (a); $2n+2:4n:2:0$ (b); and $n+1:2n:1:0$; (c) clusters proposed respectively in the $\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$, $\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$ and $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$ solid solutions.

Materials having the highest electrical conductivity between the limit $\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$ and $\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$ solid solutions can be written respectively as:

Table 1

Analytical expressions of y_{int} , $y_{\square}$, $y_{F'}$, $y_{F''}$ for the $\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$, $\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$ and $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$ solid solutions.

	$\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$	$\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$	$\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$
cluster	$2n+2:3n:2:0$	$2n+2:4n:2:0$	$n+1:2n:1:0$
y_{int}	$(3x^3+5x_2^2x)/(x^2+x_2^2)$	$(4x^3+6x_2^2x)/(x^2+x_2^2)$	$(2x^3+3x_2^2x)/(x^2+x_2^2)$
$y_{\square}$	$(2x^3+4x_2^2x)/(x^2+x_2^2)$	$(2x^3+4x_2^2x)/(x^2+x_2^2)$	$(x^3+2x_2^2x)/(x^2+x_2^2)$
$y_{F'}$	$3x$	$4x$	$2x$
$y_{F''}$	$2x_2^2x/(x^2+x_2^2)$	$2x_2^2x/(x^2+x_2^2)$	$x_2^2x/(x^2+x_2^2)$
x_2	0.118	0.118	0.236
$y_{F'}/y_{F''}$	$3(x^2+x_2^2)/2x_2^2$	$2(x^2+x_2^2)/x_2^2$	$2(x^2+x_2^2)/x_2^2$
$n_{F'}/n_{F''}$	$3n/2$	$2n$	$2n$

Fig. 7. Representation of the $\text{Pb}_{1-x}\text{In}_x\text{Zr}_y\text{F}_{2+x+y}$ compositions in the orthonormal (Ax , Ay) reference.

and

Both compositions are characterized by the same number of normal F_N - and interstitial F'' - fluoride ions; consequently, the substitution process along the D_n lines could be written:

In a similar way the solid solution range with

Fig. 8. Variation of $\log \sigma_{60^\circ\text{C}}$ as a function of y for the $\text{Pb}_{1-x}\text{In}_x\text{Zr}_y\text{F}_{2+x+y}$ ($0 \leq y \leq x_n$) materials relative to fixed n values.

fluorite-type structure shown in the $\text{PbF}_2\text{-ZrF}_4\text{-BiF}_3$ system can be represented in the orthonormal (Ax , Ay) reference (fig. 9). The materials characterized by formation of clusters of n dimension are located on the D_n line parallel to Ay and correspond to the general formulation $\text{Pb}_{1-x_n-y}\text{Zr}_{x_n-y}\text{Bi}_{2y}\text{F}_{2+2x_n}$ ($0 \leq y \leq x_n$). The limit compositions are $\text{Pb}_{1-x_n}\text{Zr}_{x_n}\text{F}_{2+2x_n}(\text{L}_{\text{Zr}})$ and $\text{Pb}_{1-2x_n}\text{Bi}_{2x_n}\text{F}_{2+2x_n}(\text{L}_{\text{Bi}})$. Crossing from L_{Zr} to L_{Bi} corresponds to substitution process: $y\text{Pb}^{2+} + y\text{Zr}^{4+} = 2y\text{Bi}^{3+}$. This process results in replacement of a number of Zr^{4+} clusters by a number of Bi^{3+} clusters twice larger.

Fig. 9. Representation of the $Pb_{1-x-y}Zr_{x-y}Bi_{2y}F_{2+2x}$ compositions in the orthonormal (Ax, Ay) reference.

Fig. 10. Variation of $\log \sigma_{60^\circ C}$ as a function of y for the $Pb_{1-x-y}Zr_{x-y}Bi_{2y}F_{2+2x}$ ($0 \leq y \leq x_n$) materials relative to fixed n values.

Fig. 10 gives the variation of $\log \sigma_{60^\circ C}$ as a function of y for various series of $Pb_{1-x-y}Zr_{x-y}Bi_{2y}F_{2+2x}$ ($0 \leq y \leq x_n$) materials corresponding to fixed values of n . These results are analogous to those obtained for the $Pb_{1-x-y}In_{x-y}Bi_{2y}F_{2+2x}$ compositions [5]:

- Whatever the value of n , a conductivity maximum is observed for a particular value y_{max} of y .
- The values of y_{max} correspond to $y_{max} \approx x_n/5$,

i.e. to materials characterized by the value $r = 1/2$ of the Bi/Zr ratio ($z = 1/3$).

- Compositions relative to different values of n and y_{max} are located on a C-curve which shows a maximum when $n = 2$ (fig. 10).

4. Discussion

Comparison of electrical and structural properties of the particular $Pb_{1-x}M_x^{2+\alpha}F_{2+\alpha x}$ ($M' = In, Zr, Bi$) compositions characterized by the presence of clusters of $n = 2$ dimension shows that the highest conductivity is observed for the material which has the lowest activation energy, the largest percentage of F'' -ions and the smallest cluster concentration (table 2). Recall, on the other hand, that the $(F_i)_m$ ions responsible for long range motions within these solid solutions are the interstitial fluoride ions of F'' -type [1,4].

Let us consider the $Pb_{1-x_n}In_{x_n-y}Zr_yF_{2+x_n+y}$ compositions located on a D_n line, the extremities of which are L_{In} and L_{Zr} (fig. 7). Going from L_{In} to L_{Zr} corresponds to a decrease of the $y_{F''}$ percentage when the number of clusters of n size is constant. The replacement in the L_{In} phase of $(y/n) In^{3+}$ clusters by $(y/n) Zr^{4+}$ clusters results in an increase of cationic disorder and a cluster disorder which favor enhancement of electrical conductivity but simultaneously in a decrease of the $y_{F''}$ percentage which is unfavorable. The observed conductivity increase shows that disorder is prevailing. On the contrary, replacement in the L_{Zr} phase of $(y/n) Zr^{4+}$ clusters by $(y/n) In^{3+}$ clusters leads to increasing disorder and simultaneously to higher percentage of $y_{F''}$ which are both favorable to larger conductivity. A conductivity maximum occurs consequently for a particular value y_{max} of y . Along the D_n lines cationic disorder is maximum for the $Pb_{1-x_n}In_{x_n-y}Zr_yF_{2+x_n+y}$ compositions corresponding to $y = x_n/2$ and the highest value of the $y_{F''}$ -percentage is obtained for L_{In} ($y = 0$). This results in the appearance of a conductivity maximum for $0 < y < x_n/2$. It is actually observed for $y_{max} \approx x_n/3$ ($z = 1/3$).

Let us consider now the $Pb_{1-x_n-y}Zr_{x-y}Bi_{2y}F_{2+2x}$ compositions located on a D_n line, whose limits are L_{Zr} and L_{Bi} (fig. 9).

Table 2

Electrical and structural properties for the $\text{Pb}_{1-x}\text{M}_x^{2+\alpha}\text{F}_{2+\alpha x}$ ($\text{M}' = \text{In, Zr, Bi}$) compositions characterized by the formation of clusters of $n=2$ extension.

	$\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$	$\text{Pb}_{1-x}\text{Zr}_x\text{F}_{2+2x}$	$\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$
	L_{In} phase ($n=2$)	L_{Zr} phase ($n=2$)	L_{Bi} phase ($n=2$)
x	0.118	0.118	0.236
$\sigma_{600^\circ\text{C}} (\Omega \text{ cm})^{-1}$	7×10^{-4}	6×10^{-4}	3×10^{-4}
$\Delta E_g (\text{eV})$	0.34	0.37	0.39
$(y_{\text{F}''}) (\%)$	5.57	5.27	5.27
cluster number per unit cell	0.059	0.059	0.118

Crossing from L_{Zr} to L_{Bi} , which corresponds to a $y\text{Pb}^{2+} + y\text{Zr}^{4+} = 2y\text{Bi}^{3+}$ substitution process, is characterized by increasing cluster concentration when the $y_{\text{F}''}$ -percentage is constant. As a decrease of the cluster concentration and an increase of the $y_{\text{F}''}$ percentage have a similar influence on transport properties, the behavior with y of the conductivity of the $\text{Pb}_{1-x_n-y}\text{Zr}_{x_n-y}\text{Bi}_{2y}\text{F}_{2+2x_n}$ materials can be explained. For a given n -parameter the maximum of disorder corresponds to the $\text{Pb}_{1-4x_n/3}\text{Zr}_{2x_n/3}\text{Bi}_{2x_n/3}\text{F}_{2+2x_n}$ compositions ($y = x_n/3$) relative to the value $r=1$ of the Bi/Zr ratio ($z=1/2$). The L_{Zr} phase ($y=0$) is characterized by the smallest cluster concentration. y_{max} must consequently be within the $0 < y_{\text{max}} < x_n/3$ range: it is observed for $y_{\text{max}} \approx x_n/5$ ($z=1/3$).

Similar features characterize the $\text{Pb}_{1-x_n-y}\text{In}_{x_n-y}\text{Bi}_{2y}\text{F}_{2+x_n+y}$ ($0 \leq y \leq x_n$) compositions with the fluorite-type structure belonging to the wide range of solid solutions observed in the $\text{PbF}_2\text{-InF}_3\text{-BiF}_3$ system [5]: the dependence of electrical properties with y , at fixed x_n , shows a conductivity maximum when the Bi/In ratio is equal to 1/2. As a consequence the materials with the best electrical conductivities belonging to the $\text{Pb}_{1-x_n}\text{In}_{x_n-y}\text{Zr}_y\text{F}_{2+x_n+y}$, $\text{Pb}_{1-x_n-y}\text{Zr}_{x_n-y}\text{Bi}_{2y}\text{F}_{2+2x_n}$ and $\text{Pb}_{1-x_n-y}\text{In}_{x_n-y}\text{Bi}_{2y}\text{F}_{2+x_n+y}$ series and involving clusters of the same n dimension are characterized, whatever n , by the $r=1/2$ value of the Zr/In, Bi/Zr and Bi/In ratios ($z=1/3$). The occurrence of a conductivity maximum for y_{max} has been explained on the one hand by the influence of disorder, on the other hand by those of the $y_{\text{F}''}$ percentage (Pb-In-Zr) or the cluster concentration (Pb-Zr-Bi). All

Table 3

Values of $\sigma_{400\text{ K}}$ for ($\text{M}_{\text{In,Zr}}$), ($\text{M}_{\text{Zr,Bi}}$), ($\text{M}_{\text{In,Bi}}$) and $\beta\text{-PbSnF}_4$.

	$\sigma_{400\text{ K}}$ ($\Omega \text{ cm}$) ⁻¹
($\text{M}_{\text{In,Zr}}$) $\text{Pb}_{1-x_n}\text{In}_{2x_n/3}\text{Zr}_{x_n/3}\text{F}_{2+4x_n/3}$	$\approx 2 \times 10^{-2}$
$x_n = \sqrt{2}/12$ ($n=2$)	
($\text{M}_{\text{Zr,Bi}}$) $\text{Pb}_{1-6x_n/5}\text{Zr}_{4x_n/5}\text{Bi}_{2x_n/5}\text{F}_{2+2x_n}$	$\approx 1.3 \times 10^{-2}$
$x_n = \sqrt{2}/12$ ($n=2$)	
($\text{M}_{\text{In,Bi}}$) [5] $\text{Pb}_{1-6x_n/5}\text{In}_{4x_n/5}\text{Bi}_{2x_n/5}\text{F}_{2+6x_n/5}$	$\approx 1.7 \times 10^{-2}$
$\beta\text{-PbSnF}_4$ $x_n = \sqrt{2}/12$ ($n=2$)	$\approx 5 \times 10^{-2}$
[10]	

three phenomena occur simultaneously for the (Pb-In-Bi) compositions, according to the $y\text{Pb}^{2+} + y\text{In}^{3+} = 2y\text{Bi}^{3+} + y\text{F}^{1-}$ substitution process.

Within three domains of solid solutions, the highest ionic conductivity is observed for the materials called ($\text{M}_{\text{In,Zr}}$), ($\text{M}_{\text{Zr,Bi}}$) and ($\text{M}_{\text{In,Bi}}$) which are characterized by the presence of column clusters of $n=2$ dimension ($x_n = \sqrt{2}/12$) and values of y_{max} equal respectively to $x_n/3$, $x_n/5$ and $x_n/5$. These phases are among the best fast fluoride ion conductors so far obtained (table 3).

5. Conclusions

New fast ionic conductors with the $\text{Pb}_{1-x}\text{In}_{x(1-z)}\text{Zr}_{xz}\text{F}_{2+x(1+z)}$ and $\text{Pb}_{1-x}\text{Zr}_{x(1-z)}\text{Bi}_{xz}\text{F}_{2+x(2-z)}$ ($0 \leq z \leq 1$) formulations have been found in the $\text{PbF}_2\text{-InF}_3\text{-ZrF}_4$ and $\text{PbF}_2\text{-ZrF}_4\text{-BiF}_3$ systems. Whatever z , an ionic conductivity maximum appears for x_{max} and the compositions relative to x_{max} are characterized by for-

mation of $n=2$ extension column clusters.

The variation with y of the F^- ion conductivity for the $Pb_{1-x_n}In_{x_n-y}Zr_yF_{2+x_n+y}$ and $Pb_{1-x_n-y}Zr_{x_n-y}Bi_{2y}F_{2+2x_n}$ ($0 \leq y \leq x_n$) series involving clusters of similar size has been determined. Materials with the best electrical properties are those for which the Zr/In and Bi/Zr ratios are close to 1/2. These results confirm those previously obtained in investigating the $Pb_{1-x_n-y}In_{x_n-y}Bi_{2y}F_{2+x_n+y}$ solid solutions.

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