Combined use of Mössbauer spectroscopy and X-ray diffraction for the study of order-disorder in tin(II)-containing fluoride ion conductors

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Abstract

In some materials, cationic or anionic disorder can take place, and the knowledge of the extent of this disorder and how it varies with preparation conditions and temperature can be essential, since key properties of the materials can vary drastically with the presence of disorder. In addition, we have discovered a method for disordering, by ball-milling, fluoride-ion conductors, the structure of which is derived from the fluorite-type. The presence of the disorder raises critical questions about the electronic structure of tin(II) and the possibility of mixed conduction due to the unhybridized tin(II) non-bonded pair having the option to add electron motion to the fluoride-ion conductivity. The study of disordered materials by X-ray diffraction does not reveal a full understanding of the tin situation, particularly its electronic structure. In addition, in many of the ordered tin(II) containing phases, very highly enhanced preferred orientation put some limits on the usefulness of X-ray diffraction, while, however, generating new knowledge. A unique method has been designed in our laboratory to determine unambiguously the lone pair stereoactivity in disordered systems, and to use it in highly oriented systems, by use of ^{119}Sn Mössbauer spectroscopy. Examples taken from our work on high fluoride ion conductors in the SnF_2/MF_2 system (M = Ca, Sr, Ba and Pb) have been studied.

Keywords: fluoride ion conductors, fluorite-type structure, order-disorder, Mössbauer spectroscopy, X-ray diffraction.

1 Introduction

Tin (II) fluoride SnF_2 is a fluoride ion conductor with a conductivity similar to that of β-PbF_2, which is the best fluoride conductor among the fluorite-type MF_2 fluorides [1]. Combinations of SnF_2 with fluorite-type MF_2 (M= Ca, Ba & Pb) have been carried out in our laboratory and have generated new materials, some of which are among the highest performance fluoride ion conductors, in some cases up to three orders of magnitude superior to that of the corresponding MF_2 [2]. The understanding of the electrical properties of these new materials requires acquiring appropriate knowledge about their structures. More particularly, a detailed crystal structure is required in order to fathom the pathways the fluoride ion may use for long distance motion. In addition, one must have information on the presence or absence of possible mechanism that electrons could use in order to estimate whether a significant participation of electrons in the total conductivity is feasible.

Tin belongs to group 14 and period 5 of the periodic table of the elements, and therefore it has 4 valence electrons. It results that it forms two stable oxidation states, +2 and +4, both of which are diamagnetic. In the full oxidation state, +4, all valence electrons are used to form covalent bonds, since the charge density on the Sn^{4+} ion makes it highly polarizing, and it would be too high to make ionic bonding possible, except perhaps in SnO_2. In the suboxidation state, +2 tin has a non-bonded electron pair (lone pair), two types of bonding can be found in halides: ionic bonding (most iodides and some bromides) or covalent bonding (all fluorides and chlorides, and most bromides). Many of the new materials prepared by combination of SnF_2 and fluorite type MF_2 have structures derived from the fluorite structure, either with a distorted supercell (M/Sn order) or with a cubic fluorite type unit-cell (M/Sn disorder). In both cases, diffraction alone is not sufficient to provide a full characterization of the tin site(s). The reasons are the following. Most ordered phases crystallize in the form of very thin and highly fragile sheets and are poorly crystalline, that result in no suitable single crystal being obtained, and in extreme cases, of preferred orientation that cannot be reduced by milling since an order/disorder phase transition was found to take place in call cases after a short time ball-milling (a few minutes) [3]. For disordered phases, only average M/Sn values can be obtained by diffraction alone.

The 119 isotope of tin is the second best Mössbauer nuclide. Its relatively low γ-ray energy makes it possible to have reasonably strong spectra for most compounds at ambient temperature. Since Mössbauer spectroscopy probes only tin sites, it provides information about the tin situation in the material, regardless of crystallinity or disorder. Used in conjunction with X-ray powder diffraction, it has made possible the characterization of tin in the SnF_2/MF_2 materials.

2 Experimental

Synthesis was carried out either in aqueous medium or at high temperature in dry conditions. Tetragonal α-$PbSnF_4$ was obtained by precipitation, on addition of an aqueous solution of lead(II) nitrate to a solution of SnF_2. Orthorhombic o−$PbSnF_4$ was prepared by the same method, using a SnF_2 solution slightly acidified with HF. $Ca_{1-x}Sn_xF_2$ precipitated when a solution of calcium nitrate was added to a solution of SnF_2 at high Ca/Sn ratio, or was formed by leaching, on stirring $CaSn_2F_6$ in a large amount of water. Dry synthesis was carried out under nitrogen, in sealed copper tubes, heated at 300 ^{o}C ($PbSn_4F_{10}$) or at 500 ^{o}C (β−$PbSnF_4$ and $BaSnF_4$) and quenched. The nanocrystalline μγ-$MSnF_4$ phases were obtained by a short time ball-milling (1-30 min.) of the crystalline phases. X-ray powder diffraction was carried out on a PW-1050/25 *Philips* diffractometer automated with the SIE RAY 122® system from *Diffraction Technology*, using the K_α radiation of copper ($\lambda_{K\alpha 1}$ = 1.54051 Å) and a monochromator. Mössbauer spectra were recorded in a TN7200® multichannel analyzer from *Tracor Northern*, using an *Elscint* driving system, a *Harshaw* (Tl)NaI detector and a 10 mCi $CaSnO_3$ γ-ray source. All chemical isomer shifts were referenced relative to a $CaSnO_3$ absorber. The spectra were fitted using the GMFP software [4].

3 Results and discussion

3.1 Ordered phases

The diffraction pattern of $BaSnF_4$ (fig. 1a) is related to that of cubic fluorite type BaF_2 (fig. 1c). In additional to the peak splitting, e.g. $(200)_{BaF2} \rightarrow [(110)$ and $(004)]_{BaSnF4}$ indicative of a tetragonal distortion with a 45^{o} rotation of the *a* and *b* axes within the *(a,b)* plane, the (001) and (003) low angle Bragg peaks (superstructure reflections) show that the *c* axis is doubled (1x1x2 superstructure). The superstructure parallel to the *c* axis suggests that Sn and Ba are ordered in that direction. The new (002) peak is not a superstructure reflection. Indexed (100) in BaF_2, it was forbidden by the absence conditions of the F Bravais lattice. The powder diffraction pattern of precipitated α-$PbSnF_4$ (fig. 2) has the same set of peaks as $BaSnF_4$ (fig. 1a) and has therefore a similar tetragonal cell with the same superstructure. The (00l) peaks of α-$PbSnF_4$ are much stronger due to extremely high preferred orientation. In addition, (110) is much broadened by internal strain. These features make it difficult to get accurate atomic positions from diffraction, let alone finding a possible solution.

The ^{119}Sn isotope has spins 1/2 and 3/2 in the nuclear ground state and first excited state, respectively. This gives a single line in the case when no efg (electric field gradient) is present on tin, and a doublet when efg $\neq 0$ (fig. 3). A sextuplet would be obtained if a magnetic field were present at tin, however, there is no paramagnetic ion in the samples studied, and no external magnetic field was applied. The efg acting at tin is mainly due to the non-spherical valence electron distribution, the largest contribution of which originates from the stereoactive lone pair located on a hybrid orbital when tin forms covalent bonds (Fig. 3b). In a single crystal, the doublet is asymmetric, and the relative intensity of the two lines is a function of the angle θ between the directions of the γ-ray beam and of V_{zz}, the main axis of the electric field gradient [5]. For $\theta = 0$, the theoretical line intensity ratio $I_{1/2\rightarrow 3/2}/\ I_{1/2\rightarrow 1/2} = 3$, and for 45^{o}, it is equal to 1.3. Samples of precipitated α-$PbSnF_4$ obtained with extremely high preferred orientation were pressed between two thin aluminum plates to enhance further the preferred orientation, and the Mössbauer spectrum was recorded at different orientations in the γ-ray beam. Figure 4 shows that the spectrum asymmetry is close to the expected values for a single crystal with V_{zz} perpendicular to the flat sample. It also showed that the alignment of the sheet-like crystallites parallel to one another obtained by pressing the sample was close to perfection. The next step consisted in relating the Mössbauer results to a possible structural solution. The enhancement of the intensity of the (00l) peaks of α-$PbSnF_4$ with increasing preferred orientation (fig. 2) shows that the *c* axis of the unit-cell is normal to the sheet-like crystallites (fig. 5a). The 3/1 ratio of the Mössbauer peaks for $\theta = 0$ (fig. 4a) proves that V_{zz} is normal to the flat sample, and since the sheet-like crystallites are parallel to the flat sample, it is concluded that V_{zz} is normal to the sheets, and therefore parallel to the *c* axis of the tetragonal unit-cell (fig. 5c).

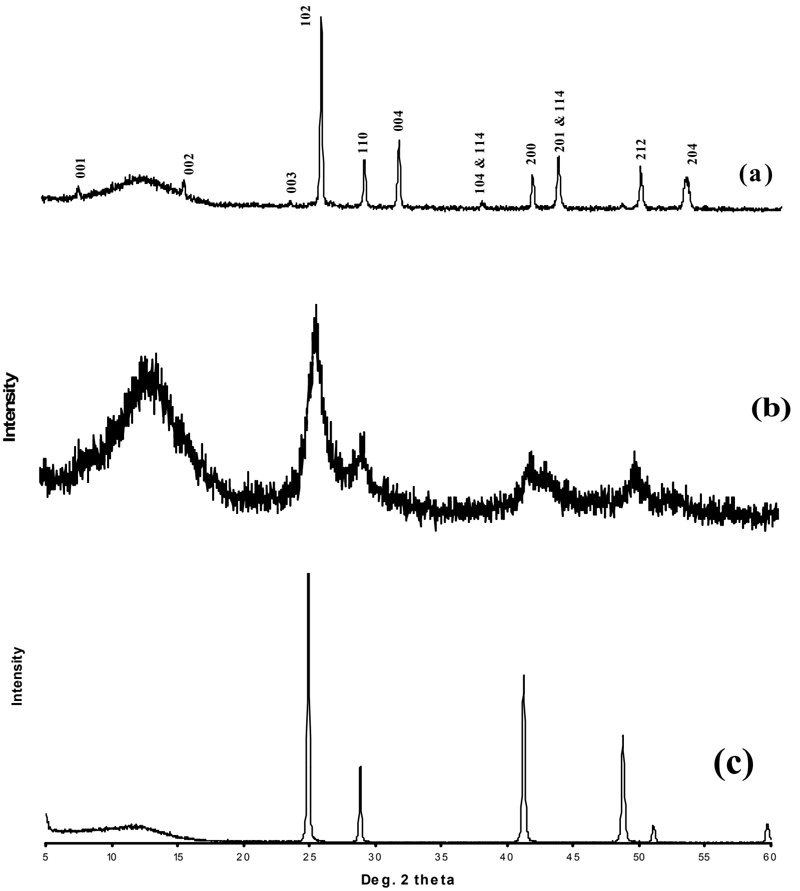


Figure 1: X-ray diffraction pattern of: (a) BaSnF4 prepared at 500 °C, (b) ball-milled $BaSnF_4$, (c) BaF_2.

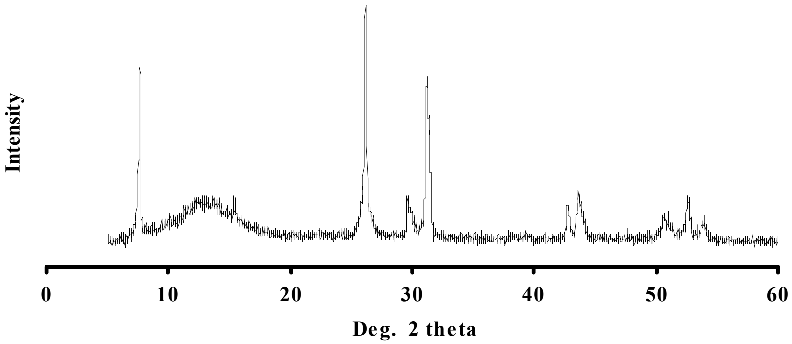


Figure 2: X-ray powder diffraction pattern of precipitated α-$PbSnF_4$.

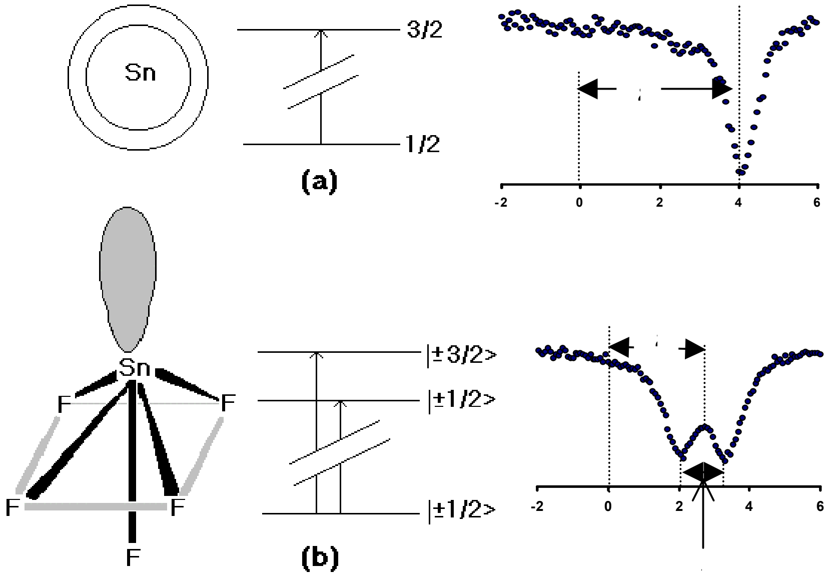


Figure 3: Electrical monopolar and electrical quadrupolar interactions generated versus the bonding type of divalent tin, and their effect on the Mössbauer spectrum. (a) ionic bonding: unhybridized lone pair and undistorted site (e.g. $CsSnBr_3$), (b) covalent bonding: hybridized lone pair (e.g. $BaSnF_4$).

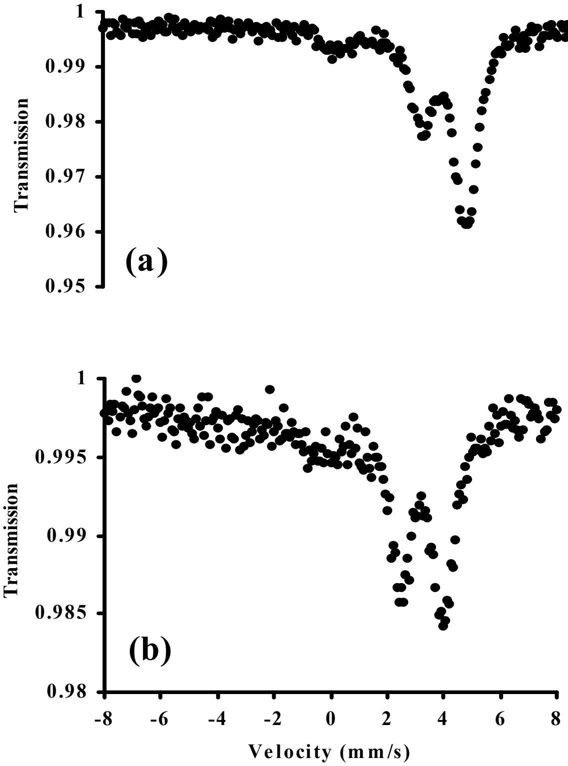


Figure 4: Tin-119 Mössbauer spectrum of α-$PbSnF_4$ versus the angle θ between V_{zz} and the γ-ray beam: (a) $\theta = 0^0$, (b) $\theta = 45^{o.}$

Since the main contributor, from far, to V_{zz} is the tin lone pair when it is stereoactive, and since the quadruple splitting Δ is large, the lone pair is stereoactive, i.e. Sn-F bonding is covalent, and the lone pair axis is parallel to *c* (fig. 5b). This is consistent with the tetragonal symmetry of the unit-cell. Taking into account the above conclusions, a model of the structure could be built. Using the superstructure (*c* doubled) and the same general metal distribution as in the fluorite structure, … Ba Ba Sn Sn… order parallel to *c* accounts for both the superstructure and the extremely high preferred orientation, since two adjacent tin sheets, with their lone pairs parallel to *c* must point their lone pairs in the space between the tin layers, thereby creating sheets of lone pairs that are perfect cleavage planes, resulting in a highly layered structure and therefore a huge preferred orientation and extremely thin flat crystallites (fig. 6). Then, using this model, the structure was completed and refined from powder diffraction. It must be noted that the layer of fluoride ions that would be located between the tin sheets like in BaF_2 if the lone pairs were not there, has moved to adjacent F_8 cubes that were previously empty, and form a short apical Sn-F bond (2.029 Å), much shorter than the sum of the ionic radii of $Sn2^+$ and F^- (2.28 Å), thereby confirming the covalency of the bonds and the hybridization of the tin orbitals, that make the lone pair strongly stereoactive. It should be noted that in $BaSnF_4$, there is no empty [] F8 cubes ([]: metal ion vacancy) like in BaF_2, that can be used as instertitial sites for long-range fluoride ion motion. However, the fluoride ion conductivity of $BaSnF_4$ is three orders of magnitude higher than that of BaF_2, therefore another easy pathway for their motion must exist. Subsequent neutron diffraction has shown that F in FSn_2Ba_2 coordination is preferentially partially depopulated, and secondarily the F in FBa_4 site, and that the fluoride ions missing from these sites go on loose sites within the sheets of lone pair, where they can easily wiggle their way between the lone pairs to give superionic conductivity.

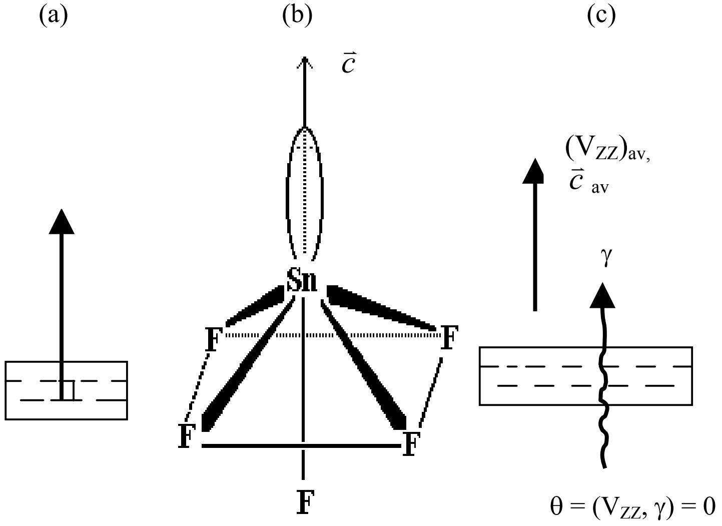


Figure 5: Mössbauer spectroscopy of highly oriented α-$PbSnF_4$: (a) *c* axis is normal to sheet-like crystallites, (b) *c* axis is parallel to lone pair axis and to V_{zz}, (c) $\theta = 0$ in highly oriented α-$PbSnF_4$ when the γ-ray beam is normal to sheets.

3.2 Disordered phases

In contrast with the above ordered phases, the diffraction pattern of some other materials made by combining MF_2 and SnF_2, where MF_2 has also the fluorite type structure, is undistorted (cubic), i.e. there is no peak splitting that would show a lattice distortion, and in addition, there is no superstructure reflection (figs. 1b & 7Ab). In some cases, no line broadening is observed ($Pb_{1-x}Sn_xF_2$, ball-milled phases) therefore the crystallite diameter is well above 1000 Å.

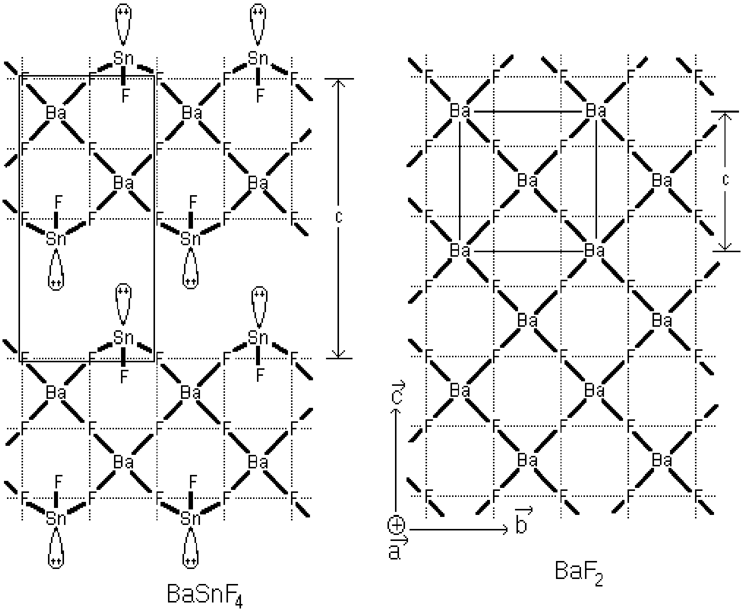
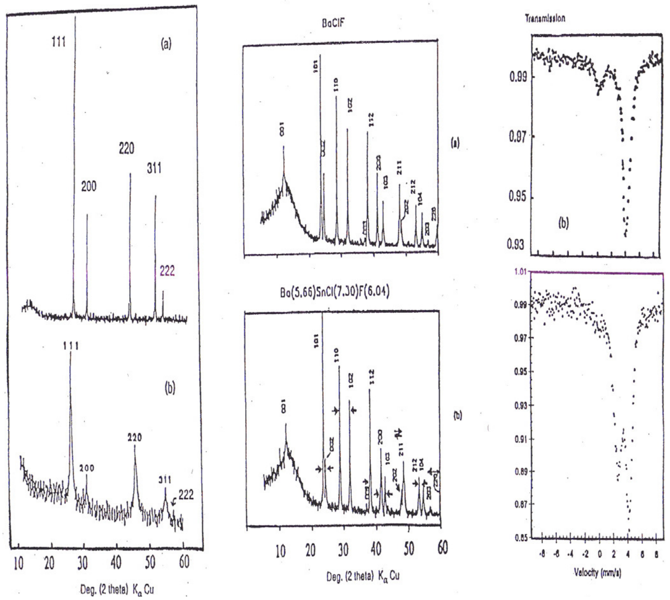


Figure 6: Projection of the structures of $BaSnF_4$ and BaF_2.



(A) **(B)** **(C)**

Figure 7: (A) X-ray powder diffraction pattern of CaF_2 and $Ca_{1-x}Sn_xF_2$ ($x = 0.27$), (B) X-ray powder diffraction pattern of BaClF and $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ ($x = 0.15$, $y = 0.094$), (C) ^{119}Sn ambient temperature Mössbauer spectrum of $Ca_{1-x}Sn_xF_2$ ($x = 0.27$) and $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ ($x = 0.15$, $y = 0.094$).

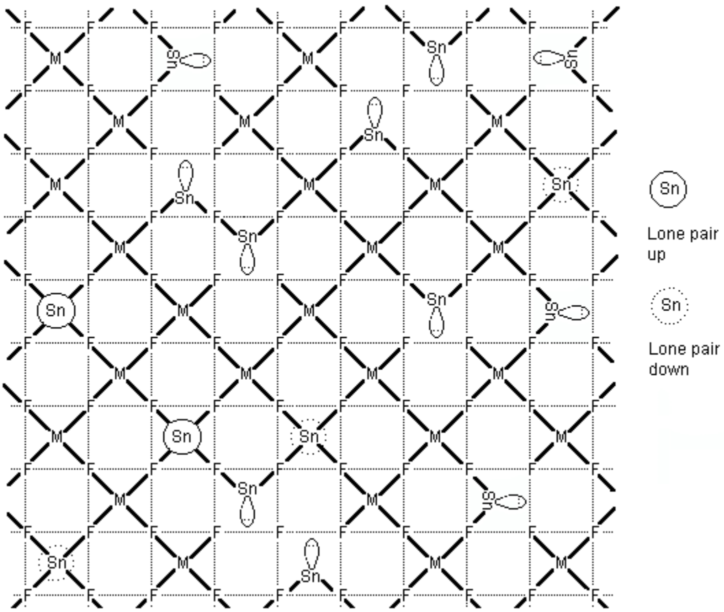


Figure 8: Model of a disordered fluorite type $M_{1-x}Sn_xF_2$ structure.

However, in other cases, such as in all ball-milled phases (fig. 1b) and in precipitated $Ca_{1-x}Sn_xF_2$ (fig. 7Ab), the lines are clearly broadened, and the average crystallite diameter was calculated from the line broadening, by use of the Scherrer method, after applying Warren correction to account for instrumental broadening, to be in most cases within the 100-130 Å range. The absence of lattice distortion or superstructure makes it that the unit-cell and space group are the same as that of the MF_2 fluorite, with however, a small difference of the numerical value of the unit-cell parameter. It results from their cubic unit-cell and absence of superstructure that the metal ion M^{2+} and Sn are disordered on the same site, since there is only one metal site in the fluorite structure. Accepted rules for partial ion substitutions state that the two types of ions must have similar sizes and the same type of bonding, particularly accept the same coordination, otherwise substitution would not be possible. Accordingly, the presence of M/Sn disorder implies that Sn-F bonding is ionic like for M-F despite the large size difference and the well known habit of tin to bind covalently to fluorine, and indeed, no example of Sn-F ionic bonding to tin(II) is known. The size difference would also tend to make the ionic substitution unlikely. Mössbauer spectroscopy can easily and quickly provide the answer. In the case of ionic bonding, tin(II) would be present in the form of the Sn^{2+} stannous ion, with no orbital hybridization, and the lone pair being located on the *5s* native orbital. Since *s* orbitals are spherical, it would generate no efg and a Mössbauer single line would be obtained (fig. 3a). However, all disordered MF_2/SnF_2 materials give a large quadruple doublet (fig. 7C down), showing the presence of a large efg at tin. Only a *stereochemically active* lone pair can generate such a large quadruple splitting, therefore Sn-F bonding is covalent in the disordered fluoride. Polarization could distort the lone pair, and a mildly distorted environment could generate a small efg, giving only a line broadening. Recently, a $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ solid solution, a disordered BaClF type structure, was prepared in our laboratory, and there too, Mössbauer spectroscopy was essential in establishing tin bonding, that was found to be ionic, since the spectrum is a single line (fig. 7B and 7C up). In the disordered fluorides, Sn and its lone pair are located inside F_8 cubes, with tin being shifted quite substantially towards one of the faces of the cube, to which it binds (coordination 4 like in SnO) and the lone pair points towards the opposite face (fig. 8). The lone pair is locked on a hybrid orbital and is not a charge carrier in agreement with transport number measurements. A non-stereoactive lone pair could be a charge carrier.

Acknowledgements

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