TIN(II)-CONTAINING FLUORIDE ION CONDUCTORS: HOW TIN MULTIPLIES THE FLUORIDE ION CONDUCTION BY UP TO THREE ORDERS OF MAGNITUDE

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ABSTRACT

Electrical conduction by the motion of ions in the solid state was considered to be impossible for a long time. When Michael Faraday discovered that solid lead(II) fluoride conducts electricity when heated, it was an anomaly and the conduction mechanism remained ununderstood for long. Nowadays, several ions of small size and low charge, such as H^+, Li^+ and F^-, are known to be highly mobile in solid compounds provided the crystal structure contains pathways that make possible easy ionic motion. We have prepared new compounds, $PbSnF_4$ and $BaSnF_4$ and other phases in the PbF_2-SnF_2 system that increase the conduction efficiency by up to three orders of magnitude relative to the corresponding MF_2. Solid state fluoride ion batteries (FIBs) promise high specific energy and thermal stability. High potential solid state rechargeable fluoride ion batteries are being designed and $BaSnF_4$ has been used as one of the ingredients to form an interlayer solid electrolyte with high conductance. In the current work, we have analyzed the role of divalent tin in these structures, in terms of crystal structure and of local bonding to fluorine, in an effort to understand how it can result in such a high enhancement of the conductivity. Diffraction methods were used to investigate the crystal structures and ^{119}Sn Mössbauer spectroscopy for studying the mode of Sn-F bonding and the electron configuration of tin.

Keywords: ionic conductivity, fluoride ion mobility, divalent tin, lone pair stereoactivity, X-ray diffraction, Mössbauer spectroscopy.

1 INTRODUCTION

Electrical conductivity in solids was for long thought to be a property of metals only, in contrast with ionic compounds that were known to be insulators. When Faraday discovered in 1838 that lead(II) fluoride PbF_2 becomes an electrical conductor at high temperature, the reasons for this unusual behavior were not understood at the time [1]. Ions were not expected to be mobile in solids, where they are held in deep potential wells in the ionic lattice. Later studies lead to the conclusion that ionic compounds conduct electricity by the motion of ions in the liquid state and in solutions, where ions are free to move. Many more recent studies of the conductivity of PbF_2 have shown that Faraday's observations were correct and that the conductivity of PbF_2 increases substantially at the $\alpha \rightarrow \beta$ (orthorhombic → cubic) phase transition [2]. The cubic phase has the fluorite-type crystal structure and the high conductivity is attributed to the high mobility of the fluoride ions by means of Frenkel defects, and at higher temperature to the presence of a diffuse superionic transition resulting in a "sublattice melting" [3]. However, the mobility, of the fluoride ions is related to the room available to lodge temporarily the fluoride ions in the Frenkel defect model. One of us (GD) has shown that, if only the size of the interstitial sites were the main factor for determining the ability of the fluoride ions to move, the conductivity of BaF_2 would be much higher than that of β-PbF_2, and it is the reverse that is observed [4]. It was also shown by one of us (GD) that combining the fluorite-type BaF_2 with stannous fluoride SnF_2 results in $BaSnF_4$ with a substantial increase of the conductivity, by three orders of magnitude [5]. The SnF_2-based

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fluoride ion electrolytes $MSnF_4$ (M = Ba, Pb) have now reached the stage where they are being considered for application in room-temperature solid-state fluoride ion batteries [6], [7].

The aim of the present work is (i) to study how SnF_2 manages to increase the conductivity of the fluorite type MF_2 fluorides by such a dramatic amount (a thousand times), and (ii) how to design a method for determining rapidly whether a tin(II)-containing compound may be an electronic conductor or an ionic conductor.

2 THEORETICAL BACKGROUND REGARDING MÖSSBAUER SPECTROSCOPY RELATED TO ELECTRONIC STRUCTURE AND BONDING IN DIVALENT TIN

Crystallography uses X-ray or neutron diffraction to study of the whole crystal lattice. On the other hand, Mössbauer spectroscopy is a local probe. It is a nuclear spectroscopy, and therefore, it probes only specific nuclides, such as ^{119}Sn in this work. Therefore, by use of ^{119}Sn Mössbauer spectroscopy, we can study tin in compounds, and the way it interacts with its neighbors and with the entire solid lattice. The nuclear spins on ^{119}Sn are 1/2 in the ground state and 3/2 in the first excited state. The ground state has no quadrupole moment, therefore it remains unsplit (|±1/2>) in the absence of a magnetic field, even if an electric field gradient (e.f.g.) is present, while the first excited state has a quadrupole moment, that interacts with an e.f.g. to give rise to two sublevels, |±1/2> and |±3/2>. Therefore, the resonant absorption of γ-rays by the ^{119}Sn nuclide for each tin site will give either a doublet (|±1/2>→|±1/2> and |±1/2>→|±3/2> transitions), or a singlet (|±1/2>→|±1/2> only), depending on whether there is an e.f.g. acting at the nucleus or not. No six line hyperfine magnetic field was observed since tin is diamagnetic in all its oxidation states, there was no transferred field in any of the compounds studied since they are diamagnetic and no external magnetic field was applied. The line position is called *isomer shift δ*, and it is a function of the amount of valence *s* electron density acting at the nucleus. This makes it a function of the oxidation state of tin, of the mode of bonding and of the electronegativity of the elements bonded to tin. To a lesser extent, it is also a function of temperature (*second order Doppler shift*). In Fig. 1(a), the Sn^{2+} stannous ion gives a single peak at high isomer shift (ca. 4 mm/s). The line is a singlet because the lone pair is located on the native *5s* orbital that is spherical and therefore it generates no e.f.g. The fact that the lone pair is purely *5s* makes it that its electron density is unshared and therefore there is a non-negligible amount of *5s* electron density acting at the nucleus, resulting in a high isomer shift. An e.f.g. due to lattice distortion is possible, however its effect on the spectrum is much weaker. Fig. 1(b) shows the case of tin(II) covalently bonded to fluorine. The stereoactive lone pair (non-bonded electron pair) at tin generates a very large e.f.g., hence a large doublet is observed. Since the *5s* electron density is shared between the lone pair and the bonds, it is further away from the nucleus than in the case of ionic bonding, and this generates a smaller isomer shift. Fig. 1(c) is the spectrum of $CaSnO_3$. It contains Sn^{4+} ions that have completely lost their valence shell, therefore there is no more *5s* electron density acting at the nucleus. It results in a much smaller isomer shift, that is taken as reference of isomer shifts, hence 0 mm/s, since all isomer shifts are referenced to $CaSnO_3$ at ambient temperature. It gives a single line since $CaSnO_3$. has the perovskite structure where the Sn^{4+} ions are in an octahedral site. It results from the above that the information obtained for each tin site are (i) its oxidation number, and in this study, for tin(II), (ii) the identification of the non-metal bonded to tin, (iii) the tin site distortion, and (iv) the tin type of bonding (ionic or covalent). Fig. 1 shows the influence of oxidation number and type of bonding on the Mössbauer spectrum. In addition, the lattice strength can also be estimated. Resonant

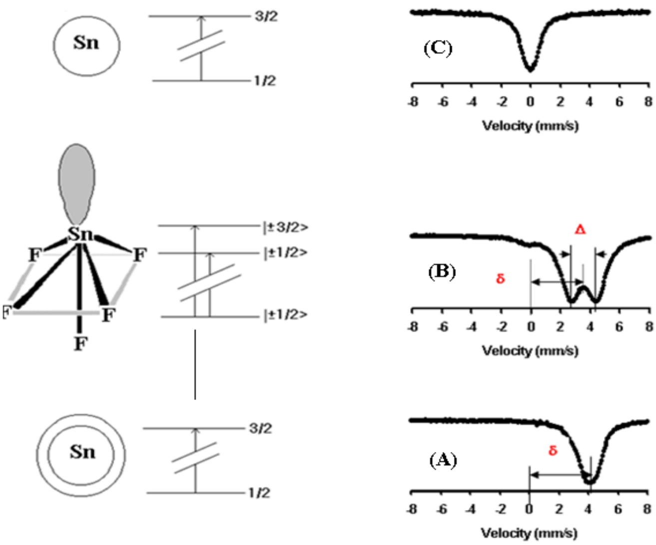

Figure 1: Mössbauer spectra for (a) Ionic Sn^{2+}; (b) Covalently bonded Sn(II) in $BaSnF_4$; and (c) $CaSnO_3$.

absorption of γ-photons is necessary in order to produce a Mössbauer spectrum, and less and less of this occurs when temperature increases and when the lattice is weak, due to phonons. Therefore, a weak lattice will result in a weaker spectrum.

3 MATERIAL PREPARATION AND CHARACTERIZATION

The following starting materials were used: SnF_2 99% from Ozark Mahoning, $BaCl_2 \cdot 2H_2O$ analytical grade from American Chemicals, BaF_2 99% from Allied Chemicals, PbF_2 99.9% from Alfa and Dye Corporations, HF 40% aqueous solution from Mallinckrodt, and doubly distilled or deionized water. All crystalline reactants were checked by X-ray powder diffraction and were found to have only the expected peaks. In addition, SnF_2 was checked by DTA and identified by the $\alpha \rightarrow \gamma$ transition at 150°C–160°C and melting point at 215°C [8]. The degree of hydration of $BaCl_2 \cdot 2H_2O$ was checked by TGA and found to be 2.04. The production of anhydrous $BaCl_2$ was verified by dehydrating the dihydrate at 140°C, significantly above the reported dehydration temperature of 113°C to ensure complete dehydration [9]. Total loss of water was confirmed by the mass loss of 14.71% (theoretical for $2H_2O$ = 14.75%).

All the materials investigated in this study were prepared either by precipitation or by solid state reactions in dry conditions. Solid state reactions were carried out by heating intimately mixed powders of the reactants in a sealed copper tube under dry nitrogen, according to the method developed by one of us (GD) [10]. The $MSnF_4$ compounds were prepared by heating stoichiometric amounts of SnF_2 and of MF_2 at 250°C for α-$PbSnF_4$ and at 500°C for $BaSnF_4$ according to the conditions determined earlier by one of us (GD) [11]. The α-phase of $PbSnF_4$ was also prepared by precipitation upon adding a solution of $Pb(NO_3)_2$ to a solution of SnF_2 upon stirring, for a molar ratio very rich in SnF_2 ($SnF_2/Pb(NO_3)_2 = 4:1$) [11].

X-ray powder diffraction was carried out by use of a Philips PW1050 diffractometer that had been automated with the Sie112 Sietronics® system from Difftech. This allowed a phase identification of phases already known, by comparison with the diffraction patterns of starting materials and other possible side products already collected in our laboratory and by use of the µPDSM Micro Powder Diffraction Search Match® from Fein-Marquat. Only the phases of interest in this study were subjected to further analysis.

The Mössbauer spectra were recorded using the following set-up. The source was a nominally 25 mCi $Ca^{119m}SnO_3$ γ-ray source from Ritverc GmbH. Isomer shifts were referenced relative to a standard $CaSnO_3$ absorber at ambient temperature. The counting system was a scintillation counter from Harshaw, equipped with a 1 mm thick (Tl)NaI crystal. A palladium foil was used to absorb the 25.04 keV and the 25.72 keV X-ray lines generated by the source decay from the 11/2 spin level of the ^{119m}Sn precursor to the 3/2 spin of the first excited state. The Doppler velocity (± 10 mm/s) was generated by use of an Elscint driving system, including a Mössbauer MVT-4 velocity transducer, a Mössbauer MDF-N-5 waveform generator and a MFG-N-5 driver. The amplifier, the single channel analyzer and the multichannel analyzer are combined in the Tracor Northern TN7200 system. After, the data were transferred to a computer for storage and processing. Low temperature spectra were recorded using an ADP Cryogenics helium closed-cycle refrigerator equipped with a two-stage Displex®. Computer processing of the data was performed using the MOSGRAF-2009 suite [12].

4 RESULTS AND DISCUSSION

4.1 Identifying the charge carriers: Electrons or ions?

Charge transport in metallic conductors results from the motion of electrons that are weakly held to metal atoms. In solid compounds, the charge carriers can also be electrons or holes, and ions in ionic conductors, also called *superionic conductors* and *solid electrolytes* when the conductivity is similar to that in the molten state. In order for electrons to be sufficiently mobile to flow over long distances in a solid when the sample is subjected to a moderate voltage, the conducting electrons must be in a conduction band, or easily promoted to such a band. Electrons in bonding orbitals are held in place simultaneously by two atoms and therefore, they cannot move without breaking chemical bonds and destroying the material. This destructive procedure would require a voltage that is much higher.

In the MF_2 fluorides with the fluorite-type structure where M is an alkaline earth metal, i.e. other than PbF_2, the M^{2+} ions have a noble gas configuration and hence they have no valance electron, therefore they cannot contribute to electronic conductivity. The case of β-PbF_2 is different since lead is not an alkaline earth metal. It belongs to group 14, the carbon group, in period 6. The electronic structure of Pb is [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$, hence it has four valence electrons, in agreement with its group number of 14. Ionization to the +2 oxidation number results in the loss of the $6p^2$ electrons, therefore the electronic structure of the Pb^{2+} ion is [Xe] $4f^{14}$ $5d^{10}$ $6s^2$. While the core electronic structure of the Pb^{2+} ion is [Xe] $4f^{14}$ $5d^{10}$, the $6s^2$ valence electrons are still present on the ion and, since they are not involved in bonding, they can be suspected to be sufficiently mobile and give rise to electronic conduction. Transport number measurements in a polarization cell at a constant voltage using a gold blocking electrode according to the method designed by Agrawal [13] have shown that the transport number for fluoride ions is ≥99% in all cases, including in the case of β-PbF_2.

The case of stannous fluoride SnF_2 is more surprising. It shows three solid phases: (i) α, obtained by crystallization from aqueous solutions, monoclinic, (ii) γ, obtained by heating α, stable only above the α → γ transition temperature (142–165°C, depending on particle size), tetragonal, and (iii) β, exists only below 66°C, obtained by cooling γ through a second order paraelastic → ferroelastic phase transition and is always metastable, orthorhombic [8], [14]–[17]. Bonding is strongly covalent in the three phases: α-SnF_2 has a tetrameric molecular structure while the two others form a polymeric network. Despite, the strong covalency of the bonds, the electrical conductivity of SnF_2 is similar to that of β-PbF_2 at high temperature, the conductivity of α being the highest, and the transport number for fluoride ions is above 97%, therefore the lone pair present on tin seems to not participate in the conduction mechanism [18]. The mechanism of formation of free F^- ions is not understood. In addition, the structure shows no obvious site that could give rise to Frenkel defects. In some divalent tin compounds, electrons from the lone pair are the charged mobile species. This was shown to occur in the perovskite structure $CsSnBr_3$ where the compound is a semi-conductor at ambient temperature and becomes a metal conductor at high temperature, with the transition being fully reversible on cooling [19].

We have designed a simple spectroscopic method to determine the possible role of the tin lone pair in the conduction mechanism. Three possible cases were identified and can be easily characterized by ^{119}Sn Mössbauer:

(a) The tin lone pair is stereoactive, i.e. on a hybrid orbital: Tin belongs to the same group as lead, group 14, and it has therefore four valence electrons. The electronic structure of the tin atom is [Kr] $4d^{10}$ $5s^2$ $5p^2$. In that case, bonding is covalent, the tin orbitals are hybridized sp^3 (tetrahedral electron pair geometry, three Sn-F bonds in a triangular pyramidal molecular geometry), or tin is hypervalent with five orbitals (trigonal bipyramidal electron pair geometry, see-saw molecular geometry with four bonds) or with six orbitals (octahedral electron pair geometry and square pyramidal molecular geometry with five bonds). In all cases, two of the valence electrons are used for bonding and the two others form the lone pair that occupies one of the hybrid orbital and distorts the coordination, and is said to be *stereoactive*. The above geometries are in agreement with Gillespie and Nyholm's VSEPR (Valence Shell Electron Pair Repulsion) theory [20]. The lone pair, being localized on a hybrid orbital, creates a highly distorted tin coordination that generates a large e.f.g. acting at the tin site, hence a large quadrupole splitting similar to that in Fig. 1(b). The presence of the 5*s* electrons, partly in bonds and partly in the lone pair, due to orbital mixing at hybridization, results in a significantly positive isomer shift. When the lone pair is stereoactive, it is locked in a hybrid orbital. Moving such electrons would destroy the hybridization, changing the bonding system and thus probably destroy its crystal structure. Therefore, if the Mössbauer spectrum is similar to that of Fig. 1(b), the lone pair electrons cannot move and therefore the compound is very unlikely to be an electronic conductor. If it is a good electric conductor, ions are likely to be the charge carriers.

The Mössbauer spectrum of α-SnF_2 (Fig. 2) and that of α-$PbSnF_4$ (Fig. 3) clearly show a large quadrupole doublet at positive isomer shifts similar to that of Fig. 1(b), characteristic of the tin lone pair being stereoactive in both cases, therefore it is locked on a hybrid orbital and cannot participate in the conduction mechanism, hence the fluoride ions must be the charge carriers.

(b) The tin lone pair is not stereoactive, i.e. it is located on the native 5*s* orbital: In this case, bonding is ionic. The electronic configuration of the Sn^{2+} stannous ion is [Kr] $4d^{10}$ $5s^2$. The spherical Sn^{2+} ion allows a highly symmetrical tin coordination resulting in little or no lattice e.f.g. In addition, since *s* orbitals are spherical, they generate no valence e.f.g. It results a total e.f.g. that is zero or near zero. This gives a single Mössbauer line. Furthermore, since there is no orbital mixing, all the 5*s* electron density is in the spherical orbital around the core of the Sn^{2+} ion, resulting in a higher isomer shift. In short, a single line at ca. 4 mm/s is

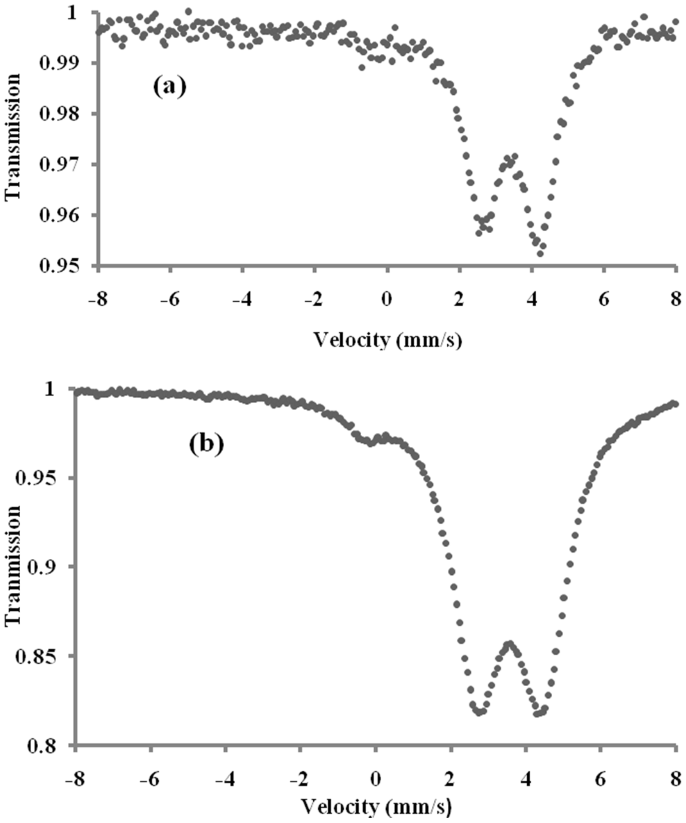

Figure 2: ^{119}Sn Mössbauer spectrum of α-SnF_2: (a) at ambient temperature, (b) at 12.5 K.

obtained. This is the case of $CsSnBr_3$ below the temperature where it becomes metal conductor (Fig. 1(a)).

(c) The tin lone pair moves to a conduction band, i.e. it is no longer located in the vicinity of the tin core. Tin behaves like a Sn^{4+} ion. Bonding is ionic The electronic configuration of the Sn^{4+} stannous ion is [Kr] 4d^{10}. The spherical Sn^{4+} ion allows a highly symmetrical tin coordination resulting in little or no lattice e.f.g. In addition, since there are no more valence electrons, there is no valence e.f.g. Like in the previous case, it results a total e.f.g. that is zero or near zero. This gives a single Mössbauer line. Furthermore, since there is no more valence electron near tin, it is locally a Sn^{4+} ion, and it gives the Mössbauer spectrum of a tin (IV) compound with no quadropole splitting. This is the same spectrum as that of $CaSnO_3$, a single line at 0 mm/s (Fig. 1(c)).

4.2 How the presence of tin(II) in $MSnF_4$ enhances the conductivity by up to 10^3

Even though covalently bonded SnF_2 is an ionic conductor equivalent to fluorite-type β-PbF_2, the structure of which is ionic, it seems hard to understand how combining covalently bonded SnF_2 with ionic MF_2 (M = Pb and Ba) increases the fluoride ion conductivity by three orders of magnitude. It would seem that replacing half of the other metal by tin would replace half

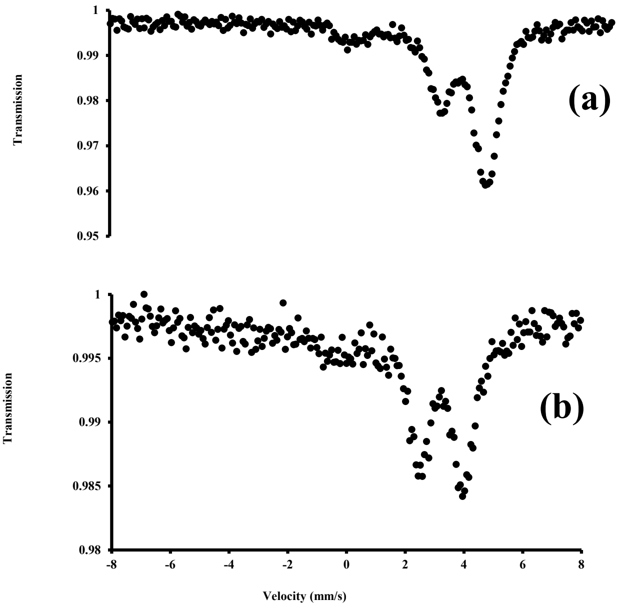

Figure 3: Ambient temperature Mössbauer spectra of highly oriented α-$PbSnF_4$: change of the asymmetry of the quadrupole doublet with the orientation of the sample relative to the γ-ray beam direction: (a) $\theta = 0°$, (b) $\theta = 45°$. θ is the angle between the γ-ray beam and the normal to the plane of the sample.

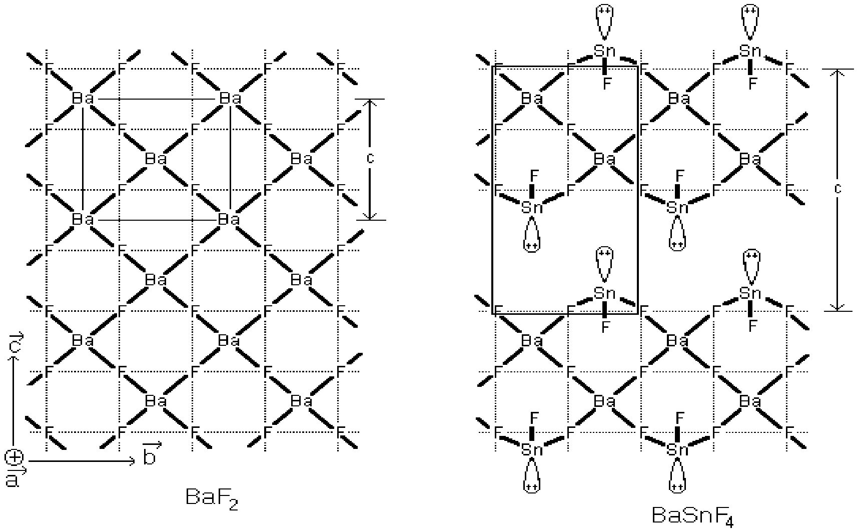

Figure 4: Projection of a slice of the structure of BaF_2 and $BaSnF_4$ on the *(a,b)* plane in the BaF_2 axes.

of the fluoride ions by covalently bonded fluorine, hence decreasing the number of charge carriers (F^-) by 50%. This should reduce substantially the conductivity. Since it increases it instead, the answer is elsewhere. Since the number of charge carriers does not seem to be the key factor, perhaps it is the ability of the charge carriers to move. The Frenkel defect model suggests that the interstitial sites for lodging the F^- ions during the motion are located inside the $\square F_8$ cubes ($\square$ = metal ion vacancy) and the high conductivity of the fluorite-type compounds is attributed to the large number of such sites: half of the F_8 cubes have no metal ion in their center. It can be seen on Fig. 4 that for BaF_2, BaF_8 cubes and $\square F_8$ cubes alternates parallel to the *b* and *c* axes of the unit-cell, and the same happens parallel to the *a* axis, perpendicular to the figure, due to the cubic symmetry.

The crystal structure of $BaSnF_4$ (α-$PbSnF_4$ type) is a superstructure of that of BaF_2 by doubling the periodicity along the *c* axis with a. ... Ba Ba Sn Sn Ba Ba Sn Sn. ... order parallel to *c*. The general network or alternating MF_8 and $\square F_8$ cubes is still present within planes parallel to *(a,b)*, it is interrupted along the *c* axis where the following order is observed:

[MF_8 $\square F_8$ sheet] [MF_8 $\square F_8$ sheet] [lone pair sheet] [MF_8 $\square F_8$ sheet] [MF_8 $\square F_8$ sheet].

The tin lone pair axis for all Sn atoms is parallel to *c* and all cluster in sheets parallel to *(a,b)*. These sheets of lone pairs create a direction of structural weakness in the material and is responsible for the two-dimensional crystallite shape in the form of very thin sheets. This creates an enormous amount of preferred orientation in polycrystalline samples, that is responsible for the large asymmetry of the Mössbauer spectrum (Fig. 3(a)) that is considerably reduced by rotation of the sample relative to the γ-ray beam (Fig. 3(b)). On the other hand, the asymmetry of the Mössbauer spectrum of α-SnF_2 does not change with the sample orientation in the γ-ray beam. The significant asymmetry at ambient temperature (Fig. 2(a)) disappears upon cooling the sample to cryogenic temperatures (Fig. 2(b)). This temperature dependent asymmetry is due to the anisotropy of the thermal vibrations and it is called the Goldanskii–Karyagin effect [21].

How can the fluoride ions move so efficiently in the α-$PbSnF_4$ type structure? All the $\square F_8$ cubes that contain no metal ion are occupied by a fluorine atom that forms an axial bond to tin, in trans-position with the lone pair. This is a very short, very strongly covalent Sn-F bond, therefore that fluorine atom cannot be mobile. In addition, that axially bonded fluorine atom leaves no room to lodge interstitial fluoride ions in the $\square F_8$ cubes. I seems therefore that all the potential interstitial sites present in the fluorite type MF_2 have disappeared in the $MSnF_4$ structure. The mobile fluoride ions must be those bonded to barium only since any fluorine atom bonded to tin forms a Sn-F covalent bond. The only room available for the motion of the fluoride ions is in the sheets of lone pairs. The presence of the lone pairs will prevent any bonding to tin and the repulsions between the charge of the lone pair and that of the F^- ions, both negative, will result in no attraction of the fluoride ions in this space and therefore they will be highly mobile.

5 CONCLUSION

In this study, the mechanisms of electrical conduction in ionic solids were analyzed with emphasis on fluorides with the fluorite-type structure and related $MSnF_4$. The method of determining by ^{119}Sn Mössbauer spectroscopy whether the tin(II) lone pair can be conducting or not was described. The possible pathways for the long distance motion of fluoride ions in both structures were evaluated. A particular question, why covalently bonded SnF_2 increases the ionic conductivity of the MF_2 in $MSnF_4$, was studied in details.

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