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Structure versus relaxor properties in Aurivillius type compounds

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Abstract

Structure refinements in $M^{II}Bi_4Ti_4O_{15}$ ($M^{II} = Ca, Ba$), $Bi_{4-x}Ba_xTi_{3-x}Nb_xO_{12}$, $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xBi_4Ti_4O_{15}$ and $Bi_4Ti_3O_{12}$–$PbTiO_3$ systems are used to report structural features of relaxor Aurivillius phases. In compounds with relaxor-like behaviour, the average structure is almost undistorted, closed to the archetypal HT paraelectric phase, with a tolerance factor $\gtrsim 0.996$. The coordination number of Bi^{3+} in fluorite layers changes from $\{4+2\}$ for ferroelectrics to $\{4\}$ for relaxors. Transmission Electron Microscopy reveals some characteristic features of relaxors such as micro-twinning, shearing-type defects which attest from the existence of a compositional inhomogeneity and a disorder at a local scale.

Keywords: Perovskite; Ferroelectric properties; Powders solid state reaction; X-ray methods

1. Introduction

The ferroelectric properties of the Aurivillius type compounds of general composition $A_{m+1}B_mO_{3m+3}$ currently arouse a keen interest because of their potential application in the fabrication of ferroelectric non-volatile memories (FeRAM). Members of this family of bismuth layered oxides are well known ferroelectric materials which can be described as the regular stacking of $[A_2O_2]^{2+}$ slabs (usually A = Bi) and perovskite-like $[A_{m-1}B_mO_{3m+1}]^{2-}$ blocks where m corresponds to the number of sheets of corner-sharing BO_6 octahedra.[1] For most of the ferroelectric Aurivillius phases, the structure observed at RT presents three structural distortions from the archetypal HT paraelectric phase: two tiltings of the octahedra around the *a*- and *c*-axis and atomic displacements along the polar *a*-axis.

Crystallographic studies have demonstrated the key role of the A-site cation in the ferroelectric behaviour of these materials and, at first approximation, a direct relation between the average ionic radii of the A-site cation and the temperature of the ferroelectric–paraelectric transition (T_c) can be has been established.[2,3] This will be illustrated in the present article for a series of Aurivillius phases: $M^{II}Bi_4Ti_4O_{15}$, ($M^{II} = Ba^{2+}$ or Ca^{2+}), the two solid solutions $Bi_{4-x}Ba_xTi_{3-x}Nb_xO_{12}$ ($0 \leq x \leq 1.2$), and $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xBi_4Ti_4O_{15}$ ($0 \leq x \leq 1$) and the system $Bi_4Ti_3O_{12}$–$PbTiO_3$ ($3 \leq m \leq 6$). As the Aurivillius phases existing within these systems possess either a "normal" or a "relaxor-like" ferroelectric behaviour in terms of dielectric properties (see references for $M^{II}Bi_4Ti_4O_{15}$,[4] $Bi_{4-x}Ba_xTi_{3-x}Nb_xO_{12}$,[5] $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xBi_4Ti_4O_{15}$,[6] and $Bi_4Ti_3O_{12}$–$PbTiO_3$[7,8]), we will point out some structural specificities related to this "relaxor" behaviour.

2. Experimental

Pure powder samples were prepared by a solid state reaction of the precursor oxides and carbonates. Stoichiometric amounts of high purity $BaCO_3$, Nb_2O_5, Na_2CO_3, $PbCO_3$, Bi_2O_3 and TiO_2 were mixed, pressed into pellets and then heated at 850–1000 °C for 2–10 h depending on the composition. When necessary, a two-step procedure was used and, for each thermal treatment, the pellets were reground and pressed again. The XRD patterns used for the structural determination were recorded in the 2θ range of 10–100°, with a 0.02° step using a Siemens D5000 diffractometer (Cu Kα, graphite monochromator).

For the $M^{II}Bi_4Ti_4O_{15}$ compounds, single crystals were grown using a flux method in Bi_2O_3 excess: heating up to 1150 °C at 5 °C min^{-1}, dwelling at 1150 °C for 5 h, cooling down to 500 °C

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at 3 °C h^{-1} and finally free cooling down to room temperature. Platelet-shaped transparent thin crystals were extracted using hydrochloric acid and then washed in hot water. After observation in polarised light optical microscope, those which presented only one ferroelectric domain or nearly so were selected for XRD experiments using a Siemens-Bruker KAPPA-CCD four-circle diffractometer equipped with a CCD detector and a graphite-monochromatized Mo Kα wavelength.

The electron microscopy study was carried out with a JEOL 2010 microscope working at 200 kV and fitted with a double-tilt (±30°) rotating sample holder.

Structure refinements were performed with the Jana2000 software[9] using single crystals or powder X-ray diffraction data and for both 3D or 3 + 1D superspace group approach (useful for long period structures).[10]

3. Results and discussion

Previous works have shown, considering the perovskite tolerance factor $t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$ of a number of Aurivillius phases, that both the structural distortion and the Curie temperature T_C increase as t decreases.[11,3] Regarding the Aurivillius members of different series, the variation of the "reduced" unit cell volume with the tolerance factor highlights a critical value of t around 0.996 (Fig. 1). Above this value, all considered Aurivillius phases present a relaxor-like behaviour.

All structures are closely related and only the number m of octahedral sheets in perovskite blocks differs from one compound to another. Complete results of the structure refinements are not the aim of this paper and can be found elsewhere.[12] As supposed by the values of the tolerance factor, refined structures of ferroelectric compounds are more distorted than those of relaxor compounds. As an example, Fig. 2 shows the representations of two members of the $Bi_{4-x}Ba_xTi_{3-x}Nb_xO_{12}$ ($m = 3$) solid solution: $Bi_4Ti_3O_{12}$, a "classical" ferroelectric and $Ba_{1.2}Bi_{2.8}Ti_{1.8}Nb_{1.2}O_{12}$, a "relaxor" ferroelectric. The classical ferroelectric compound is characterized by structural distortions, i.e. double tilting of octahedra around a and c axes and atomic displacement along a-axis. In agreement with the tolerance factor, the level of these structural distortions decreases as the average ionic radius of the A-site cation in the perovskite blocks increases. Hence, for the relaxor ferroelectrics, no or only small distortions with respect to the HT prototype paraelectric structure ($I4/mmm$) can be observed. This is a structural feature common to all relaxor compounds.

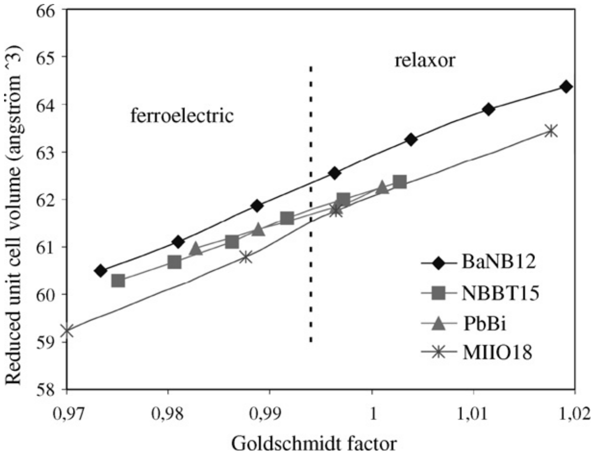

Fig. 1. Evolution of "reduced" unit cell volume ($a \approx 5.4$ Å, $b \approx 5.4$ Å and $c \approx 8.2$ Å) with increasing Goldschmidt tolerance factor for $Bi_{4-x}Ba_xTi_{3-x}Nb_xO_{12}$ (BaNB12), $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xBi_4Ti_4O_{15}$ (NBBT15), $Bi_4Ti_3O_{12}$–$PbTiO_3$ (PbBi) and $M^{II}Bi_4Ti_5O_{18}$ (MIIO18). Relaxor compounds are characterised by $t \gtrsim 0.996$. "Reduced" means unit cell parameters used in the 3D + 1 description.

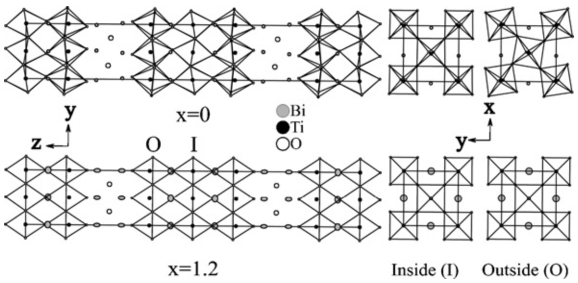

Fig. 2. Representation of $Bi_4Ti_3O_{12}$ ($x = 0$, classic ferroelectric) and $Ba_{1.2}Bi_{2.8}Nb_{1.2}Ti_{1.8}O_{12}$ ($x = 1.2$, relaxor); projections into yOz and xOy plans. Double tilting of octahedral around a- and c-axis and atomic displacement along a axis have disappeared for $x = 1.2$.

This structural evolution can be observed in the reciprocal space using selected area electron diffraction (SAED). Subtle modifications from the archetypal structure as well as existence of a structural disorder were observed. In particular the [1 2 0] or [2 −1 0] zone axis patterns (ZAP) are sensitive to twinning and/or local disorder.[12,13] Examples of patterns of the relaxor-like compound $Pb_2Bi_4Ti_5O_{18}$ are given in Fig. 3. The [0 1 0] ZAP exhibits sharp spots compatible with the B2cb space group whereas in the [1 2 0] or [2 −1 0] ZAP the $[h\,k\,\ell]^*$ rows with $h + k \neq 2n$ appear either as sharp spots or diffuse streaks along c^* depending on crystallites. These SAED patterns show the existence of micro-twinning (thin 90° twins domains with $a \leftrightarrow b$ permutation) along the c direction and, also, attest of inhomogeneities at a local scale.

Another difference between ferroelectric and relaxor-like compounds is the need to introduce a significant amount of non-Bi cations into the fluorite layers during the structure refinements (Fig. 4). This result might be related to the existence of shearing defects, observed in the studied relaxor compounds. These defects, highlighted with white arrows in Fig. 5, keep the global

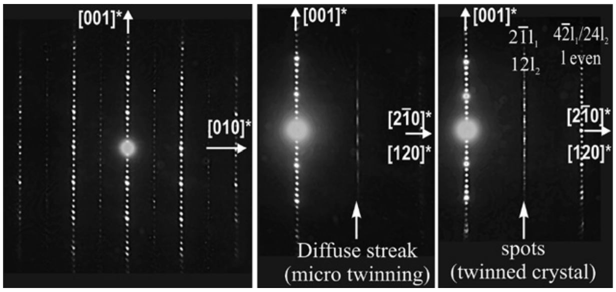

Fig. 3. SAED patterns of relaxor $Pb_2Bi_4Ti_5O_{18}$. [1 2 0] ZAP patterns show sharp spots or diffuse streaks on [2 −1 ℓ] rows, depending on considered crystallites.

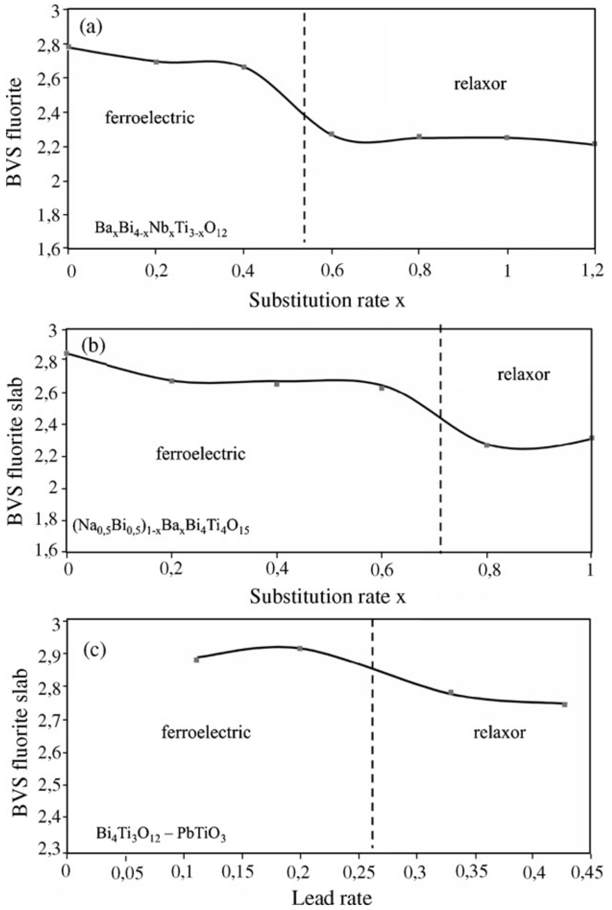

Fig. 4. Bond valence sum calculated for A-site cations of fluorite slabs in (a) $Bi_{4-x}Ba_xTi_{3-x}Nb_xO_{12}$, (b) $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xBi_4Ti_4O_{15}$ and (c) $Bi_4Ti_3O_{12}$-$PbTiO_3$. Significant decreasing of its value for relaxor compounds is related to the presence of divalent non-Bi cations in these sites.

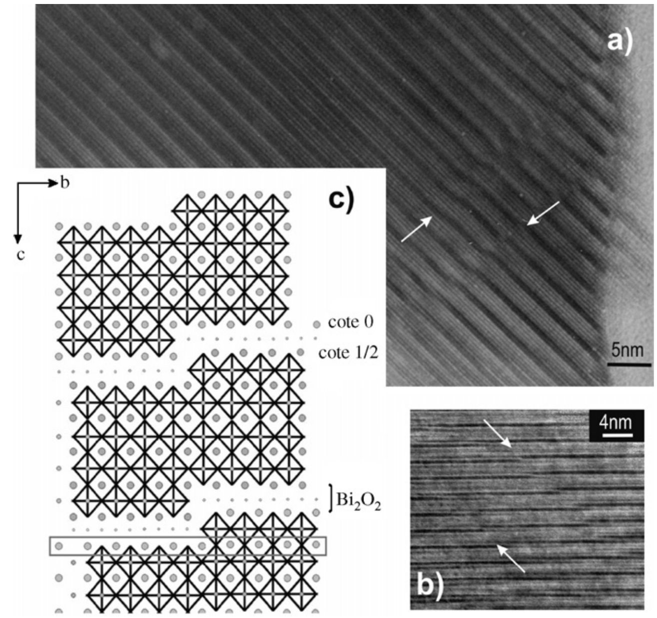

Fig. 5. Shearing-type defects observed in relaxor compounds, (a) $BaBi_4Ti_4O_{15}$ and (b) $Pb_2Bi_4Ti_5O_{18}$. (c) Model for defect zone.

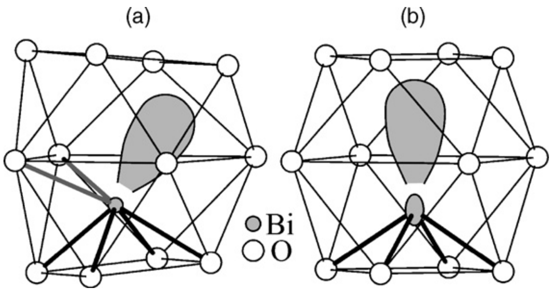

Fig. 6. Oxygen environment of Bi^{3+} in the fluorite slabs for (a) ferroelectric and (b) relaxor compounds. Coordination of cations is represented by black and grey Bi–O bonds.

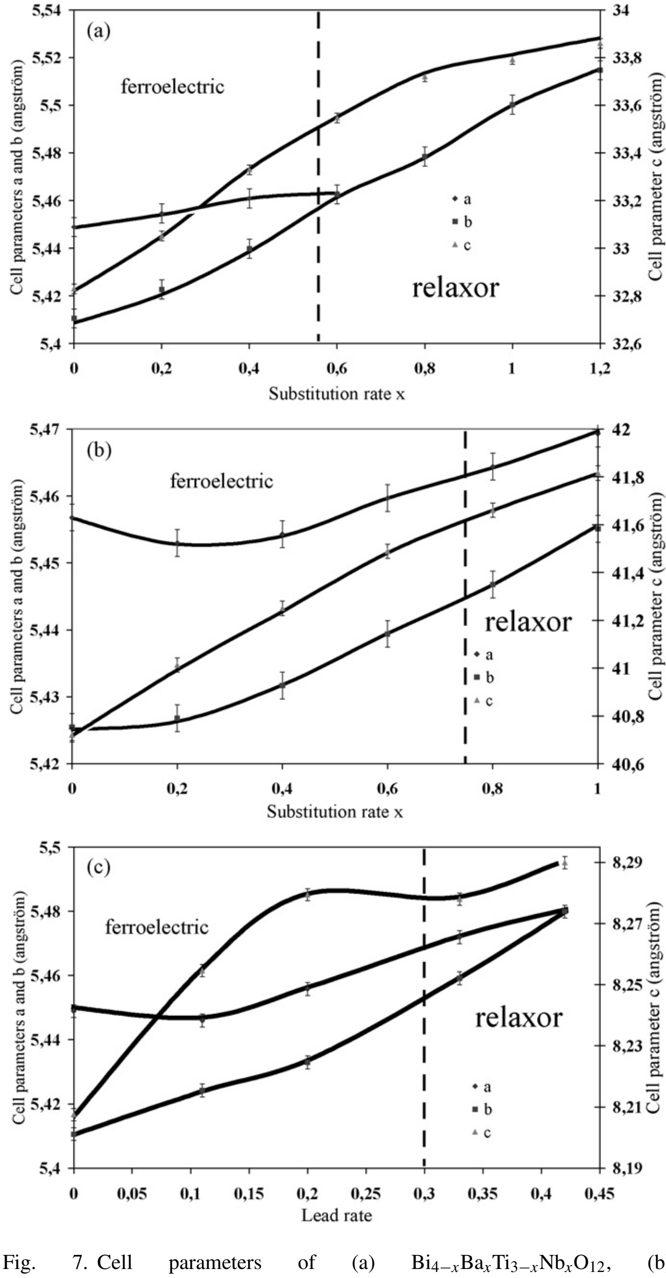

Fig. 7. Cell parameters of (a) $Bi_{4-x}Ba_xTi_{3-x}Nb_xO_{12}$, (b) $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xBi_4Ti_4O_{15}$ and (c) $Bi_4Ti_3O_{12}$–$PbTiO_3$ series. Pseudo-tetragonal metric is not always verified for relaxor compounds.

stoichiometry unchanged with the same thickness of the perovskite blocks. In the grey rectangle, the cationic row belonging to the fluorite slab in the average structure contains some non-Bi cations coming from the adjacent perovskite block. Details on such faults would need further investigations to ensure this feature is actually related to relaxor behaviour and not only a general characteristic of Aurivillius phases.

In relaxor compounds the coordination number of Bi^{3+} in fluorite layers decreases. It changes from $\{4+2\}$ with four short distances and two longer for ferroelectrics to $\{4\}$ for relaxors (Fig. 6). This latter configuration leads to a modification of the direction of the Bi lone pair that moves to be parallel to the c direction. Its stereo-chemical role weakens the Bi–O bonds between the perovskite blocks and the $[Bi_2O_2]^{2+}$ slabs.

Lastly, for the $BaBi_4Ti_4O_{15}$, $Bi_{4-x}Ba_xTi_{3-x}Nb_xO_{12}$ and $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xBi_4Ti_4O_{15}$ relaxor compositions, the refined structures show a positional static disorder on every A-site. This phenomenon, not noticed in the $Bi_4Ti_3O_{12}$–$PbTiO_3$ system where Bi^{3+} and Pb^{2+} have the same environment, can be related to the averaging of different atomic positions at a local scale and thus cannot be considered as a condition of the apparition of a relaxor-like behaviour. Also, pseudo-tetragonality is not a necessary condition as metrically orthorhombic compounds can have a relaxor-like behaviour (Fig. 7).

4. Conclusion

In this paper, the structural features of relaxor-like Aurivillius compounds are reported considering $M^{II}Bi_4Ti_4O_{15}$, $Bi_{4-x}Ba_xTi_{3-x}Nb_xO_{12}$, $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xBi_4Ti_4O_{15}$ and $Bi_4Ti_3O_{12}$–$PbTiO_3$ systems. Compared to ferroelectric ones, relaxor compounds show a less distorted average structure that approach the prototype undistorted one, with a tolerance factor above 0.996. Fluorite slabs are slightly bonded to perovskite blocks, in relation with the decrease of coordination number of its cationic sites. The introduction of an amount of non-Bi cations into them can be related to observation of shearing defects in relaxor compounds. SAED study reveals inhomogeneities within crystallites, with probably local changes in Bi/non-Bi ratio leading to local variation of the tolerance factor and to micro-twinning. Some structural aspects do not seem to be relevant, as the static disorder and the pseudo-tetragonality of the unit cell have not been observed in all relaxor compounds. The introduction of an amount of non-Bi cations in these slabs might be related to observation of shearing defects. TEM study reveals structural inhomogeneities, with probably local changes in Bi/non-Bi ratio leading to local variation of the tolerance factor and to micro-twinning. Obviously, a more precise local analysis may enable to determine the role of microstructural features in the onset of a relaxor-like behaviour in the Aurivillius phases.

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