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2002 J. Phys.: Condens. Matter 14 11849

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Magnetic-field-induced orientation in Co-doped SrBi₂Ta₂O₉ ferroelectric oxide

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Received 22 July 2002, in final form 8 October 2002

Published 1 November 2002

Online at stacks.iop.org/JPhysCM/14/11849

Abstract

Co-doped SrBi₂Ta₂O₉ (SBT) compounds have been synthesized using solid-state reaction between the starting oxides Bi₂O₃, Ta₂O₅ and CoO and the carbonate SrCO₃. High-resolution x-ray diffraction data were collected on a four-circle diffractometer using synchrotron radiation. The structure of the orthorhombic phase (space group A_12am , *one formula unit*, $a = 5.5194_{(1)} \text{ \AA}$, $b = 5.5191_{(1)} \text{ \AA}$ and $c = 25.0309_{(2)} \text{ \AA}$) has been refined using the Rietveld method. Chemical occupancies, atomic positions and spontaneous polarization were deduced from the structural refinement. In order to determine the effects on ferroelectric properties of the Sr-by-Co substitution, the dielectric response was measured over the temperature range 450–750 K on heating and cooling and at several frequencies. Finally, the magnetic field effect on Co-doped SBT powder was investigated by means of x-ray diffraction. It appears that the magnetic field induces a strong fibre texture, with the \vec{c} -axes of grains being aligned with the direction of the applied field. This original and unusual phenomenon suggests a new method for the deposition of SBT thin films with enhanced ferroelectric properties.

1. Introduction

Non-volatile memories using ferroelectric film have attracted a lot of attention in recent years and are proposed as next-generation memory material [1–3]. Ferroelectric SrBi₂Ta₂O₉ (SBT) thin films are largely studied on account of their fatigue-free properties and low coercive field [4–6] in comparison to the PbZr_{1-x}Ti_xO₃ (PZT) oxides. To obtain ferroelectric thin films

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with optimum performances, several compositions in the solid solution series $\text{Sr}_{1-x}\text{Bi}_{2+x}\text{Ta}_2\text{O}_9$ have already been studied [7–11]. It was recently reported that SBT films synthesized with Sr-deficient and Bi-excess compositions (such as $\text{Sr}_{0.8}\text{Bi}_{2.2}\text{Ta}_2\text{O}_9$) present enhanced ferroelectric properties.

The structure of SBT, called a ‘Bi-layered Aurivillius compound’ [12], consists of double-perovskite-type SrTa_2O_7 units between Bi_2O_2 layers perpendicular to the \bar{c} -axis. Strontium atoms are 12-fold coordinated in the perovskite sublattice, tantalum atoms are placed on the octahedral sites and the bismuth atoms form the rock-salt type interlayer. At room temperature, the compound crystallizes in a ferroelectric orthorhombic phase (space group $A2_1am$) [13, 14] and above the Curie temperature, the oxide presents a tetragonal paraelectric phase (space group $I4/mmm$). In the ferroelectric phase, the spontaneous polarization is along the \bar{a} -axis. Therefore, the ferroelectric properties for thin films will be optimized when the polarization is perpendicular to the substrate plane (for films with a (100) texture).

In this work, Co-doped SBT has been fabricated by a solid-state reaction route in order to:

- refine the crystal structure and precise chemical occupancies, from Rietveld whole-pattern fitting;
- measure the dielectric response and study the effect of the cobalt substitution on the Sr sites;
- investigate the magnetic-field-induced orientation.

2. Experimental details

2.1. Sample synthesis

Co-doped SBT samples were synthesized using a solid-state reaction route. SrCO_3 , Bi_2O_3 , Ta_2O_5 and CoO precursors were ground in an agate mortar (with proportions corresponding to the formula $\text{Sr}_{1-x}\text{Co}_x\text{Bi}_2\text{Ta}_2\text{O}_9$) and then annealed at 973 K for 12 h under air in an alumina crucible. The strontium ions were partially substituted for with cobalt cations with nominal substitution levels of 2, 5 and 15%. The resulting powder was ground in an agate mortar, pressed and heated at 1373 K for 12 h under air. This last operation was repeated with an annealing at 1423 K. Finally, the specimen was ground and annealed at 1373 K for 12 h under air without pressing in order to improve the powder crystallinity. For the dielectric measurements, the powdered samples were pressed to form cylindrical pellets of 9 mm diameter and then annealed at 1473 K for 12 h.

In the following, the structural and electrical characterizations will be focused on the compound $\text{Sr}_{0.85}\text{Co}_{0.15}\text{Bi}_2\text{Ta}_2\text{O}_9$ which presents enhanced properties.

2.2. Magnetic-field-induced orientation

The stable valence of cobalt cations is 2+ and, on account of their magnetic moment, some attempts have been made to induce a texture under a magnetic field. The $\text{Sr}_{0.85}\text{Co}_{0.15}\text{Bi}_2\text{Ta}_2\text{O}_9$ powder was mixed with Araldite glue to form a cylindrical pellet. This sample was placed, at room temperature, in a 1 T magnetic field H_a generated by an electromagnet. The effect of the magnetic field, applied perpendicular to the cylinder faces, was analysed by *ex situ* x-ray diffraction, the diffracting planes being either parallel or perpendicular to the sample faces. The diffraction pattern of the oriented cylindrical sample was recorded at room temperature over the angular range 20°–60°. The data were collected on a Siemens–Bruker D5000 diffractometer configured in Bragg–Brentano geometry, operating with $\text{Cu K}\alpha$ radiation and equipped with a

diffracted beam monochromator and Soller slits. A rocking curve scan of the (0010) reflection was also recorded.

2.3. Data collection and fitting procedure

For the $\text{Sr}_{0.85}\text{Co}_{0.15}\text{Bi}_2\text{Ta}_2\text{O}_9$ oxide, a high-resolution x-ray powder diffraction pattern was recorded at 300 K on the four-circle diffractometer of the synchrotron W22 beamline at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique LURE (Orsay, France). The incident wavelength of 0.6918 Å was selected by a double-Si(111) monochromator with sagittal focusing. In the high-resolution mode, a Ge(111) crystal analyser was placed on the detector arm. The powder diffraction pattern was obtained from $\theta/2\theta$ scans (in Bragg–Brentano geometry) over the 2θ angular range 6° – 46° with steps of 0.004° in 2θ . The sample was continuously rotated about its surface normal.

Full profile fitting refinement of the powder diffraction pattern was performed using the program *Fullprof* based on the Rietveld method [15]. The experimental profiles were modelled using a pseudo-Voigt profile function ($\eta \approx 0.6$) and the angular broadening of the diffraction lines reflected the Caglioti function $H = \sqrt{U \tan^2 \theta + V \tan \theta + W}$, where U , V and W are refinable parameters [16]. Systematic error corrections (zero-point shift and asymmetry) were applied; the background was adjusted from a polynomial function.

2.4. Dielectric measurements

The dielectric permittivity, as a function of temperature and frequency, was determined using a conventional-computer-controlled LCR meter, HP4284 A, measuring the capacitance and the dielectric losses of cylindrical ceramics in an electrical field of 1.5 V mm^{-1} . The experimental device also included a multimeter, HP34401 A, allowing measurement of the sample temperature controlled by an Eurotherm-920P regulator. The dielectric measurements were performed between 400 and 800 K on heating and on cooling (at a rate of 2.5 K min^{-1}) and over the frequency range 5–960 kHz.

3. Structural refinement of the ferroelectric phase

The powder diffraction data collected at 300 K were fitted using the orthorhombic structural model of SBT [7, 8], the atomic positions being described in the space group $A2_1am$ (No 36). The diffraction pattern is presented in figure 1 and shows the Co-doped SBT and an undesirable phase. The Bragg peaks of this last phase were excluded during the refinement. At the beginning of the refinement, the cell parameters and the atomic coordinates were simultaneously refined with the scale factor and the polynomial function describing the background. Independent isotropic atomic displacement parameters for the Sr, Bi and Ta atoms and the overall isotropic atomic displacement parameters for the O atoms were refined. At this stage, the chemical occupancies were fixed at 0.85/0.15 and 1 for Sr/Co and Bi respectively. In these conditions, the structural refinement leads to negative values of the isotropic atomic displacement parameters for the Sr/Co and O sites, this phenomenon being probably associated with a cationic disorder in the structure.

In earlier studies, disagreements are reported on the cationic disorder in a Bi-layered Aurivillius compound family [7, 8, 10, 17]. Neutron diffraction is ideally sensitive to the positions of the lighter O atoms whereas x-ray diffraction provides evidence of cationic disorder. Indeed, Macquart *et al* [17] have mentioned obtaining conclusive evidence for cation disorder using synchrotron x-ray diffraction on the $\text{ABi}_2\text{Ta}_2\text{O}_9$ ferroelectric oxides. For the

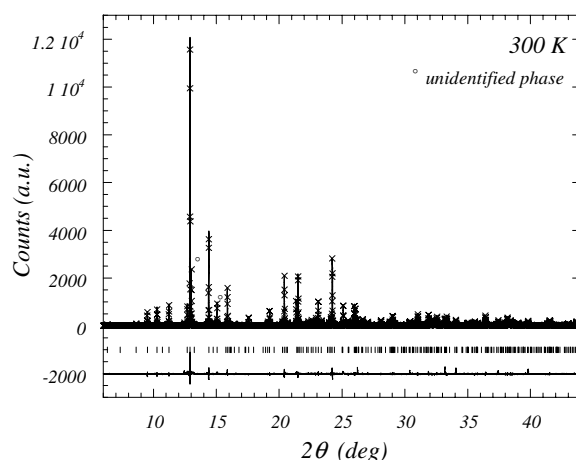


Figure 1. Observed, calculated and difference x-ray diffraction patterns for the Co-doped SBT powder with the nominal composition $\text{Sr}_{0.85}\text{Co}_{0.15}\text{Bi}_2\text{Ta}_2\text{O}_9$. Lower sticks correspond to the orthorhombic phase.

Table 1. Atomic positions, chemical occupancies and atomic displacement parameters obtained from the Rietveld refinement of the powder with the nominal composition $\text{Sr}_{0.85}\text{Co}_{0.15}\text{Bi}_2\text{Ta}_2\text{O}_9$. Refinement of high-resolution x-ray diffraction data. Space group: $A2_1am$; $a = 5.5194_{(1)} \text{ \AA}$, $b = 5.5191_{(1)} \text{ \AA}$ and $c = 25.0309_{(2)} \text{ \AA}$. X-ray data: $\lambda = 0.6918 \text{ \AA}$; pseudo-Voigt function ($\eta = 0.59$); angular range: 6° – 46° in 2θ ; step size: 0.004° in 2θ ; $U = 0.012_{(1)}$, $V = -0.0009_{(4)}$, $W = 0.00033_{(3)}$; $R_p = 11.7\%$, $R_{wp} = 17.3\%$, $R_{exp} = 12.4\%$, $\chi^2 = 1.94$, $R_{Bragg} = 5.3\%$, $R_F = 6.5\%$.

Atom	x	y	z	$B_{iso} (\text{\AA}^2)$	Chemical occupancy
Sr	0	$0.259_{(1)}$	0	$0.52_{(12)}$	$0.81_{(2)}$
Co on Sr site	0	$0.259_{(1)}$	0	$0.52_{(12)}$	$0.07_{(2)}$
Bi on Sr site	0	$0.259_{(1)}$	0	$0.52_{(12)}$	$0.12_{(2)}$
Bi	$0.469_{(1)}$	$0.7751_{(4)}$	$0.2006_{(1)}$	$0.75_{(6)}$	$0.96_{(2)}$
Sr on Bi site	$0.469_{(1)}$	$0.7751_{(4)}$	$0.2006_{(1)}$	$0.75_{(6)}$	$0.04_{(2)}$
Ta	$0.520_{(1)}$	$0.7475_{(4)}$	$0.4149_{(1)}$	$0.17_{(9)}$	1
O(1)	$0.560_{(8)}$	$0.294_{(7)}$	0	$0.04_{(3)}$	0.5
O(2)	$0.548_{(6)}$	$0.703_{(4)}$	$0.340_{(1)}$	$0.04_{(3)}$	1
O(3)	$0.730_{(5)}$	$1.021_{(13)}$	$0.249_{(1)}$	$0.04_{(3)}$	1
O(4)	$0.755_{(6)}$	$0.955_{(6)}$	$0.070_{(1)}$	$0.04_{(3)}$	1
O(5)	$0.790_{(7)}$	$0.997_{(8)}$	$0.583_{(1)}$	$0.04_{(3)}$	1

stoichiometric oxide SBT, Kim *et al* have determined the chemical occupancy on the Sr site (Sr/Bi = 0.91/0.09) and have described the location of Bi^{3+} ions on the Sr^{2+} sites as a function of the Bi excess in the structure [10]. In our case, the introduction of Bi atoms on the Sr sites and Sr atoms on the Bi sites of the perovskite units gives a positive value of the isotropic atomic displacement parameters, the chemical occupancies on Sr/Co/Bi and Bi/Sr sites being equal to $0.81_{(2)}/0.07_{(2)}/0.12_{(2)}$ and $0.96_{(2)}/0.04_{(2)}$ respectively (the chemical occupancy of the Ta atoms remaining full). The general chemical formula is $(\text{Sr}_{0.81}\text{Co}_{0.07}\text{Bi}_{0.12})(\text{Bi}_{1.92}\text{Sr}_{0.08})\text{Ta}_2\text{O}_9$. Considering these results, it is possible to state that the unidentified phase contains near to 7 at.% of Co. The structural refinement leads to satisfactory reliability factors with $R_p = 11.7\%$, $R_{wp} = 17.3\%$, $R_{Bragg} = 5.3\%$, $R_F = 6.5\%$, $\chi^2 = 1.94$. The structural data are given in table 1.

The shifts along the ferroelectric \vec{a} -axis of the Bi^{3+} , Ta^{5+} cations and O^{2-} anions have been calculated by setting the position of the Sr site at the origin. The cation shifts being directly related to the ferroelectric character of the structure, a spontaneous polarization P_S due to the relative ion displacements can be estimated by considering a purely ionic crystal and neglecting the electronic polarization:

$$P_S = Z \sum_i \frac{\delta x_i q_i}{V}$$

where δx_i is the cation shift along the ferroelectric \vec{a} -axis of the i th ion carrying a charge q_i , and V the volume of the unit cell. The calculation leads to a spontaneous polarization of about $19.8 \mu\text{C cm}^{-2}$ at 300 K, this polarization being close to those determined for the SBT and $\text{Sr}_{0.8}\text{Bi}_{2.2}\text{Ta}_2\text{O}_9$ compounds (respectively 18.2 and $20 \mu\text{C cm}^{-2}$ at 300 K) [8].

4. Dielectric properties of Co-doped SBT ceramics

Figure 2 presents the temperature dependence of the dielectric constant, ϵ_r , for the Co-doped SBT sample at several frequencies on heating and on cooling. The substitution of cobalt atoms for strontium atoms conserves the ferroelectric character of the oxide, since a high maximum of the dielectric constant is observed around 660 K on cooling. Furthermore, the maximum of ϵ_r exhibits a slight thermal shift with the frequency from 656 at 5 Hz to 663 K at 960 kHz, this phenomenon being probably attributable to a relaxor behaviour. The maximum of the dielectric permittivity associated with the ferroelectric–paraelectric transition exhibits a thermal hysteresis of about 13 K between heating and cooling. This seems to favour a first-order ferroelectric-to-paraelectric phase transition. Finally, the evolution of the dielectric constant with temperature for various compositions of SBT oxides is presented in figure 3. The dielectric response of Co-doped SBT is higher than those observed in the stoichiometric and the Bi-rich SBT samples (the maxima of ϵ_r for SBT, $\text{Sr}_{0.8}\text{Bi}_{2.2}\text{Ta}_2\text{O}_9$ and Co-doped SBT compounds are respectively 402, 415 and 640 at 300 kHz). The ferroelectric–paraelectric transitions for SBT, $\text{Sr}_{0.8}\text{Bi}_{2.2}\text{Ta}_2\text{O}_9$ and Co-doped SBT samples appear on heating at 605, 680 and 658 K respectively. These results are in agreement with those reported by Shimakawa *et al* [8]. As a partial conclusion, the substitution of Co^{2+} for Sr^{2+} cations seems to enhance the dielectric response and increase the transition temperature.

5. Analysis of the magnetic-field-induced texture

X-ray diffraction patterns were collected for free $\text{Sr}_{0.89}\text{Co}_{0.07}\text{Bi}_{2.04}\text{Ta}_2\text{O}_9$ powder (figure 4(a1)) and an oriented cylindrical sample (figures 4(a2) and (a3)). The diffraction pattern corresponding to the scattering vector parallel to the magnetic field direction presents a strong preferred orientation of (00ℓ) reflections (figure 4(a2)). Moreover, the pattern registered when the scattering vector is perpendicular to the magnetic field direction (figure 4(a3)) is similar to the one measured for the free powder (figure 4(a1)), the (00ℓ) reflections being nevertheless absent. Therefore, the magnetic field clearly induces an alignment of the \vec{c} -axes with the direction of \vec{H} .

The degree of orientation of the cylindrical sample was investigated from a rocking curve for the (0010) reflection at 36° in 2θ . Figure 4(b) presents the scan and the fit used to determine a full width at half maximum (FWHM) of about 3.5° . One can consider the \vec{c} -axes to be dispersed over a revolution cone centred on the \vec{H} -direction and with no more than 3.5° FWHM. Although this value is not as good as the one obtained for epitaxially grown thin film, this result clearly shows that the cylindrical sample is well aligned. Song *et al* [18] have investigated the \vec{c} -axis

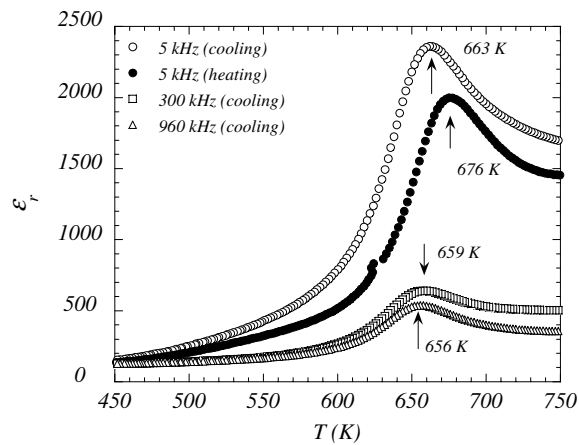


Figure 2. Dielectric constant as a function of the temperature for the Co-doped SBT ceramic at several frequencies, on heating and on cooling (5, 300 and 960 kHz).

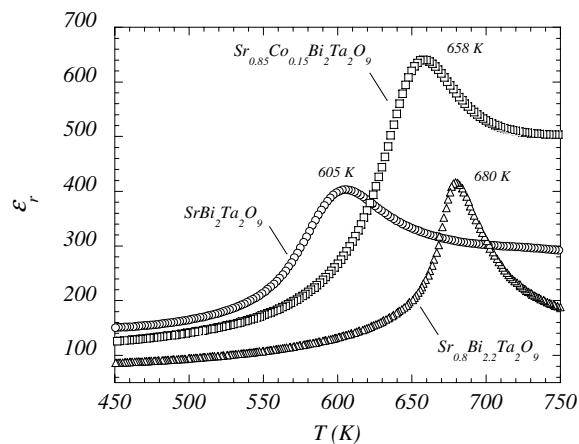


Figure 3. Temperature-dependent evolution of the dielectric constant measured at 300 kHz for SBT, $\text{Sr}_{0.8}\text{Bi}_{2.2}\text{Ta}_2\text{O}_9$ and Co-doped SBT compounds.

orientation of SBT thin film by means of a rocking curve scan of the (006) Bragg reflection and have determined a FWHM of about 3.2° . It seems that, in our case, the magnetic field induces a \bar{c} -axis orientation for the Co-doped SBT powder as good as the one obtained for SBT thin films deposited on Pt(111)/Ti/SiO₂/Si(001) substrate [18].

6. Discussion

Cobalt atoms have been introduced on the Sr site because this isovalent substitution (Co^{2+} for Sr^{2+}) does not modify the global electroneutrality and does not create oxygen vacancies. The substitution of divalent cations for trivalent or tetravalent cations could induce the number of oxygen vacancies and increase the number of fatigue defects [12, 19, 20]. The introduction of 15 at.% of cobalt atoms on the Sr site leads to the formation of an undesirable phase which coexists with the ferroelectric SBT phase. Co-doped samples with different substitution

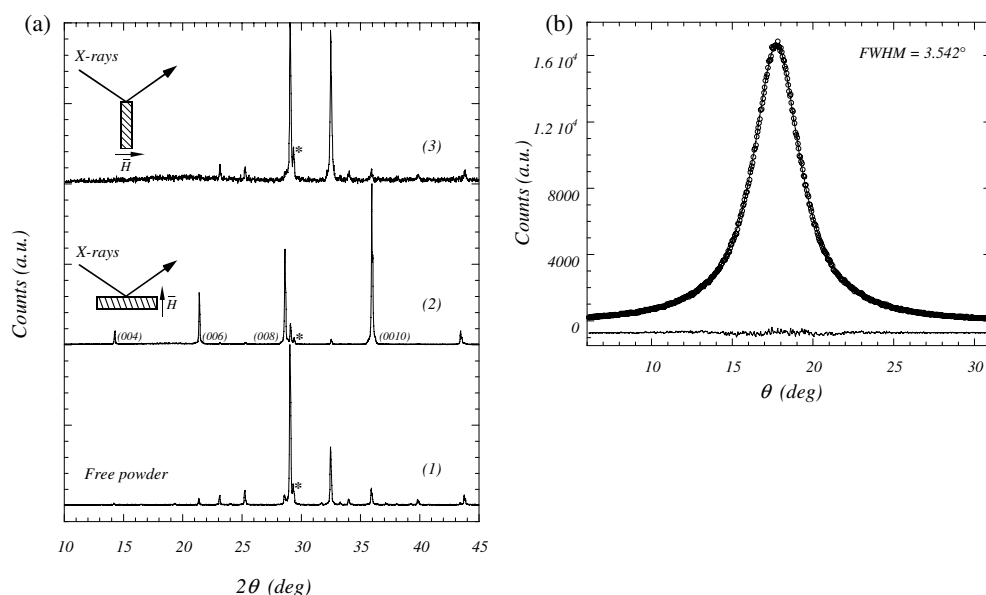


Figure 4. (a) X-ray diffraction diagrams for free Co-doped SBT powder (1) and a magnetic-field-oriented cylindrical samples (2 and 3). The diffracting planes are either perpendicular (2) or parallel (3) to the magnetic field direction. The stars indicate the Bragg reflections of the small impurity. (b) A rocking curve scan of the (0010) Bragg reflection. The continuous curve corresponds to the adjusted profile with a Lorentzian function for which the full width at half-maximum (FWHM) is equal to 3.5° in 2θ .

rates have been synthesized (2, 5 and 15 at.%) and it appears that the increase of Co in the solid solution increases the proportion of the undesirable phase. $\text{Sr}_{0.98}\text{Co}_{0.02}\text{Bi}_2\text{Ta}_2\text{O}_9$ and $\text{Sr}_{0.95}\text{Co}_{0.05}\text{Bi}_2\text{Ta}_2\text{O}_9$ compounds exhibited the undesirable phase in lower quantities but the magnetic field induced no orientation. By Rietveld refinement, we have determined that Co-doped SBT contains 7% of cobalt atoms for a nominal composition of 15%. Therefore, it seems that it is necessary to introduce a large excess of Co atoms during the synthesis to obtain a sufficient percentage of cobalt in the structure.

The cationic substitution of Co^{2+} for Sr^{2+} does not remove the ferroelectric character of the structure and leads to unusual characteristics as compared to the undoped SBT oxides. The spontaneous polarization calculated from the Rietveld refinement is close to the one obtained for the non-substituted compound [8], but the dielectric response is larger. Furthermore, the cobalt doping induces a thermal shift of the permittivity maximum with frequency, this phenomenon being unreported in the literature for SBT-derived oxides. This probable relaxor behaviour is in agreement with the larger measured dielectric permittivity. Finally, the cobalt doping also increases the temperature of the ferroelectric-to-paraelectric phase transition, this divalent substitution (Sr^{2+}) probably having a similar influence on the transition temperature to Bi in Bi-rich compounds.

The magnetic field effect on the Co-doped SBT has been investigated by means of x-ray diffraction. The x-ray diffraction pattern of the oriented cylindrical sample shows a strong texture along the \vec{c} -axis. Following magnetic characterization results obtained on the Aurivillius phase $\text{Bi}_4(\text{V}_{0.85}\text{Co}_{0.15})_2\text{O}_{11-\delta}$ [21], it is emphasized that the Co^{2+} atoms have an anisotropic magnetic moment parallel to the \vec{c} -axis. When this material was embedded in Araldite glue, the \vec{c} -axes of the grains were aligned parallel to the applied magnetic field

direction. The x-ray diffraction pattern, corresponding to the scattering vector perpendicular to the magnetic field direction, is similar to the one obtained for a free SBT powder without (00ℓ) reflections. This result can be interpreted as a fibre texture with a stacking of (00ℓ) planes perpendicular to the magnetic field direction and a random orientation in the (\vec{a}, \vec{b}) planes. This peculiar behaviour opens a new way to deposit SBT thin films with improved ferroelectric properties. Indeed, in applying a magnetic field during the deposition it should be possible to force the \vec{c} -axis to be in the plane of the substrate with a direction parallel to the applied field. Consequently, the spontaneous polarization, which is along the \vec{a} -axis, will be distributed over a disc perpendicular to the substrate (random orientation of the (\vec{a}, \vec{b}) planes). In these conditions and after poling, the global remanent polarization should be enhanced as compared to that obtained for a non-textured polycrystalline film.

7. Conclusions

Cobalt-doped SBT powder has been synthesized using solid-state reaction. The structural refinement performed from the fitting of high-resolution x-ray powder diffraction data has revealed a cationic disorder on Bi^{3+} and Sr^{2+} crystallographic sites, the Sr atoms occupying the Bi sites and vice versa. On the other hand, the substitution limit of Co^{2+} cations on the Sr sites has been estimated at 7 at.%. From the cationic shifts, a spontaneous polarization of $19.8 \mu\text{C cm}^{-2}$ has been determined.

The substitution of Co^{2+} ions for Sr^{2+} cations leads to unusual properties of this SBT-derived compound. The following characteristics have been observed:

- (i) This partial substitution strongly enhances the dielectric response, especially around the ferroelectric-to-paraelectric phase transition. Furthermore, the Co-doped SBT undergoes this phase transition 50 K above the temperature generally encountered for the stoichiometric SBT compound. In agreement with the larger dielectric constant, a slight relaxor behaviour has been inferred from the frequency-dependent dielectric measurements.
- (ii) A magnetic field orientates Co-doped SBT powders using the anisotropic magnetic moment carried by Co^{2+} cations. The resulting sample presents a fibre texture with a stacking of the (00ℓ) planes perpendicular to the magnetic field direction and a random orientation in the (\vec{a}, \vec{b}) plane.

These results suggest a new method for depositing SBT thin films with enhanced ferroelectric properties. Indeed, if a magnetic field is applied during the deposition, it should be possible to control the orientation of the film on the substrate. Attempts are now under development to constrain the \vec{c} -axis to be in the substrate plane in order to have a more favourable distribution of the polarization.

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