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Lanthanum-doped $Bi_4Ti_3O_{12}$ prepared by the soft chemical method: Rietveld analysis and piezoelectric properties

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Abstract

$Bi_{4-x}La_xTi_3O_{12}$ (BLT) thin films and powders with x ranging from 0 to 0.75 were prepared by the polymeric precursor solution. The effect of lanthanum on the structure of BIT powders was investigated by Rietveld Method. The increase of lanthanum content does not lead to any secondary phases. Orthorhombicity of the bismuth titanate (BIT) crystal lattice decreased with the increase of lanthanum content due the reduction of a/b ratio. The BLT films show piezoelectric coefficients of 45, 19, 16 and 10 pm/V for $x = 0$, 0.25, 0.50 and 0.75, respectively. The piezoelectric response is strongly reduced by the amount of lanthanum added to the system.

Keywords: A. Sintering; Ceramics; Crystal structure

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1. Introduction

In recent years, several studies have been reported on thin films for memory applications. The most popular ferroelectric material for nonvolatile memories is lead zirconate titanate (PZT). However, the PZT thin films on platinum electrode show serious problems of degradation due to oxygen vacancies created at the interface [1]. As alternative a new class of ferroelectric based on Bi-layered perovskites has been attempted. The bismuth layer structure was originally described by Aurivillius to have the formula $(Bi_2O_2)^{2+}$–$(A_{m-1}B_mO_{3m+1})^{2-}$, where A is Bi, Ba, Sr, Ca, Pb, K or Na; B is Ti, Nb, Ta, Mo, W or Fe. Recently, Bi-layered perovskite thin films such as $Bi_4Ti_3O_{12}$, $SrBi_2Ta_2O_9$ (SBT) or $SrBi_2Nb_2O_9$ (SBN) have been developed. Because of the fatigue-free behavior of lanthanum-substituted bismuth titanate [Bi_{x}-$La_{1-x}Ti_3O_{12}$ (BLT)], a Bi-layered perovskite oxide with a platinum electrode has received increasing attention on ferroelectric applications, such as nonvolatile memory [2,3]. Compared with $SrBi_2Ta_2O_9$ (SBT), another well-known fatigue-free ferroelectric material which is also a Bi-layered perovskite oxide, BLT has many attractive properties, such as low processing temperature and large values of remnant polarization. Two reasons for the fatigue-free behavior of BLT have been found. One is the charge-compensating role of the (Bi_2O_2) layers. Another is the higher chemical stability of the perovskite layers compared to oxygen vacancies after substituting Bi by La atom. The oxygen ions near Bi ions in BIT are likely to be less stable than those near Sr ions in SBT due to the high volatility of Bi ions [3–5].

Obviously, the substitution of bismuth by lanthanum influences on the ferroelectric properties of this material dramatically. Bu et al. [6] prepared thin films of BIT doped with lanthanum by pulsed laser deposition. The authors found that these films were appropriate for non-volatile random access memory devices. It is known that BIT compounds have a high leakage current and domain pinning due to defects such as Bi vacancies (V'''_{Bi}) accompanied by oxygen vacancies $(V_O^{\circ\circ})$. In order to minimize these defects the substitution of Bi by La ion on A-site is required [3]. It is known that the role of A-site substitution is to displace the volatile Bi with La to suppress the A-site vacancies which are accompanied by oxygen vacancies

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that act as space charges. It has been reported that ferroelectric properties were improved by ion doping on A- or B-site [7]. Recently, effects of ion doping on ferroelectric properties and electrical conduction have been widely studied [8]. For practical FRAM application, it is necessary to obtain BLT thin film with high remnant polarization and low leakage current.

In recent years sol–gel processing and the co-precipitation method have become popular for producing ceramic materials with improved compositional homogeneity and with lower sintering temperature. Although the sol–gel process utilizes expensive precursors and depends of a critical drying process, the co-precipitation process is limited by cation solutions with similar solubility constants. On the other hand, polymeric precursor process which employs complexing of cations in an organic media, makes use of low cost precursors and results in a homogeneous ion distribution at molecular level [9]. Due to the formation of a polyester resin during the synthesis, no segregation of cations was observed during the thermal decomposition of organic material. The polymeric precursor method presents many advantages, such as the possibility to work in aqueous solutions with the high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method (inexpensive precursors and equipments). Crystal structure analysis is an important step to get the high quality of BIT. XRD method is general technique to find out micro-parameter of materials, otherwise another technique is needed to refine data from XRD data which uses more accurate data. Due the fact that recently, more and more efforts have been undertaken to develop nontoxic lead-free piezoelectric materials, we report the Rietveld analysis to refine the crystal structure of BLT systems. Also, the effect of crystal structure on piezoelectric properties of La-doped bismuth titanate thin films prepared from polymeric precursors was investigated.

2. Experimental procedure

Titanium isopropoxide (Hulls AG), hydrated lanthanum carbonate (Aldrich) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth, titanium and lanthanum were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Ti, Bi and La were mixed and homogeneized by stirring at 90 °C. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. Films were spin-coated from $Bi_{4-x}La_xTi_3O_{12}$ ($x = 0$, 0.25, 0.50 and 0.75) solutions onto $Pt/Ti/SiO_2/Si$ substrate. BLT films were completely crystallized at 700 °C for 2 h in static air atmosphere according to a previous paper [10]. Multilayered films were obtained by spinning 10 times the deposition solution on the surface of the substrate at 5000 rpm. In this work, an excess of 5 wt% of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Phase analysis was performed at room temperature by X-ray powder diffraction (XRD) using a Bragg-Brentano diffractometer (Rigaku 20–2000) and Cu Kα radiation. For Rietveld analyses, X-ray diffraction data of the powders calcinated at 750° C for 4 h were collected on a diffractometer under the following experimental conditions: 40 kV, 30 mA, $20° \leq 2\theta \leq 120°$, $\Delta 2\theta = 0.02°$, λCu Kα monocromatized by a graphite crystal, divergence slit = 2 mm, reception slit = 0.6 mm, step time = 10 s. The Rietveld analysis was performed with the refinement program DBWS-941 1 [11]. The profile function used to adjust the calculated to the observed diffractograms was the modified Thompson–Cox-Hasting pseudo-Voigt. In this profile, the Lorentzian fraction of the function (η) changes with the Gauss and Lorentz components of the full width at half maximum. The lattice parameters, atomic positions, occupation factors of the calculated XRD pattern is adjusted to the observed one until a minimal deviation is reached. The best-fitting curve obtained from the least square method assumes the minimal sum of squared deviations (least square error) from a given set of data.

The thickness of the annealed films was studied using scanning electron microscopy (Topcon SM-300) by looking at the transversal section. In this case back scattering electrons were utilized. The thickness results obtained from SEM represent an average value of three measurements. A 0.5 mm diameter top Pt electrode was sputtered through photolitopraphy at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace, at 300 °C, in oxygen atmosphere for 1 h to decrease eventually present oxygen vacancies.

Piezoelectric measurements were done using a setup based on an atomic force microscope in a Multimode Scanning Probe Microscope with Nanoscope IV controller.

3. Results and discussion

Fig. 1 illustrates the XRD analyses of pure and lanthanum-doped BIT thin films. All reflections are addressed to the perovskite and residual oxide bismuth phases. No additional

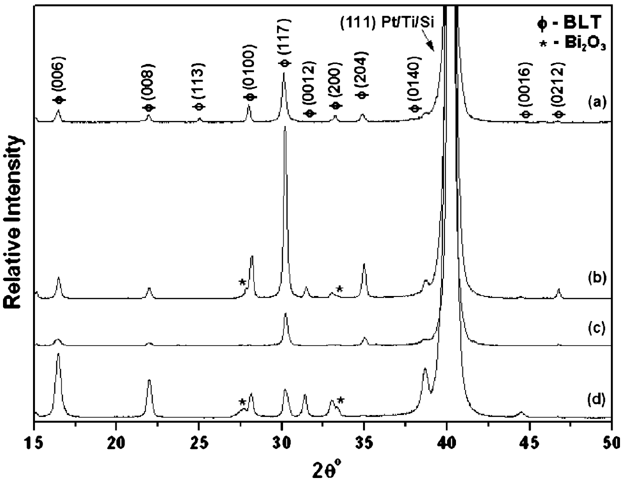

Fig. 1. XRD for $Bi_{4-x}La_xTi_3O_{12}$ films deposited on (1 1 1) $Pt/Ti/SiO_2/Si$ and annealed at 700 °C/2 h in static air: (a) $x = 0$; (b) $x = 0.25$; (c) $x = 0.50$; (d) $x = 0.75$.

secondary phases were evident after the addition of lanthanum in the system. A shift of some peak positions was noted after the addition of lanthanum and can be ascribed to the change of crystal structure from orthorhombic to tetragonal as already discussed in reference [12].

The BIT system has already been investigated from a fundamental point of view, regarding the role of dopant in the crystal structure of pure bismuth titanate [13]. In the present study, we have adopted the Rietveld refinement technique to investigate the crystal structure of the BIT and BLT systems, and have obtained adequate evidence for the preferred site for lanthanum substitution (Table 1). Table 1 illustrates the R_{wp}, R_{exp}, and S indexes, as well as the lattice parameters (a, b and c) and the unit cell volume (V). The phase identification was carried out in the PDF data bank, resulting in an orthorhombic structure type. The structural model (available on ICSD data bank) that allows the best-fitting was the orthorhombic one (ICSD no. 24735 with space group *Fmmm*). The quantitative phase analyses for the orthorhombic phase were calculated according to the reference of Young and Wiles [11]. No changes occurred in the refinements when Bi^{3+} ion was substituted by La^{3+} ion in the orthorhombic BIT phase. It was observed that La^{3+} substitutes Bi^{3+} only in a perovskite-type unit cell, causing a distorted structure whereby distortion increases with raising lanthanum content.

The covalent interaction, which originates from the strong hybridization between Ti 3d and O 2p orbitals, plays an important role in the structural distortion of these materials. It can be assumed that doping with La improves oxygen ion stability in the lattice because some of the Bi ions in the pseudo-perovskite layers containing Ti–O octahedra were substituted by La ions. The low S values ($S = R_{wp}/R_{exp}$) obtained in our investigation indicates that the refinement was successfully performed with all parameters close to literature data [14]. Lanthanum addition elongates c-axis due the differences in charge density of lanthanum and bismuth atoms. Also, the addition of lanthanum that has a radial substitution effect higher than bismuth is to stabilize the oxygen vacancies and consequently the structure. As a consequence, a and b parameters became closer indicating that the orthorhombic

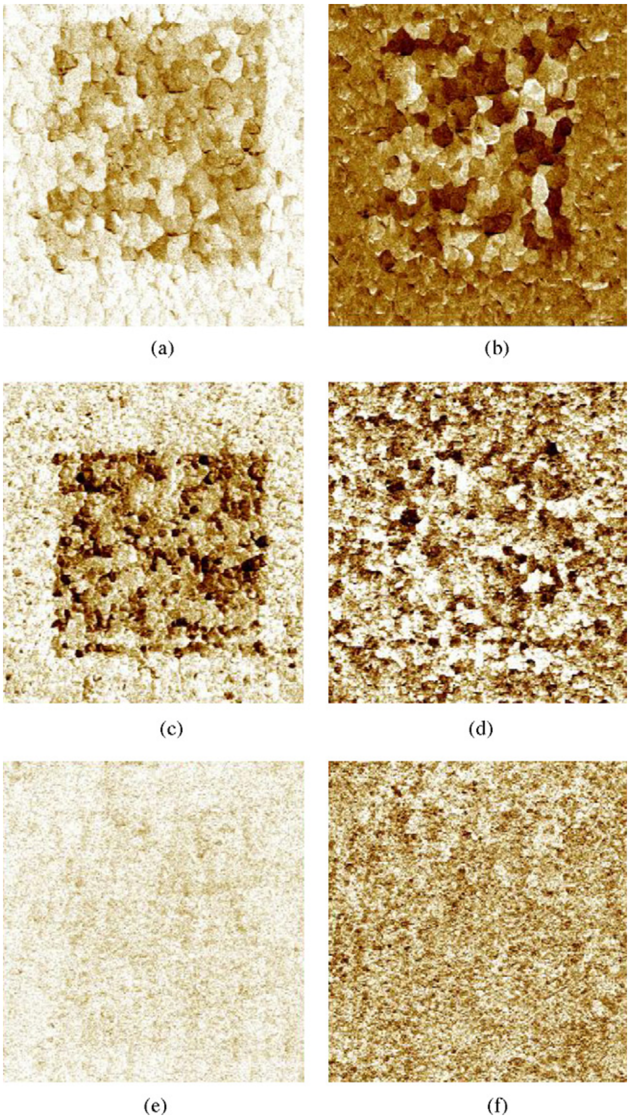
(a) (b) (c) (d) (e) (f)

Fig. 2. Domain images obtained from top-electrode-coated $Bi_{4-x}La_xTi_3O_{12}$ thin films for different compositions and views: (a) $x = 0.0$, out-of-plane view; (b) $x = 0.0$, in-plane view; (c) $x = 0.25$, out-of-plane view; (d) $x = 0.25$, in-plane view; (e) $x = 0.75$, out-of-plane view; (f) $x = 0.75$, in-plane view.

Table 1
Index refinements for $Bi_{4-x}La_xTi_3O_{12}$ calcinated powders at 750 °C for 4 h with different lanthanum contents: (a) $x = 0$; (b) $x = 0.25$; (c) $x = 0.50$ and (d) $x = 0.75$

Parameter	BIT	BTL25	BTL50	BTL75
Refinement index				
R_{wp} (%)	11.12	12.57	10.78	10.19
R_{exp}	7.06	9.00	6.60	7.02
S	1.57	1.39	1.62	1.44
Lattice parameters				
a (Å)	5.4175	5.4141	5.4151	5.4208
b (Å)	5.4403	5.4377	5.4310	5.4213
c (Å)	32.7862	32.8409	32.8578	32.8924
V (Å^3)	966.30	966.85	966.33	966.64
D (g/cm^3)	8.02	7.89	7.78	7.67
Perovskite (mol%)	97.5 ± 0.5	97.1 ± 0.4	98.4 ± 0.4	97.7 ± 0.4
Stoichiometry	$Bi_4Ti_3O_{12}$	$Bi_{3.75}La_{0.25}Ti_3O_{12}$	$Bi_{3.50}La_{0.50}Ti_3O_{12}$	$Bi_{3.25}La_{0.75}Ti_3O_{12}$
Refinement	$Bi_4Ti_3O_{11.6}$	$Bi_{3.75}La_{0.25}Ti_3O_{11.6}$	$Bi_{3.50}La_{0.50}Ti_3O_{11.6}$	$Bi_{3.25}La_{0.75}Ti_3O_{11.8}$

structure tends to transforms into a tetragonal one with the increase of lanthanum content.

Fig. 2a–f illustrates the piezoelectric response of BLT films for several compositions. Here, the negative pole of the 12 V power supply was applied to the substrate bottom electrode in order to check the piezoelectric activity. Two regions with different contrasts can be distinguished; the light contrast corresponds to the as-grown film, the dark one arose upon application of the dc voltage, which results in a polarization vector along the electric field, pointing perpendicular into the film plane. In the out-of-plane image (Fig. 2a, c and e) the color contrast indicates domains oriented in direction to the bottom electrode and the AFM tip, respectively. Usually, the dark region indicates that the polarization vector is oriented in the tip direction. Generally, inside the darker quadratic regions that exhibit a small piezoelectric response, are always unpolarized crystallites (light regions).

This is a common result for bismuth-layered ferroelectrics, which exhibit a great polarization in *a*-axis direction, besides a smaller polarization along the *c*-axis and reflects the different orientation of the grains, i.e. the light regions are *c*-axis oriented crystallites. Since the image does not change even for high voltages, it can be concluded that it is impossible to align their polarization vector, so the total polarization in field direction is always moderate. By changing the polarity of the applied voltage it can be easily demonstrated that the light regions present a polarization vector perpendicular to the film surface, whereas in the dark regions the polarization vector lies in the film plane.

From the obtained results, it can be inferred that the piezoelectric properties are strongly influenced by the La content. The $x = 0.50$ composition possesses already highly diminished piezoelectricity, which vanishes completely for the $x = 0.75$ composition. The decrease in piezoelectric response with increasing La concentration originates from a reduced polarizability along the *a*-axis, which contributes significantly to the ferroelectric properties of bismuth titanate. The in-plane images show light-colored grains presenting a polarization vector in the positive *y*-axis direction and dark grains with exactly opposite polarization. Grains with intermediate contrast do not present overall piezoelectricity, probably due to pinned domains. In this way, La is changing the crystal structure of BIT affecting the piezoelectric properties.

Fig. 3 illustrates the piezoelectric hysteresis loop obtained for the pure and lanthanum-doped BIT system. The hysteresis in the piezoresponse signal is directly associated with the polarization switching. The maximum d_{33} value, ~45 pm/V, is higher for the pure system and approaches the reported value for a BIT single crystal [15]. Here, we point out that it is difficult to compare these values to the piezoelectric coefficients of bulk material since the measurement was performed on a local area that has a relatively intricate field distribution and vibrational modes. Considering the polycrystalline nature of our films the effective piezoelectric coefficient depends on grain orientation. Therefore, the piezoelectric response decreases with the increase in lanthanum content due to the change in crystal structure from orthorhombic to tetragonal and reduction in the strain energy and the pinning effect of charged defects after doping. Although the PZT films still have higher d_{33} values, ranging from 40 to 110 pm/V [16], the presented values reported for our pure BIT films suggest that this material can be considered as a viable alternative for lead-free piezo-ferroelectric devices. In comparison with other lead free ferroelectrics, 40 pm/V is more than two times the d_{33}

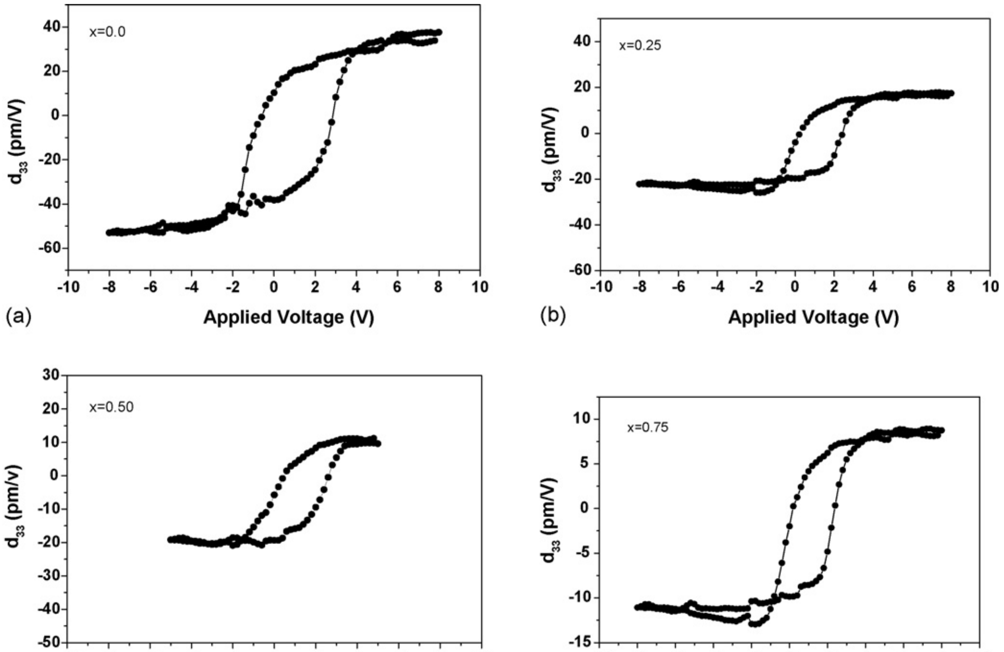

Fig. 3. Piezoresponse loops of $Bi_{4-x}La_xTi_3O_{12}$ thin film deposited on (1 1 1) Pt/Ti/SiO$_2$/Si substrate and annealed at 700 °C for 2 h: (a) $x = 0$; (b) $x = 0.25$; (c) $x = 0.50$; (d) $x = 0.75$.

value of $SrBi_2Ta_2O_9$ films [17] (17 pm/V) and close to the reported value of Nd-doped $Bi_4Ti_3O_{12}$ [17] (38 pm/V).

4. Conclusions

Pure and lanthanum modified bismuth titanate thin films and powders were obtained from the polymeric precursor method through annealing in static air atmosphere. XRD analyses demonstrated that lanthanum addition does not lead to additional secondary phases indicating the formation of solid solution. Rietveld refinement indicated a tendency to phase transition from orthorhombic to tetragonal structure when the lanthanum content is increased. Increasing lanthanum content decreases strongly the piezoelectric response.

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