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Structure of sol-gel prepared ferroelectric $Bi_{3.4}La_{0.6}Ti_3O_{12}$

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Abstract The $Bi_{3.4}La_{0.6}Ti_3O_{12}$ (BLT) thin film and powder have been prepared by a sol-gel method with annealing at 700°C. Randomly oriented BLT thin film exhibits a large remanent polarization, $2P_r = 72\ \mu C/cm^2$, with a dc applied field strength of 320 kV/cm. Structure of sol-gel derived BLT powder has been investigated by neutron scatterings, and refined by a Rietveld method resulting a reasonable goodness of fit ($wR_p = 6.7\%$, and $R_p = 5.7\%$) using an orthorhombic (*B2cb*, $a = 5.4221$ Å, $b = 5.4032$ Å, and $c = 32.8361$ Å). Two different TiO_6 octahedra exhibit different polarization directions; (100) from $Ti(1)O_6$, and (011) from $Ti(2)O_6$, which explains the observed large $2P_r$ of the randomly oriented BLT thin film.

1 Introduction

Ferroelectrics have been extensively studied for applications on nonvolatile ferroelectric random access memories (FeRAMs) [1–3]. Among them, lanthanide doped $Bi_4Ti_3O_{12}$ (BIT) thin films have been extensively investigated, since they exhibit several advantages, such as a large remanent polarization, a good fatigue resistance, and a relatively low processing temperature [4–9].

It is worthwhile to study ferroelectric properties of lanthinium-substituted bismuth titanate, $(Bi_{4-x}La_x)Ti_3O_{12}$, since La is a member of lanthanide expected to improve ferroelectric properties by reducing Bi and O vacancies in the structure. Furthermore, the 6-coordinated ion radius of La^{3+} (0.1172 nm) is similar to that of Bi^{3+} (0.117 nm), which suggests that an easy replacement of La to Bi without a large lattice distortion. Pulsed laser deposited $(Bi_{4-x}La_x)Ti_3O_{12}$ thin film has been known to improve ferroelectric properties [4].

In order to understand ferroelectric nature of the Bi-layered perovskite, the structure must be investigated. Furthermore, it has been widely accepted that the ferroelectric properties of the layered perovskite heavily depend on the TiO_6 octahedron in the unit cell, which would determine the magnitude and orientation of polarization vector in the structure.

In this study, lanthinium-substituted bismuth titanate, $Bi_{3.4}La_{0.6}Ti_3O_{12}$ (BLT), thin films were grown on Pt(111)/$Ti/SiO_2/Si(100)$ substrates by a sol-gel spin coating process followed by annealing process (700°C). Furthermore, BLT powder prepared by the same sol-gel process with annealing at 700°C has been investigated by neutron scatterings to understand structure of the BLT powder. The structure of BLT has been refined by a Rietveld analysis using the neutron scattering data.

2 Experiments

Precursor solution of ferroelectric $Bi_{3.4}La_{0.6}Ti_3O_{12}$ have been prepared by a conventional sol-gel process. Bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$], praseodymium nitrate [$La(NO_3)_3 \cdot 6H_2O$] and titanium isopropoxide [$Ti[OCH(CH_3)_2]_4$] were used as starting materials for Bi, La and Ti, respectively. Detailed process was described in the elsewhere [9]. The final mixture of BLT precursor has been coated on Pt(111)/$Ti/SiO_2/Si$ substrates by spin coating at 3000 rpm,

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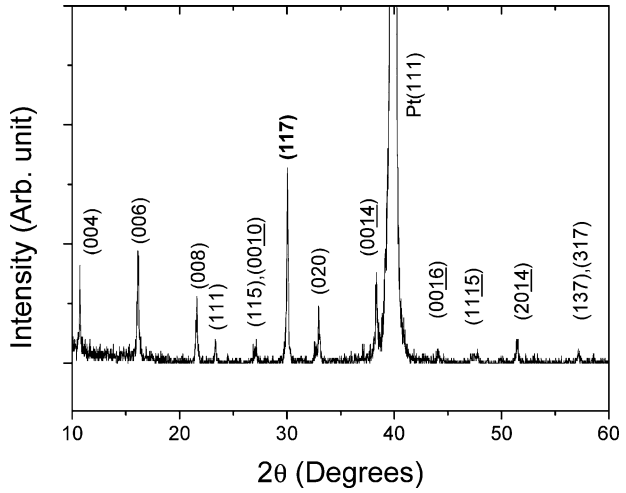

Fig. 1 X-ray diffraction pattern of BLT thin film grown on Pt(111)/Ti/SiO_2/Si

and annealed at 700°C to fabricate thin crystallized film. At the same time, the final mixture of BLT has been dried and annealed to produce powder sample with the same procedure described for film preparation.

The crystallization of the BLT film and powder have been investigated by an X-ray diffractometer equipped with Cu Kα (Philips, APD system. For measurements of electrical properties, gold electrodes were deposited by a thermal evaporation method on the surface of the BLT thin film with an area of approximately 7.85×10^{-5} cm^2 using a metal mask and then heated at 400°C for 15 s by a rapid thermal annealing process before measurements to improve adhesion between the metal and ferroelectrics. The electrical properties of the ferroelectric film capacitors were measured using a ferroelectric tester (Radiant, RT66A), a low frequency impedance analyzer (HP4192A) and an electrometer (Keithley 6517A).

Neutron scattering data of BLT powder was collected by a high resolution powder diffractometer in HANARO neutron reactor in Daejon, Korea with a wavelength of 0.18339 nm with a vanadium charge tube. The neutron scattering data was fitted by a Rietveld analysis method using a GSAS program [10].

3 Electrical properties of BLT thin film

X-ray diffraction pattern of the BLT thin film annealed at 700°C for 30 min in oxygen atmosphere are shown in Fig. 1. From the XRD patterns, it is clear that the reflection peaks can be indexed as a bismuth layered perovskite structure. It is reasonable that the BLT thin film annealed at 700°C is randomly orientated polycrystalline, since strong (117) reflection was observed.

Remanent polarization ($2P_r$) and coercive electric field ($2E_c$) of the BLT thin films were measured with a dc sweep voltage of $-20 \sim +20$ V across a 400 nm of film thickness (Fig. 2). At an applied electric field of 320 kV/cm, the measured remanent polarization ($2P_r$) is 72 μC/cm^2. This large remanent polarization from randomly oriented BLT film is very unusual since spontaneous polarization of BIT family have been known to be along *a* axis [11, 12].

4 Structural properties of BLT powders

The sol-gel prepared BLT powder annealed at 700°C has been analyzed by a Rietveld method using GSAS. Lanthanide substituted BIT powders prepared by solid state reaction experiencing high temperatures (normally higher than 1100°C) have been refined to be orthorhombic (*B*2*cb*) and mono-

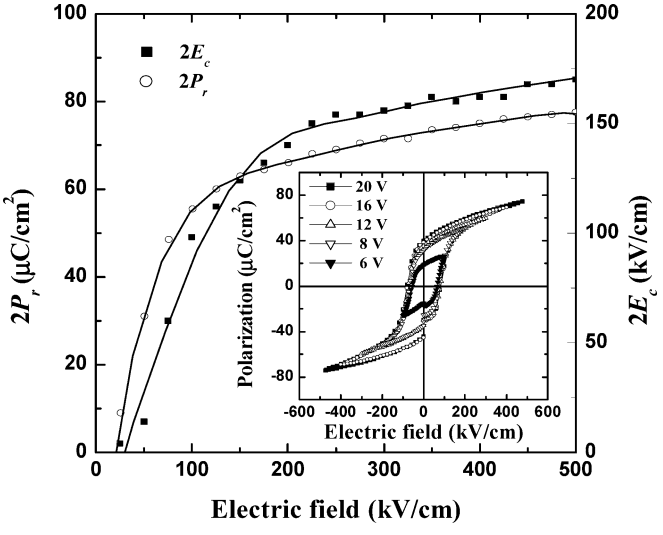

Fig. 2 Electric field dependent remanent polarizations and coersive field of BLT thin film

Table 1 Refined atomic data of BLT

	Position						
Name (Type)	X	Y	Z	Ui/Ue*100	Site sym	Mult	Frac
Bi1	0.0146(15)	0.9969(11)	0.06660(10)	0.81(09)	1	8	0.558(20)
La1	0.0146(15)	0.9969(11)	0.06660(10)	0.81(09)	1	8	0.442(20)
Bi2	0.0174(13)	0.0145(12)	0.21127(9)	0.76(12)	1	8	1.0000
Ti1	0.0354(40)	0.000000	0.500000	0.15(17)	2(100)	4	1.0000
Ti2	0.0357(31)	0.991(4)	0.37076(19)	0.68(21)	1	8	1.0000
O1	0.3284(18)	0.2697(16)	0.00639(24)	1.17(18)	1	8	1.0000
O2	0.2796(24)	0.2611(19)	0.25045(29)	0.49(12)	1	8	1.0000
O3	0.0501(24)	0.0541(17)	0.44125(16)	1.66(16)	1	8	1.0000
O4	0.0520(29)	0.9537(19)	0.31850(15)	1.41(17)	1	8	1.0000
O5	0.3069(26)	0.2612(27)	0.11281(25)	2.62(22)	1	8	1.0000
O6	0.2508(23)	0.2170(21)	0.87845(21)	0.83(19)	1	8	1.0000

clinic ($B1a1$) [13–16]. However, the difference between two structures is undistinguishable with such a low temperature annealed sol-gel powder, because it may contain a large number of defects and a relatively poor crystalline. Therefore, it is reasonable to use simple structure, such as orthorhombic, as a starting structure.

For the first step, basic parameters, such as lattice constant, zero shift, wavelength, background, have been fitted. Then, peak profile, atomic position, fraction, and thermal factor have been refined. Furthermore, a small amount of secondary phase (cubic $Bi_{12}TiO_{20}$, *I23*, $a = 10.177$ Å) has been subtracted from neutron scattering data to improve goodness of fit. The resulting orthorhombic *B2cb* structure ($a = 5.4171(4)$ Å, $b = 5.4113(4)$ Å, and $c = 32.8948(11)$ Å) exhibits a reasonable goodness of fit; $wR_p = 6.7\%$, $R_p = 5.7\%$. The resulting atomic parameters are shown in Table 1, and simulated diffraction pattern is shown in Fig. 3. Schematics of the atomic model is shown in Fig. 4.

Interestingly, atomic position uncertainties reported in the parenthesis of Table 1 is relatively larger than other cases reported for BIT family prepared by solid state reaction. This may attribute to the poor crystallinity of the sol-gel derived BLT powders, because it was annealed at a mere 700°C.

From the refinement result, it is found that approximately 3.5 out of 8 Bi(1) atoms have been replaced by La atoms. The calculated chemical composition, $Bi_{3.12}La_{0.88}Ti_3O_{12}$, from

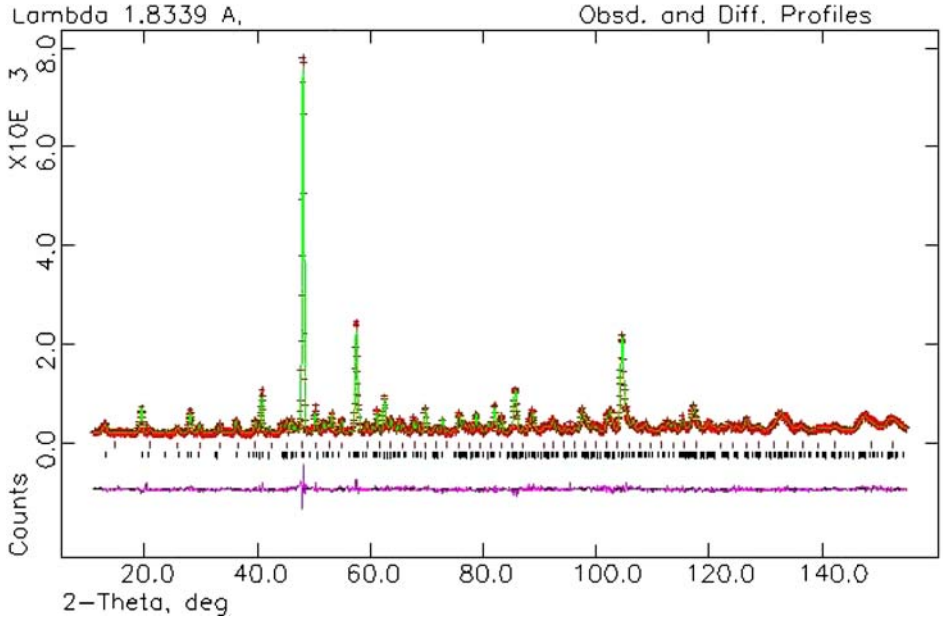

Fig. 3 Calculated and measured neutron scattering pattern of BLT powders. Difference between calculated and measured profiles is shown at the bottom of the figure. Caculated peak positions are marked

Table 2 Information of TiO_6 octahedra extracted from the structure refinement

Type of bond	Ti-O Distance (Å)	Oxygen coordination x	y	z
		$Ti(1)O_6$ octahedron		
Ti1_01	2.02868(11)	0.32842	0.23026	0.50639
Ti1_01	2.02868(11)	0.32842	−0.23026	0.49361
Ti1_01	1.85276(18)	−0.17158	0.26974	0.50639
Ti1_01	1.85276(10)	−0.17158	−0.26974	0.49361
Ti1_03	1.95627(6)	0.05009	0.05408	0.44125
Ti1_03	1.95627(6)	0.05009	−0.05408	0.55875
Average oxygen center		0.06898	0	0.5
Ti(1) coordinator		0.0354(40)	0	0.5
O_6-Ti(1) difference		0.0336	0	0
O_6-Ti(1) distance		0.182 Å	0	0
		$Ti(2)O_6$ octahedron		
Ti2_03	2.34466(7)	0.05009	1.05408	0.44125
Ti2_04	1.73357(6)	0.05204	0.95374	0.31850
Ti2_05	2.0035(10)	0.30694	0.76118	0.38719
Ti2_05	1.92230(10)	−0.19306	0.73882	0.38719
Ti2_06	1.97817(11)	0.25079	1.28302	0.37845
Ti2_06	1.98443(11)	−0.24921	1.21698	0.37845
Average oxygen center		0.03626	1.0013	0.38184
Ti(2) coordinator		0.0357(31)	0.991(4)	0.3707(2)
O_6-Ti(2) difference		−0.0006	0.0103	0.01108
O_6-Ti(2) distance		−0.003 Å	0.0557 Å	0.3644 Å

the refinement result is slightly different from the nominal composition of $Bi_{3.4}La_{0.6}Ti_3O_{12}$. This difference may come from the uncertainty of the neutron scatterings because of similar neutron scattering lengths of Bi (8.532 fm) and La (8.24 fm).

TiO_6 octahedra, Ti at center and O at vertices, responsible with the ferroelectricity in Bi-layered peroveskite have been investigated from the refinement result, which were summarized in Table 2. It is well known that the polarization of Bi-layered perovskite is related with the distance between anion and cation centers in the TiO_6 octahera. There are two types of TiO_6 octahera in the unit cell, namely $Ti(1)O_6$ and $Ti(2)O_6$. $Ti(1)O_6$ octahedron exhibit polarization along (100) axis, while that of $Ti(2)O_6$ octahedron is close to (011) axis within 1°, which is similar with those observed from $(Bi_{4-x}La_x)Ti_3O_{12}$ [17]. This suggests that there is a partial polarization along *c*-axis. Furthermore, accounting the number of $Ti(2)O_6$ is twice that of $Ti(1)O_6$, total polarization along *c*-axis is 4 times greater than that along *a*-axis. This may explain why randomly oriented BLT thin film studied in here has such a high polarization of 72 μC/cm^2, though it is randomly oriented. The randomly oriented BLT thin films with large polarization should be considered as a good candidate for memory applications.

5 Summary

The BLT thin film and powder have been prepared by a sol-gel method after annealing at 700°C. Randomly oriented BLT thin film exhibits a large remanent polarization, $2P_r = 72$ μC/cm^2. Structure of sol-gel derived BLT has been refined by a Rietveld method resulting a reasonable goodness of fit ($wR_p = 6.7\%$, and $R_p = 5.7\%$) using orthorhombic symmetry (*B2cb*). Two different TiO_6 octahedra exhibit different polarization directions; (100) from $Ti(1)O_6$, and (011) from $Ti(2)O_6$, which explains large $2P_r$ of the randomly oriented BLT thin film.

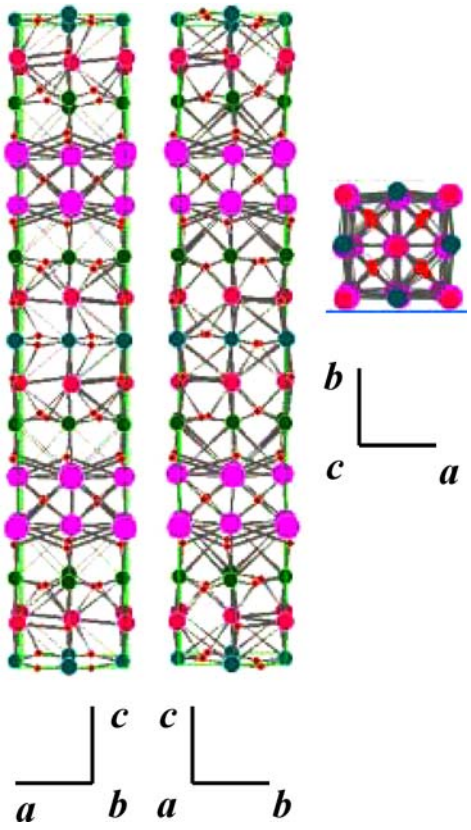

Fig. 4 Atomic model of BLT based on the refined structure listed in Table 1

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