강유전 $Bi_{3.5}A_{0.5}Ti_3O_{12}$ (A=La, Ce)의 합성 및 XRD를 이용한 구조분석

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Synthesis and structure analysis of ferroelectric $Bi_{3.5}A_{0.5}Ti_3O_{12}$ (A=La, Ce) using XRD

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Introduction

The Aurivillius family of layered bismuth oxides [1] have been widely studied since the early work of Smolenski et al. [2] and Subbarao [3]. Recently, ferroelectric materials have been attracted much attention for application to ferroelectric random access memory (FERAM) devices, which realized both nonvolatile operation and high-speed access.

Ferroelctric $Bi_4Ti_3O_{12}$ crystals have a typical perovskite-layered structure and show strong anisotropic properties: [4] coercive field values of 3.5 and 50 kV/cm, and spontaneous polarization of 4.0 and 50 mC/cm2 along the *c*- and *a*-axes, respectively. When BTO was synthesised as thin film, it has potential problems such as low spontaneous polarization along *c*-axis and fatigue failure in order to apply to memory [5]. Therefore, it is important to fabricate highly *a*-axis oriented and fatigue-free BTO thin films. Especially, fatigue failure of BTO should be removed in order to sustain a memory operation for a long time. Actually, it was reported that $(Bi,La)_4Ti_3O_{12}$ (BLT) thin film, La substituted BTO thin film, prepared by pulsed laser ablation show fatigue free behavior [6]. From this report, we wanted to know the structure change when La was substituted and if Ce which has smaller ionic radii than La is substituted instead of La (BCT) crystal structure of BTO will change. In the previous report [7], crystal structure of BTO was determined to have the space group of B2cb and other report [8] suggested that BLT has the space group of I4/mmm. In this research, we synthesised ferroelectric $Bi_{3.5}A_{0.5}Ti_3O_{12}$ (A=La, Ce) powder by sol-gel method for structure analysis using XRD.

Experimental

(1) Synthesis of $Bi_{3.5}A_{0.5}Ti_3O_{12}$ (A=La, Ce) powders.

We dissolved proper amount of bismuth nitrate in acetic acid and lanthanium (or cerium) nitrate in 2-metoxyethanol, respectively. After mixing of two solutions, we added titanium isopropoxide. The final solution was dried at 80°C in vacuum and calcined at 750°C.

(2) Characterization by XRD

X-ray powder diffraction data were collected over the range of $10^\circ < 2\Theta < 130^\circ$ in 0.02° steps on Rigaku Dmax/200V equipment (CuKα radiation).

(3) Structure refinement

X-ray data analysis was carried out by the Rietveld method using the Fullprof program suite [9]. We assumed that $Bi_{3.5}A_{0.5}Ti_3O_{12}$ (A=La, Ce) have the same crystal structure of

orthohombic and space group of B2cb with BTO. And that assumption was confirmed by profile matching mode of Fullprof program [10]

Results and Discussion

Refinement results for the lattice parameters were a=5.444, b=5.409 and c=32.83 for BTO. And that of BLT and BCT were a=5.420, b=5.416, c=32.85 and a=5.399, b=5.396, c=33.11, respectively. Atomic position of three materials were shown in shown in Table 1. In Table 1, significant result is that atomic position of Ti1, Ti2, O1, O2, O3, O5 and O6 along the x axis has changed very much as the substitution of La and Ce. In the introduction part, we already commented that the remanent polarization of BTO is occured along the a axis. From this result, we can conclude that the increase of remanent polarization of BLT is influenced from atomic displacement of those components. And for BLT, the occupancy of La for site B1, perovskite-like block, and B2, fluorite-like block, was about 5:1 which means that almost La atoms are substituted to bismuth atoms of perovskite-like block which agreed to the result of BCT. For this propose to be more accurate we may have to repeat the same process for samples which has other concentration of La and Ce. Fig. 1. and Fig. 2. show the refinement result of BLT and BCT, respectively. All peaks were matched and R_B was 4.79 for BLT and 12.72 for BCT. For the result of BCT, refinement error is somewhat large and further refinement is required because the thermal isotropic factor and asymmetry constants are not finally confirmed yet. To predict exact remanent polarization of BLT and BCT, we need reflection data using neutron scattering because the reflection data of XRD are dependent on the atomic number of component. Therefore, for BLT and BCT the reflection data of oxygen is not reliable as that of bismuth and titanium. But, neutron scattering does not depend on the atomic number which can show the exact displacement of oxygen which has important role in the prediction of remanent polarization of BLT and BCT.

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BTO	x	y	z	BLT	x	y	z	BCT	x	y	z
Bi1	0.00000	0.99950	0.06651	Bi1, La1	0.00000	0.99480	0.06724	Bi1, Ce1	0.00000	0.99385	0.06740
Bi2	0.00234	0.01469	0.21128	Bi2, La2	0.00120	0.02078	0.21091	Bi2, Ce2	0.00125	0.02042	0.21090
Ti1	0.05567	0.00000	0.50000		0.03463	0.00000	0.50000		0.03313	0.00000	0.50000
Ti2	0.04961	0.00168	0.37083		0.03559	0.00520	0.37086		0.03615	0.00523	0.37094
O1	0.32311	0.26234	0.00703		0.22436	0.18881	0.01174		0.22871	0.18243	0.01231
O2	0.26459	0.26122	0.24807		0.21600	0.25165	0.24303		0.23540	0.28542	0.24253
O3	0.08154	0.06512	0.44025		0.06586	0.03714	0.44028		0.05757	0.04553	0.44009
O4	0.05716	0.94351	0.31941		0.05637	0.97056	0.32469		0.04925	0.96784	0.32471
O5	0.29407	0.26491	0.11123		0.19611	0.25194	0.11108		0.22857	0.20107	0.11116
O6	0.21901	0.20120	0.87553		0.17430	0.23983	0.87499		0.17758	0.24654	0.87514

Table 1. Atomic position of BTO, BLT, BCT

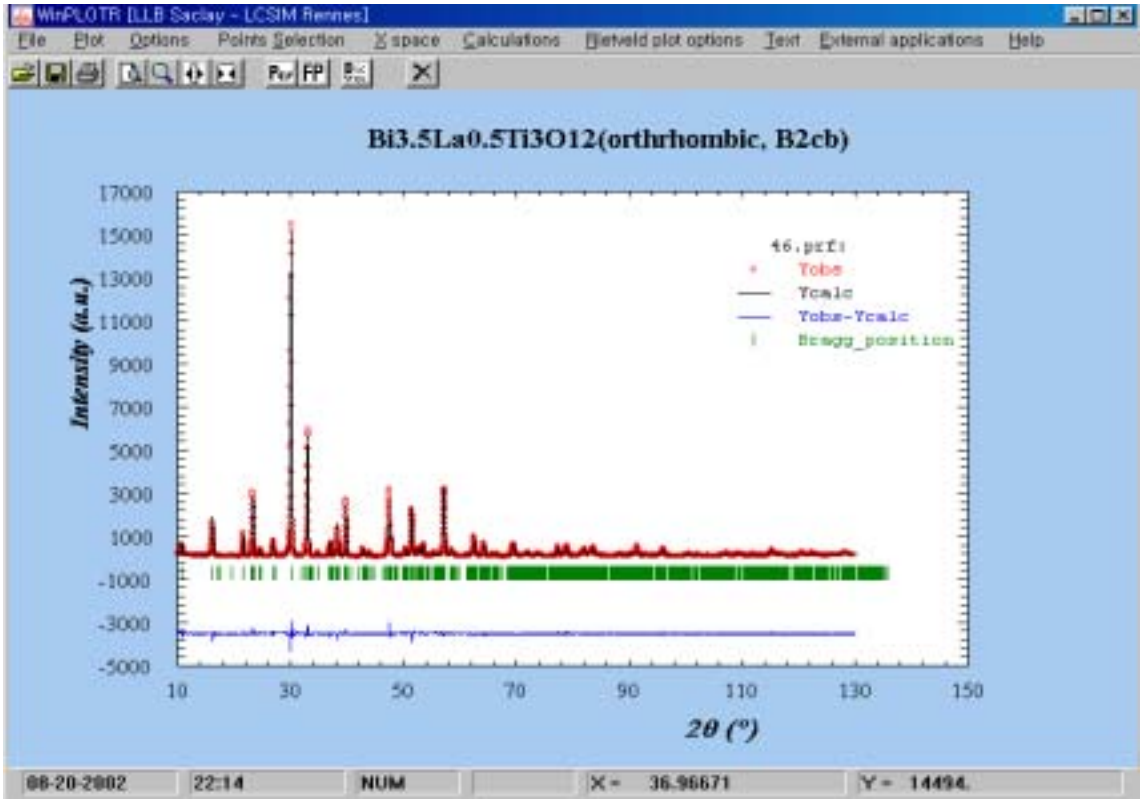

Fig. 1. Refinement result of BLT

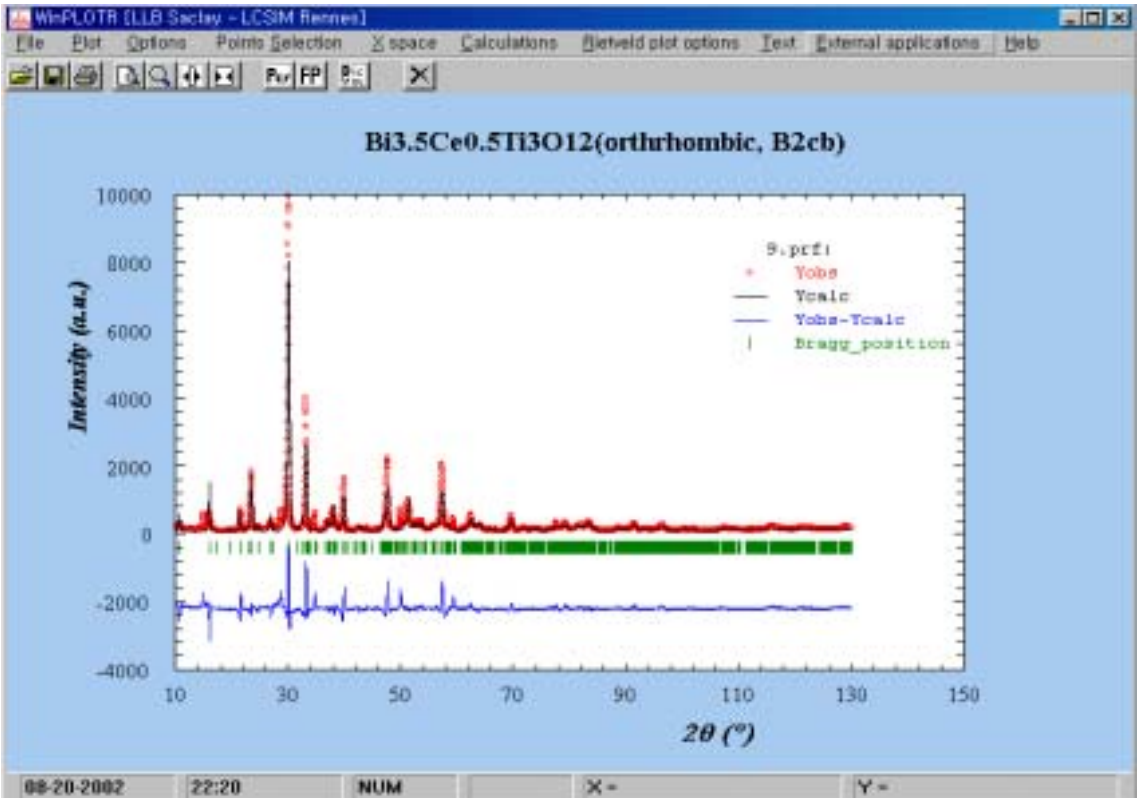

Fig. 2. Refinement result of BCT