

중성자 회절과 라만 스펙트럼을 이용한 $(\text{Bi,Ce})_4\text{Ti}_3\text{O}_{12}$ 의 조성에 따른 결정구조 변화 및 전기적 특성 변화의 상관관계 연구

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Cation disorder and spontaneous polarization study of fatigue-free ferroelectric $(\text{Bi,Ce})_4\text{Ti}_3\text{O}_{12}$ by using neutron powder diffraction and Raman spectroscopy

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Introduction

Ferroelectric materials have been widely studied, especially for application in ferroelectric random access memories (FeRAMs). FeRAMs have advantages of long lifetimes of 10^{12} read/write cycles and low power consumption. For commercial application of FeRAMs, the required properties are a large remnant polarization, a low coercive field, fatigue-free behavior, and a low process temperature [1].

Recently, Ce-substituted bismuth titanate, $(\text{Bi,Ce})_4\text{Ti}_3\text{O}_{12}$ (BCT), was introduced as an promising candidate for FeRAMs application because of large remnant polarization and fatigue-free behavior [2]. However, there have been no reports on composition dependence of polarization and crystal structure which has a close relationship and is an important point on understanding changes of ferroelectric properties.

In this study, we prepared $\text{Bi}_{4-x}\text{Ce}_x\text{Ti}_3\text{O}_{12}$ ($x = 0.25, 0.5$ and 0.75) thin films by a pulsed laser deposition method to verify composition dependence of polarization. Structural analysis was also carried out to understand relationship between structural changes and spontaneous polarization. Raman spectroscopy was measured to determine substitution site of Ce atoms between two Bi sites as it is sensitive to the coordination of local sites resulting from atomic substitution and the distortion of polyhedron. Based on the Raman spectroscopy results, Rietveld refinement was performed by using a neutron powder diffraction data which is a useful method to determine structural parameters of oxygen atoms in oxide compounds. The final structure analysis results were used for calculation of spontaneous polarization to compare with experimental results.

Experimental

The targets of BCT were prepared by a traditional solid-state reaction using Bi_2O_3 , CeO_2 and TiO_2 as starting materials with 10 % of excess Bi_2O_3 . The BCT thin-films were prepared by using a PLD technique on Pt/ TiO_2 / SiO_2 /Si substrates. The BCT films were deposited at 400 °C in 100 mTorr of oxygen with an energy density and a repetition rate of 2.5 J/cm² and 4 Hz, respectively. The deposited films were annealed at 650 °C for 1 hr in an oxygen atmosphere and the Pt top electrodes were deposited using DC magnetron sputtering. Thickness of the prepared BCT films was 100 nm.

Results and Discussion

Fig. 1A shows the hysteresis loops of the BCT films as a function of composition. The P_r values significantly decreased from 16.3 to 10.9 and 4.6 $\mu\text{C}/\text{cm}^2$ at an applied electric field of 600 kV/cm with increasing amount of substituted Ce from 0.25 to 0.5 and 0.75 indicating that P_r is closely related to the composition of Ce. Fig. 1B shows fatigue-free behavior of $\text{Bi}_{3.75}\text{Ce}_{0.25}\text{Ti}_3\text{O}_{12}$ until 1.36×10^{10} read/write cycles.

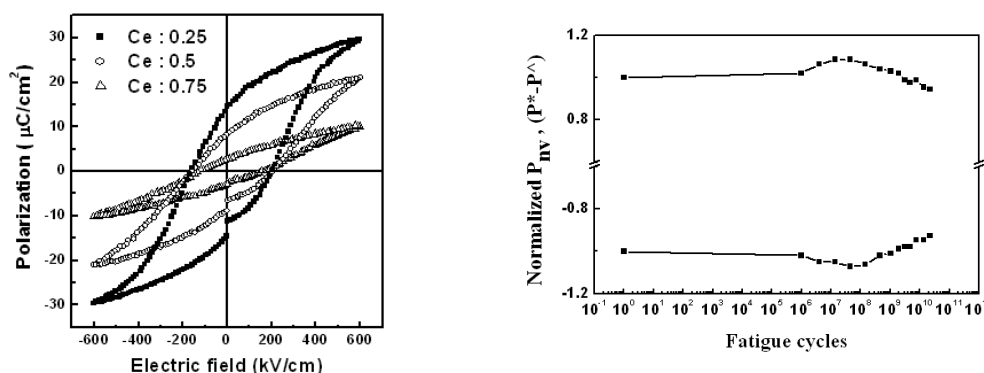


Fig. 1. (A) Hysteresis loops of BCT thin films (left) and (B) fatigue behavior test of $\text{Bi}_{3.75}\text{Ce}_{0.25}\text{Ti}_3\text{O}_{12}$ (right).

Here, the crystal structural approach was carried out for an understanding of composition dependence of the ferroelectric properties of BCT because remnant polarization values can be calculated from the displacement lengths of atoms. As the thin films can not be used for crystal structural analysis, BCT powders with the same composition as the films were prepared.

Bismuth titanate (BTO) has a crystal structure in which bismuth oxide layers, $(\text{Bi}_2\text{O}_2)^{2+}$, are interleaved with perovskite $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ blocks along the c -axis [3]. Substitution site study was performed before refinement because there are three possibilities of Ce substitution. The first possibility is that Ce atoms substitute Bi atoms in the perovskite units only and the second one is that Ce atoms substitute Bi atoms in the Bi_2O_2 layers only. The last possibility is that Ce atoms substitute Bi atoms in both of the perovskite units and the Bi_2O_2 layers. Raman spectroscopic study was carried

out for cation disorder study and Raman spectra of BTO and $\text{Bi}_{3.25}\text{Ce}_{0.75}\text{Ti}_3\text{O}_{12}$ are shown in Fig. 2. The band appeared at 65 cm^{-1} originated from the Bi atoms in the Bi_2O_2 layers. And the triple bands at 90, 119 and 148 cm^{-1} were assigned to the modes of Bi atoms in the perovskite units [4]. The band at 65 cm^{-1} showed little variation with substitution of Ce. However, the triple bands became diffusive and the frequencies increased to higher ones with increasing substitution amount of Ce. This up-shift of the triple band to higher frequencies indicates that the Ce ions were only incorporated into the Bi sites of the perovskite units, which can be explained by the smaller atomic weight of Ce. The modes at high frequencies above 200 cm^{-1} originated from the vibrational modes of TiO_6 octahedra.

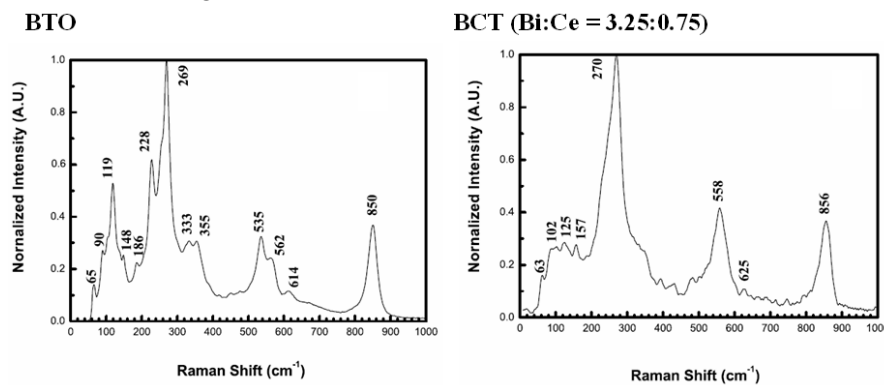


Fig. 2. Raman spectra of (A) BTO (left) and (B) $\text{Bi}_{3.25}\text{Ce}_{0.75}\text{Ti}_3\text{O}_{12}$ (right)

The BTO and BCT powders were assumed to have a monoclinic structure with a space group of $B1a1$ (non-standard setting of No. 7 $P1c1$) [5]. Substitution sites of Ce atoms were assumed to be only the Bi sites in the perovskite units following the results of Raman spectroscopy. The final weighted R -factors (R_{wp}), profile R -factors (R_p), goodness-of-fit indicator (S), and lattice parameters are summarized in Table I. The crystal structure of $\text{Bi}_{3.75}\text{Ce}_{0.25}\text{Ti}_3\text{O}_{12}$ determined from structural refinement was shown in Fig. 3.

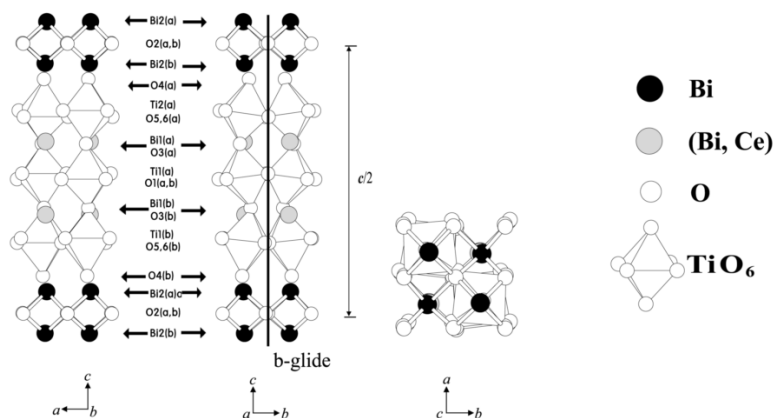


Fig. 3. Crystal structure of $\text{Bi}_{3.75}\text{Ce}_{0.25}\text{Ti}_3\text{O}_{12}$ based on the parameters obtained from the structural refinement.

We calculated spontaneous polarizations (P_s) by using an equation of

$$P_s = \sum_i (m_i \times \Delta x_i \times Q_{ie}) / V, \quad (1)$$

where m_i is the site multiplicity, Δx_i is the atomic displacement along the a -axis from the corresponding position in the tetragonal structure, Q_{ie} is the ionic charge of the i -th constituent ion, and V is the unit-cell volume [6].

We only considered polarizations along the a -axis because those along the b -axis are cancelled by b -glide and along the c -axis are much smaller than the a -axis. The calculated P_s values and lattice parameters were shown in Table I with experimental results of thin films. The calculated P_s values significantly decreased with an increase in the amount of substituted Ce. The experimental P_s values of the BCT thin-films are in accordance with the calculated ones. The P_r values were about a half of P_s values because of random orientation of the films.

	BTO	BCT (3.75:0.25)	BCT (3.5:0.5)	BCT (3.25:0.75)
R_{wp}, R_p (%)	5.36, 4.00	4.44, 3.35	5.11, 3.88	5.42, 4.11
S	1.40	1.38	1.32	1.65
A (Å)	5.4474(8)	5.4353(1)	5.4217(1)	5.4110(3)
b (Å)	5.4082(9)	5.4075(1)	5.4043(1)	5.4069(2)
c (Å)	32.8070(6)	32.8626(5)	32.8809(6)	32.9065(7)
Calculated P_s (//a) ($\mu\text{C}/\text{cm}^2$)	35.4	30.4	27.5	16.5
P_s and P_r values of films ($\mu\text{C}/\text{cm}^2$)		23.5, 16.3	14.2, 10.9	9.8, 4.6

Table I. R_{wp} and R_p factors, goodness-of-fit indicator (S), lattice parameters, calculated and experimental polarization values.

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