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Combined structural refinement and spontaneous polarization study of $\text{Bi}_{3.5}\text{Ce}_{0.5}\text{Ti}_3\text{O}_{12}$ by using x-ray and neutron powder diffraction data

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Abstract

Combined structural refinement of $\text{Bi}_{3.5}\text{Ce}_{0.5}\text{Ti}_3\text{O}_{12}$ was carried out by using both neutron and x-ray diffraction results based on the monoclinic space group of $B1a1$. Weighted R -factors were 6.29% and 8.17% for the neutron and x-ray diffraction data, respectively. The goodness-of-fit indicator (S) was 1.9 for all patterns. Lattice parameters were $a = 5.4229(6)$ Å, $b = 5.4038(6)$ Å and $c = 32.8838(5)$ Å. The β angle was $90.10(1)^\circ$. Spontaneous polarization (P_s) calculated from the refinement results was $26.7 \mu\text{C cm}^{-2}$. The contribution of each atom on the spontaneous polarization was plotted and it was clearly shown that the distortion of TiO_6 octahedrons was the key factor that determines spontaneous polarization.

1. Introduction

Ferroelectric materials have recently attracted much attention due to their special characteristic feature which does not lose polarization when the applied voltage is removed. This feature has made ferroelectric materials promising candidates for ferroelectric random access memory (FeRAM) capacitors [1]. Among various ferroelectric materials, bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BTO) has been intensively studied as a lead-free ferroelectric material [2] and, in thin films, large remanent polarization and fatigue-free behaviour have been achieved by substituting La [3], Ce [4], Sm [5] and Nd [6] for Bi sites of BTO. Many studies on the improved performance of lanthanide metal substituted BTO have been reported; however, crystal structural changes by different types of substituted metal have not yet been studied.

The crystal structure of BTO consists of Bi_2O_2 capping layers and perovskite units ($\text{Bi}_2\text{Ti}_3\text{O}_{10}$) between the Bi_2O_2 layers along the c -axis [7, 8]. In this study, we carried out combined structural refinement for the precise analysis of atomic positions which is a key factor to determine spontaneous polarization of ferroelectric materials. Combined structural refinement is a useful technique in the crystal structural analysis of metal oxide compounds because x-ray diffraction has relatively low sensitivity compared with oxygen atoms due to heavy Bi atoms and neutron diffraction is not good at determining the atomic position of Ti atoms due to negative scattering length of Ti atoms. On the other hand, neutron diffraction is more sensitive to O atoms than x-ray diffraction as neutron diffraction depends on the nuclear scattering length. Neutron coherent scattering cross section of O atom is $4.232 \times 10^{-24} \text{ cm}^2$ which is comparable to $9.148 \times 10^{-24} \text{ cm}^2$ of Bi. Thus, combined refinement of $\text{Bi}_{3.5}\text{Ce}_{0.5}\text{Ti}_3\text{O}_{12}$ (BCT) can provide precise refinement

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results through the complementary effect of neutron and x-ray diffraction. In addition to the crystal structural refinement, spontaneous polarization was calculated from the refinement results and compared with that of $\text{Bi}_{3.5}\text{La}_{0.5}\text{Ti}_3\text{O}_{12}$ (BLT) [9] which was analysed in the same manner of this study to compare the effect of substituted atoms between La and Ce on spontaneous polarization.

2. Experimental

The BCT sample was prepared by a normal solid-state reaction using Bi_2O_3 , CeO_2 and TiO_2 as starting materials [10]. The mixture was annealed at 1000°C for 24 h. A second annealing process was carried out at 1100°C for 48 h with intermediate grindings. Neutron powder diffraction data were collected over scattering angles between 0° and 160° with a 2θ step of 0.05° using 1.8343 \AA neutron on the high resolution powder diffractometer (HRPD) at the Hanaro Center of the Korea Atomic Energy Research Institute (KAERI). The x-ray diffraction data were collected over scattering angles from 5° to 100° at a 2θ step of 0.02° using $\text{Cu K}\alpha_1$ radiation at 298 K. The x-ray diffractometer was equipped with a primary asymmetric monochromator, $\text{Ge}(111)$ and a linear position sensitive detector (model: STADI MP). The samples were rotated during the measurement of the diffraction data under the transmission mode. The EXPGUI program, a graphical user interface for general structure analysis system (GSAS), was used to perform the Rietveld refinement [11, 12]. The pseudo-Voigt function was used as a profile function among those in the GSAS program [13]. The neutron scattering lengths for Bi, Ce, Ti and O atoms are $0.853 \times 10^{-12} \text{ m}$, $0.484 \times 10^{-12} \text{ m}$, $-0.3438 \times 10^{-12} \text{ m}$ and $0.5805 \times 10^{-12} \text{ m}$, respectively.

3. Results and discussion

Two important aspects of BCT were considered carrying out the Rietveld refinement. One was the crystal structural system of BCT which can be either orthorhombic [14] or monoclinic [8]. Our previous study on the crystal system of BTO [15, 16] and BLT [9, 17] showed that the monoclinic system with a space group of $B1a1$ (non-standard setting of No.7 $P1c1$) is more suitable than the orthorhombic system. The other consideration was the substitution site of Ce. In our previous report, it was proved that Ce substitutes for Bi atoms only in the perovskite units by means of Raman spectroscopy [18]. Thus, in this paper, the monoclinic system was adopted for structural refinement with an assumption that Ce atoms were substituted only in the perovskite units.

Refinement results are shown in figure 1 for (a) neutron and (b) x-ray diffraction data. Weighted R -factors (R_{wp}) were 6.29% and 8.17% for neutron and x-ray data, respectively. The goodness-of-fit indicator ($S = R_{\text{wp}}/R_e$) was 1.9 for the total refinement results. The lattice parameters were $a = 5.4229(6) \text{ \AA}$, $b = 5.4038(6) \text{ \AA}$ and $c = 32.8838(5) \text{ \AA}$. The β angle was $90.10(1)^\circ$. Compared with $5.4157(1) \text{ \AA}$, $5.3959(1) \text{ \AA}$ and $32.8383(6) \text{ \AA}$ of the neutron diffraction study results, all lattice parameters were 0.14% larger in the

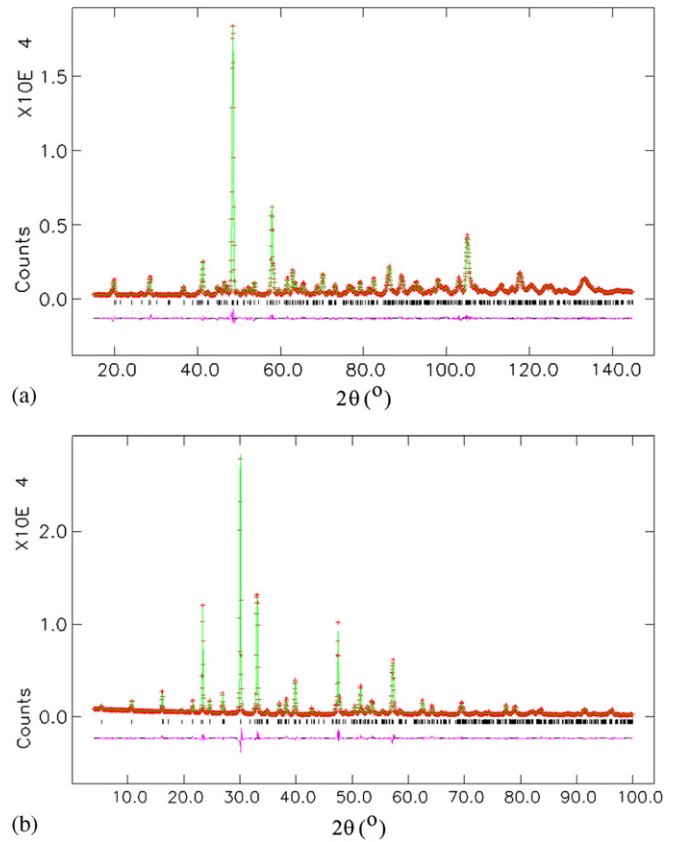


Figure 1. Rietveld refinement results by using (a) neutron and (b) x-ray powder diffraction data. Plus (+) marks represent the observed intensities and the solid lines are calculated ones. A difference (obs. – cal.) plot is shown beneath. Tick marks above the difference line indicate reflection positions.

(This figure is in colour only in the electronic version)

combined structural refinement results, which means the lattice parameters obtained from neutron diffraction only were also accurate. Other refinement results including atomic positions, occupation parameter and isotropic thermal parameters are listed in table 1. Bi and Ce atoms in the same site were assumed to have identical atomic positions and isotropic thermal parameters.

Calculation of spontaneous polarization was carried out 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 [19]. The calculated P_s was $26.7 \mu\text{C cm}^{-2}$ which was close to $27.5 \mu\text{C cm}^{-2}$ of the neutron diffraction study [18], because spontaneous polarization is determined by atomic positions of oxygen atoms. Figure 2 shows the contribution of each atom on the calculated spontaneous polarization. It was clearly shown that the displacements of Bi atoms are too small to contribute to spontaneous polarizations. In other words, atomic positions of Bi atoms are seldom changed by the substitution of Ce. Ti and O atoms exhibited large contributions to spontaneous

Table 1. Structural parameters for $\text{Bi}_{3.5}\text{Ce}_{0.5}\text{Ti}_3\text{O}_{12}$ obtained from the Rietveld refinement using neutron powder diffraction data at 298 K. The symbol, g , is the occupation factor. The numbers in parentheses are the estimated standard deviations of the last significant figure. Space group $B1a1$ (non-standard setting of No 7 $P1c1$) was used.

Atom	Site	x	y	z	g	$100 \times U_{\text{iso}} (\text{\AA})$
Bi1(a)	4a	0.0572(1)	0.5092(1)	0.5673(7)	0.90(2)	2.26(6)
Ce1(a)	4a	0.0572(1)	0.5092(1)	0.5673(7)	0.10	2.26(6)
Bi2(a)	4a	0.0592(7)	0.4794(5)	0.7122(6)	1.0	1.85(4)
Ti1(a)	4a	0.0979(8)	0.0106(3)	0.5043(2)	1.0	0.28(7)
Ti2(a)	4a	0.0993(1)	0.0083(7)	0.6248(2)	1.0	1.17(1)
O1(a)	4a	0.3342(1)	0.2803(7)	0.5107(9)	1.0	1.93(8)
O2(a)	4a	0.3307(7)	0.2457(6)	0.2484(6)	1.0	0.25(3)
O3(a)	4a	0.1358(9)	-0.0637(2)	0.5633(5)	1.0	0.21(1)
O4(a)	4a	0.1115(2)	0.0550(8)	0.6816(3)	1.0	0.89(3)
O5(a)	4a	0.3339(6)	0.2685(6)	0.6099(1)	1.0	0.52(1)
O6(a)	4a	0.3918(8)	-0.2049(6)	0.6238(2)	1.0	1.27(6)
Bi1(b)	4a	0.0649(9)	0.4979(8)	0.4334(3)	0.60(2)	0.97(1)
Ce1(b)	4a	0.0649(9)	0.4979(8)	0.4334(3)	0.40	0.97(1)
Bi2(b)	4a	0.0597(9)	0.2176(8)	0.2898(5)	1.0	1.10(1)
Ti2(b)	4a	0.0965(7)	0.0005(1)	0.3694(8)	1.0	0.37(5)
O1(b)	4a	0.4047(2)	-0.2083(2)	0.4961(6)	1.0	0.40(9)
O2(b)	4a	0.3215(8)	-0.2445(1)	0.7488(1)	1.0	0.09(1)
O3(b)	4a	0.1199(8)	0.0472(8)	0.4470(4)	1.0	1.19(7)
O4(b)	4a	0.0939(3)	-0.0356(4)	0.3187(5)	1.0	1.78(6)
O5(b)	4a	0.3485(7)	-0.2614(2)	0.3854(9)	1.0	1.11(4)
O6(b)	4a	0.3930(4)	0.2085(7)	0.3765(6)	1.0	3.00(3)

polarizations except for the O atoms in Bi_2O_2 layers, O2(a) and O2(b), indicating that the distortion of TiO_6 octahedra is the key factor of spontaneous polarization.

The calculated P_s of $\text{Bi}_{3.5}\text{La}_{0.5}\text{Ti}_3\text{O}_{12}$ (BLT) determined by the combined structural refinement at the same condition of this study was $27.0 \mu\text{C cm}^{-2}$ [9]. The similar calculated P_s values of BCT and BLT imply that substituting Ce and La of the same amount contributed to the change in P_s to a similar extent. This result might come from similar ionic radii of La^{3+} (117 pm) and Ce^{3+} (115 pm). Considering a large change in P_s by substituting a different amount of Ce [18], from the crystal structural point of view, we could conclude that the amount of the substituted atom is more important in determining P_s than the type of substituted atom between La and Ce.

4. Conclusions

Combined structural refinement of $\text{Bi}_{3.5}\text{Ce}_{0.5}\text{Ti}_3\text{O}_{12}$ was successfully performed by using both neutron and x-ray diffraction data. Precise information on the crystal structure of $\text{Bi}_{3.5}\text{Ce}_{0.5}\text{Ti}_3\text{O}_{12}$ including atomic positions and isotropic thermal parameters was obtained. Contribution of the constituent atoms to spontaneous polarization showed that the large distortion of TiO_6 octahedra determines the spontaneous polarization of BCT. The calculated P_s from the structural refinement result was $26.7 \mu\text{C cm}^{-2}$.

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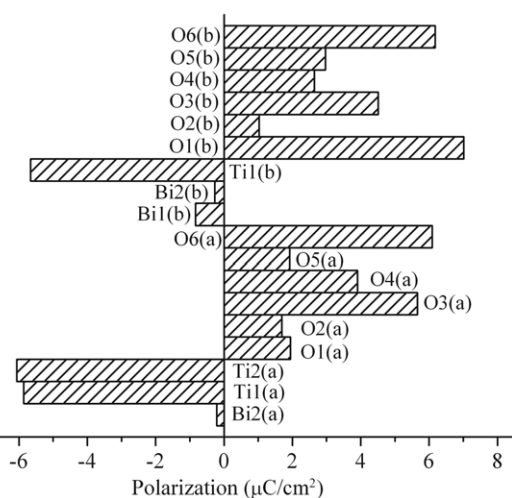


Figure 2. Contribution of constituent atoms to spontaneous polarization. Polarization of Bi1(a) is missing as it was used as a zero point.

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References

- [1] Ramesh R, Aggarwal S and Auciello O 2001 *Mater. Sci. Eng.* **R 32** 191
- [2] Cummins S E and Cross L E 1968 *J. Appl. Phys.* **39** 2268
- [3] Park B H, Kang B S, Bu S D, Noh T W, Lee J and Jo W 1999 *Nature (London)* **401** 682
- [4] Jeon M K, Chung H J, Kim K W, Oh K S and Woo S I 2005 *Thin Solid Films* **489** 1

- [5] Ruy S-O, Lee N-Y, Lee W-J and Yoon S-G 2004 *Japan. J. Appl. Phys.* **43** 6594
- [6] Zhong X L, Wang J B, Zheng X J, Zhou Y C and Yang G W 2004 *Appl. Phys. Lett.* **85** 5661
- [7] Dorrian J F, Newnham R E, Smith D K and Kay M I 1971 *Ferroelectrics* **3** 17
- [8] Rae A D, Thompson J G, Withers R L and Willis A C 1990 *Acta Cryst. B* **46** 474
- [9] Jeon M K, Kim Y-I, Nahm S-H and Woo S I 2005 *J. Phys. Chem. B* **109** 968
- [10] West A R 1984 *Solid State Chemistry and its Applications* (New York: Wiley)
- [11] Larson C and Von Dreele R B 1994 *Los Alamos National Laboratory Report No LAUR 86-748* (Los Alamos, NM: Los Alamos National Laboratory)
- [12] Toby B H 2001 *J. Appl. Cryst.* **34** 210
- [13] Thompson P, Cox D E and Hastings J B 1987 *J. Appl. Cryst.* **20** 79
- [14] Hervoche C H and Lightfoot P 1999 *Chem. Mater.* **11** 3359
- [15] Kim Y-I, Jeon M K and Woo S I 2003 *J. Mater. Sci. Lett.* **22** 1655
- [16] Jeon M K, Kim Y-I, Nahm S-H and Woo S I 2004 *J. Kor. Phys. Soc.* **45** 1240
- [17] Jeon M K, Kim Y-I, Sohn J M and Woo S I 2004 *J. Phys. D: Appl. Phys.* **37** 2588
- [18] Jeon M K, Kim Y-I, Nahm S-H and Woo S I 2006 *J. Phys. D: Appl. Phys.* **39** 5080
- [19] Shimakawa Y, Kubo Y, Nakagawa Y, Goto S, Kamiyama T, Asano H and Izumi F 2000 *Phys. Rev. B* **61** 6559