Polarization properties and crystal structures of ferroelectric (Ba,Ca)TiO₃ single crystals

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We have investigated the spontaneous polarization (P_s) of Ba_{1-x}Ca_xTiO₃ (BCT) by polarization hysteresis measurements using single crystals and by density functional theory (DFT) calculations. Single crystals of BCT ($x = 0.07$) were grown by a top-seeded solution growth (TSSG) method. The polarization measurements show that the crystals ($x = 0.07$) have a P_s of 26.0 $\mu\text{C}/\text{cm}^2$, which is slightly small compared with BaTiO₃ (27.3 $\mu\text{C}/\text{cm}^2$). Our DFT calculations based on a supercell approach show that Ca atoms are markedly displaced cooperatively with the adjacent Ti atoms along the P_s direction. It is suggested that the CaTiO₃-like octahedral rotation is constructed in the BCT supercell around the Ca atoms, which is the origin of the smaller P_s observed for the BCT crystals.

Keywords: Barium titanate; single crystals; spontaneous polarization; DFT calculations.

1. Introduction

Ferroelectricity in perovskite oxides originates from the cooperative displacements of their constituent atoms relative to the corresponding positions in cubic symmetry.¹ For BaTiO₃ (BT), the spontaneous polarization (P_s) is attributed mainly to the off-centering of Ti from the center in the relatively-rigid oxygen octahedron caused by the orbital hybridization between Ti-3d and O-2p. The spontaneous displacement of Ba is small in BT due to an ionic nature of the Ba–O bonding.² In contrast, PbTiO₃ (PT) has a strong Pb–O bonding resulting from the hybridization between Pb-6s(p) and O-2p.^{2,3} The covalent bonding not only of Ti–O but also of Pb–O enhances the spontaneous displacements of the constituent atoms, which leads to a large P_s of PT.

Recently, Ca-substituted BT has attracted a renewed interest because of its enhanced piezoelectric properties.^{4,5} Early works on Ba_{1-x}Ca_xTiO₃ (BCT) ceramics⁶ have shown that the Ca substitution remarkably lowers the transition temperature (T_{T-O}) from the tetragonal to orthorhombic phase in spite of their almost constant Curie temperature (T_C) around 405 K. BCT ($x = 0.16$) is reported to show a T_{T-O} of 150 K, which is much lower than that of BT ($T_{T-O} = 275$ K). The dependences of T_C and T_{T-O} on Ca content in BCT are quite different from those in Sr-substituted BT (BST). The Sr substitution lowers both T_C and T_{T-O} , which is considered to be due to the influences of the smaller ionic radius of Sr²⁺ than Ba²⁺. The trends of T_C and T_{T-O} in BCT cannot be explained by the simple ionic model.^{2,7}

Fu *et al.* have reported that the stabilization of the tetragonal phase by the Ca substitution in BCT is derived from the off-center displacement of Ca along the [113] direction that works cooperatively with that of Ti.⁵ Their first-principles calculations suggest a large P_s of BCT due to the Ca displacement, although BCT single crystals exhibited a low remanent polarization (P_r) compared with BT. Levin *et al.* have reported the detailed local structure of BCT.⁸ They show that Ca is displaced along the [111] direction, which leads to strained Ca–O bonds. This Ca displacement is accompanied by the enhanced off-center displacements of the adjacent Ti atoms along the [001] direction, which leads to an enhancement of P_s by the Ca substitution.

In contrast to BT, CaTiO₃ (CT) does not show ferroelectricity in spite of having a large structural distortion, i.e., the rotation of the TiO₆ octahedra.⁹ CT shows a paraelectric behavior in space group $Pbnm$ at 298 K with a large TiO₆ rotation that belongs to the irreducible representations of M_3 and R_{25} . In the crystal structure of CT, Ca with a small ionic radius is accommodated by these TiO₆ rotations and the displacements of the constituents are cancelled out. Therefore, the structural distortion around Ca accompanied by the TiO₆ rotation¹⁰ does not yield a ferroelectric polarization. To our knowledge, the possibility of the TiO₆ octahedral rotation in BCT has never been investigated. In addition, there is no report on the experimental observation of P_s of BCT by means of single-crystal measurements.

In this study, we report the P_s of BCT that is determined by the direct measurements of the polarization hysteresis

loops of BCT single crystals. It is known that BCT single crystals can be grown by the czochralski method¹¹ or floating zone (FZ) method.^{4,5} However, BCT single crystals with a low Ca content ($x < 0.02$) cannot be obtained by these methods because hexagonal crystals are formed in this composition range.⁴ We have, therefore, grown BCT single crystals by a TSSG method. It is reported that the BCT crystals has a low P_s compared with BT.

2. Experiments

Powders of BCT were prepared by a solid-state reaction from the raw materials of BaCO₃ (99.99%), CaCO₃ (99.99%) and TiO₂ (99.99%). Single crystals of BCT were grown by a TSSG method. The photographs of the crystals are shown in Fig. 1. Few cracks or inclusions were found in these crystals. The compositions of the crystals were determined by X-ray fluorescence measurements: $x = 0.07$. The crystals were cut along the $\langle 001 \rangle$ direction with a size of $1.0 \times 0.8 \times 0.5 \text{ mm}^3$. These crystals were annealed at 1523 K for 12 h in order to recover the mechanical damage induced during the cutting process. After the annealing, platinum electrodes with a thickness of 50 nm were sputtered onto both the surfaces with $0.8 \times 0.5 \text{ mm}^2$. Polarization hysteresis loops were measured

at 298 K and at 1 Hz so that an electric field (E) was applied along the $[001]$ direction.

Synchrotron radiation (SR) single-crystal X-ray diffraction (XRD) data were collected at 298 K in a transmission geometry using a large cylindrical two-dimensional imaging plate (IP) camera at BL02-B1 in the SPring-8 SR facility (35 keV, wavelength of 0.03540(2) nm).

To investigate the local structure and spontaneous polarization (P_s) of BCT, density functional theory (DFT) calculations were conducted. The calculations were performed with the generalized gradient approximation¹² using a plane wave basis set as implemented in the Vienna *ab initio* simulation package (VASP). We used the projector-augmented wave potentials¹³ with the valence-electron configurations of $5s^2 5p^6 6s^2$ for Ba, $3p^6 4s^2$ for Ca, $3p^6 3d^2 4s^2$ for Ti, and $2s^2 2p^4$ for O. The Perdew–Burke–Ernzerhof functional modified for solids (PBEsol)¹⁴ was employed for the exchange–correlation potential. A plane-wave cut-off energy of 800 eV was adopted, and electronic energy was converged to less than 10^{-6} eV in all calculations. Born effective charge (Z^*) tensors were evaluated by using a density-functional perturbation theory (DFPT).¹⁴

For the calculations of P_s , three kinds of possible space group were considered: tetragonal $P4mm$, monoclinic Cm , and orthorhombic $P2_1$. Our single-crystal SR-XRD measurements confirm that the averaged structure of BCT is tetragonal $P4mm$. The comprehensive structural analyses by Levin *et al.* have shown that Ca is displaced along the $[111]$ direction in BCT, which can be explained by adapting space group Cm . Furthermore, to take a local structure of the TiO₆ octahedral rotation observed in CT at room temperature in space group $Pbnm$ into account, $P2_1$ was also adapted, in which the antiphase rotation of TiO₆ octahedra in the $a - c$ plane and cooperative ferroelectric displacements along the b -axis are simultaneously permitted. The supercells in each space group are listed in Table 1.

To determine the crystal structures by DFT, the following two-step calculations were executed. At first, geometrical optimization (atom positions, unit cell shape and unit cell volume) was performed to obtain the cell volume in the ground state. Then, under the constraint of the fixed cell volume in the ground state, the cell shape of the geometry optimized structure was changed manually so that the cell has the same tetragonal distortion (c/a) determined by the

Fig. 1. A photo of the single crystal of BCT ($x = 0.07$) grown by a top-seeded solution growth (TSSG) method.

Table 1. Calculated and measured spontaneous polarizations of BT and BCT.

			$P_s(\mu\text{C}/\text{cm}^2)$	
	Cell composition	Crystal system (space group)	DFT calculations	Experiments
BT	BaTiO ₃ ($1a \times 1a \times 1c$)	Tetragonal ($P4mm$)	26.8	27.3
BCT ($x = 0.07$)	Ba ₁₁ CaTi ₁₂ O ₃₆ ($2a \times 2a \times 3c$)	Tetragonal ($P4mm$)	29.5	
		Monoclinic (Cm)	29.5	26.0
	Ba ₁₄ Ca ₂ Ti ₁₆ O ₄₈ ($3a \times 3a \times 2c$)	Orthorhombic ($P2_1$)	28.0	

Table 2. Parameters used for the DFT calculations of BT and BCT.

			Geometrical optimization, atomic-position optimization		Born effective charge (Z^*)	
Cell composition		Crystal system (space group)	Cut-off energy (eV)	k -mesh	Cut-off energy (eV)	k -mesh
BT	BaTiO ₃ ($1a \times 1a \times 1c$)	Tetragonal ($P4mm$)	800	$9 \times 9 \times 9$	400	$9 \times 9 \times 9$
BCT	Ba ₁₁ CaTi ₁₂ O ₃₆ ($2a \times 2a \times 3c$)	Tetragonal ($P4mm$)	800	$5 \times 5 \times 5$	400	$4 \times 4 \times 3$
		Monoclinic (Cm)				
	Ba ₁₄ Ca ₂ Ti ₁₆ O ₄₈ ($3a \times 3a \times 2c$)	Orthorhombic (P2 ₁)		$3 \times 5 \times 3$		$3 \times 4 \times 3$

SR-XRD experiments. Next, the atom positions were optimized under the constraints that the cell volume and the c/a value were fixed. From the optimized crystal structure obtained by the two-step calculations and the Born effective charges of the constituent atoms, P_s was calculated as a macroscopic polarization per unit volume.

Information of the plane-wave cut-off energy and the Monkhorst–Pack k -mesh for the geometrical optimization (1st step calculation), atomic-position optimization (2nd step calculation) and the calculations of Z^* are listed in Table 2. The adopted mesh sizes of k -point sampling grid were set to be 1.9 nm^{-1} for the structural optimization calculations and 0.25 nm^{-1} for the Z^* calculations.

We have checked the influences of the cut-off energy and the k -mesh on the Z^* for BT. The difference in Z^* for the cut-off energies of 400 eV and 800 eV was less than 0.07, which is 1.5% of the absolute value of Z^* . The k -mesh sampling of $5 \times 5 \times 5$ yielded almost the same results of Z^* as that of $9 \times 9 \times 9$ and the difference is less than 1%. Due to the restriction of the computer resources, the calculations of Z^* of the BCT supercells were conducted with a smaller cut-off energy of 400 eV and a relatively coarse k -mesh sampling compared with those with the structural optimizations, as listed in Table 2.

3. Results and Discussions

Figure 2 shows the polarization (P) hysteresis loops observed along the $\langle 001 \rangle$ direction at 298 K. To obtain the P_s from the $P(E)$ loops, a linear regression analysis was conducted using the data in the range of 1–3 kV/cm². The broken lines in Fig. 2 denote the line generated by the regression analysis. The crystals exhibit a well-saturated polarization hysteresis loop, indicating that a depolarization around $E = 0 \text{ kV/cm}$ does not influence the determination of P_s . It can be, therefore, said that an intercept of the broken lines in Fig. 2 coincides with P_s . The P_s of BT is determined to be $27.3 \text{ }\mu\text{C/cm}^2$. This value is close to the P_s reported previously.¹⁵ BCT ($x = 0.07$) is found to exhibit a P_s of $26.0 \text{ }\mu\text{C/cm}^2$. The results of the polarization measurements show that the P_s of BCT is slightly smaller than that of BT. On the contrary, several studies^{5,8} have suggested that the Ca substitution on the Ba site increases P_s without apparent experimental

Fig. 2. Polarization hysteresis loops measured at 297 K along the $\langle 001 \rangle$ direction for the single crystals of (a) BT and (b) BCT ($x = 0.07$).

evidence. The P_s of BCT was determined by our single-crystal measurements for the first time.

As a result of the single-crystal SR-XRD analysis, all diffraction spots observed were indexed to tetragonal space group $P4mm$. Table 3 lists the lattice parameters measured for

Table 3. Lattice parameters determined by the SR-XRD experiments using single crystals.

	a (nm)	c (nm)	c/a
BT	0.3990	0.4034	1.0109
BCT ($x = 0.07$)	0.3980	0.4027	1.0117

Fig. 3. Crystal structures determined by our DFT calculations: the (a) BT cell and the BCT supercells in space group (b) $P4mm$, (c) Cm and (d) $P2_1$.

the single crystals of BT and BCT ($x = 0.07$). These values agree quantitatively with the previous reports.⁶ It should be emphasized that the average structure of BCT crystals is not monoclinic or orthorhombic but indeed tetragonal $P4mm$. The monoclinic distortion reported by Levin *et al.* was not confirmed in our structural analysis.

Differential thermal analysis measurements show that BT and BCT ($x = 0.07$) crystals have a T_C of 401 K and 406 K, respectively. The increase in T_C by the Ca substitution on the Ba site agrees with the results of BCT ceramics.⁶

Figure 3 shows the crystal structures determined by DFT calculations. Table 1 represents the values of P_s determined by the single-crystal polarization experiments and by the DFT calculations. The P_s of BT obtained by the DFT calculations is $26.8 \mu\text{C}/\text{cm}^2$, which corresponds fairly to the experimental P_s of $27 \mu\text{C}/\text{cm}^2$. The DFT calculations of BCT yield a larger P_s for all the supercells. The overestimation of P_s of BCT found in our calculations is caused by the GGA problems,^{16,17} which is inevitable also in our GGA-PBESol calculations. The P_s obtained in $P4mm$ and Cm is $29.5 \mu\text{C}/\text{cm}^2$, which is larger by $3.0 \mu\text{C}/\text{cm}^2$ than that of the experimental value. The calculation in space group $P2_1$ results in a smaller P_s of $28.0 \mu\text{C}/\text{cm}^2$. It is worth noting that the calculation in $P2_1$ provides a reasonable agreement with the experimental P_s .

Our DFT calculations reveal that the optimized structures have their distinct local structures around the Ca atoms in the supercells, which leads to a characteristic feature of the electric dipole moments (p) of the constituent atoms. The p_i of the i th atom is expressed by

$$p_i = \Delta z_i \bullet Z_i^* / V_{\text{primitive}}, \quad (1)$$

where Δz_i denotes the displacement of the atom with respect to the center of gravity in each of the perovskite ABO₃ primitive unit, Z_i^* its Born effective charge and $V_{\text{primitive}}$, the cell volume of the ABO₃ unit. It is noted for the supercells that the value of p is normalized as the moment per $V_{\text{primitive}}$ not per the volume of the supercell ($V_{\text{supercell}}$). The spontaneous polarization (p_s) of each of the ABO₃ (A + B + O1 + O2 + O3) primitive unit in the supercell is written by

$$p_s = p_A + p_B + p_{O1} + p_{O2} + p_{O3}. \quad (2)$$

The macroscopic polarization (P_s) of the supercell is expressed by

$$P_s = \frac{1}{N} \sum_{j=1}^N p_{s,j}, \quad (3)$$

where N denotes the number of the ABO₃ primitive units in the supercell. In the case of BT, P_s coincides with p_s due to $N = 1$.

Figure 4 represents the p vectors along the macroscopic polarization direction in BT ($P4mm$) and BCT ($P4mm$, Cm and $P2_1$). The number in parenthesis under the atoms denotes the site multiplicity (m). For the BCT supercells, the atoms of which the p vectors are largely changed by the substitution of Ca are selected. The p vectors of BT are the standard for comparing the values of p in BCT. In the $P4mm$ supercell, the p of Ca is relatively large compared with that of Ba. The p vectors of Ti2 and O1 are markedly enhanced by the Ca substitution. In the Cm supercell, the p vectors of Ti2, O1 and Ca are large compared with those of other atoms. The p of Ca is twice as large as that in $P4mm$. This large Ca displacement is accompanied by the enhancement in the off-centering of the adjacent Ti atoms. The enhanced p vectors of Ti2 and O1 are the main reasons for the large P_s in the $P4mm$ and Cm supercells. The large p vector of Ti2 is found also for the $P2_1$ supercell. The enhanced displacement of Ti around Ca has been reported for the structural analysis by Levin *et al.*⁸ It is interesting to note for the $P2_1$ supercell that the p vector of Ca is as large as ca. $22 \mu\text{C}/\text{cm}^2$. The large displacement of Ca leading to this large p along the polarization direction originates from the CT-type rotation of the TiO₆ octahedra around Ca. The supercell in space group $P2_1$ can adopt the rotation of the TiO₆ octahedra indeed observed for CT at 298 K in space group $Pbnm$. Although the average rotation angle of the TiO₆ octahedra is as small as 0.2° in the $P2_1$ supercell, this TiO₆ rotation greatly mitigates the p vectors of the atoms around Ca such as O1 and O2. The influence of the suppressed p vectors of the atoms around Ca overcomes the enhanced p of Ca, and therefore the P_s of the $P2_1$ supercell is smaller than those of the $P4mm$ and Cm supercells.

Fig. 4. Electric dipole moments (p) of the representative constituent atoms in (a) the BT cell and the BCT supercells of (b) $P4mm$, (c) Cm , and (d) $P2_1$. The number in parenthesis denotes the site multiplicity.

Here, we focus on the bond distance of Ca–O in the supercells. In the crystal structure of CT in space group $Pbnm$ at room temperature, two kinds of short bonding appear for Ca–O: 0.236 nm and 0.238 nm. In all of the supercells, Ca is displaced along the P_s direction. The off-centering of Ca along the $[113]^5$ or $[111]^8$ direction reported for BCT is not found in our DFT calculations. The $P4mm$ supercell has four equivalent short bonding of Ca–O with 0.251 nm while the Cm supercell exhibits two short Ca–O bonding with 0.251 nm and 0.252 nm. The above-mentioned Ca–O bonding in the $P4mm$ and Cm supercells are longer than those in CT. It is interesting to note that the $P2_1$ supercell has a short Ca–O bonding with 0.246–0.249 nm. This short bonding of Ca–O is attributed to the TiO_6 octahedral rotation around Ca.

The possible crystal structure in monoclinic Cm is denied by the experimental results of the structural analysis; the single-crystal SR-XRD measurements do not observe any monoclinic distortion of the BCT crystals under their

detection limit. Our DFT calculations suggest that the $P2_1$ supercell is the most probable crystal structure representing the local structure in BCT. It is reasonable to consider that the TiO_6 octahedral rotation similar to CT appear around Ca in BCT. In BCT, Ca with a smaller ionic radius induces the rotation of the adjacent TiO_6 octahedra, which is accompanied by the enhanced Ca displacement along the P_s direction, as is exhibited in Fig. 4(d). The higher T_C observed for BCT crystals can be explained by the large Ca displacement along the P_s direction. It is concluded that the smaller P_s of BCT originates from the rotation of the TiO_6 octahedra around Ca.

The structural distortion around Ca in BCT is likely to influence the polarization switching behavior under an electric field. The $P(E)$ loops shown in Fig. 2 exhibits that the coercive field (E_c) of BCT was 0.5 kV/cm, which was Ca. two times as large as that of BT (1.3 kV/cm). It is reasonable to consider that the high E_c observed for the BCT crystals are attributed partly to the large structural distortion around Ca, i.e., the rotation of the TiO_6 octahedra around Ca.

4. Conclusions

Single crystals of BCT were grown by a TSSG method. The spontaneous polarization at 298 K was determined to be $26.0 \mu C/cm^2$ for BCT ($x = 0.07$), which was smaller than that of BT ($27.3 \mu C/cm^2$). It is shown that the substitution of Ca on the Ba site decreases P_s while raises T_C . The small P_s observed for the BCT crystals is suggested to originate from the $CaTiO_3$ -like octahedral rotations around the Ca atoms.

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