Invariant lattice strain and polarization in BaTiO$_3$–CaTiO$_3$ ferroelectric alloys

FAST TRACK COMMUNICATION

Invariant lattice strain and polarization in BaTiO₃–CaTiO₃ ferroelectric alloys

Desheng Fu[1,2]**, Mitsuru Itoh**[3] **and Shin-ya Koshihara**[4,5]

[1] Division of Global Research Leaders, Shizuoka University, Johoku 3-5-1, Naka-ku,
Hamamatsu 432-8561, Japan
[2] Collaborative Research Project of Materials and Structures Laboratory of Tokyo Institute of
Technology, 4259 Nagatsuta, Yokohama 226-8503, Japan
[3] Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta,
Yokohama 226-8503, Japan
[4] Department of Materials Science, Tokyo Institute of Technology, Meguro-ku,
Tokyo 152-8551, Japan
[5] CREST and ERATO, Japan Science and Technology Agency (JST), 3-5 Sanbanchou,
Chiyoda-ku, Tokyo 102-0075, Japan

E-mail: ddsfu@ipc.shizuoka.ac.jp

Abstract
We report the lattice strain and polarization of the BaTiO₃–CaTiO₃ solid solution. We found
that the lattice strain evaluated by the tetragonality of the tetragonal phase at room temperature
is nearly independent of the composition within the limit of the solid solution. In association
with this variation, the saturation polarization remains nearly unchanged. Such invariant lattice
strain associated with the ionic displacement in ferroelectrics is considered to be responsible for
the nearly compositional independence of the polarization and the observed ferroelectric Curie
temperature. Its relatively stable polarization compared with that of pure BaTiO₃ is very
interesting for technological applications, such as in ferroelectric memory.

(Some figures in this article are in colour only in the electronic version)

The lattice strain in ferroelectrics plays a critical role in controlling their structure, ferroelectric phase transition, polarization and dielectric properties [1–9]. Recent first-principles calculations have revealed that the large lattice strain in ABO_3 perovskite can modify the ground state and nature of the transition. A typical example is the phase transition in $PbTiO_3$, which has a larger lattice strain, as evaluated by the large tetragonality $c/a = 1.06$ (c and a are the lattice constants), and thus merely has a stable tetragonal ferroelectric phase, in contrast to BaTiO₃, which possess a smaller lattice strain ($c/a = 1.01$) and thus exhibits a ground ferroelectric state of rhombohedral phase [1]. Theoretical calculations also indicate that an increase in the lattice strain will lead to a more stable ferroelectric structure and enhancement of the polarization [2, 3]. Motivated by theoretical predictions, experimental investigations were performed in a number of epitaxial perovskite oxide thin films by utilizing the so-called strain engineering technique [4–7], which demonstrated drastic enhancements of the ferroelectric transition temperatures and polarization in coherently epitaxial thin films. For example, epitaxial strain can result in an increase in the ferroelectric Curie temperature by nearly 500 °C and the remnant polarization by 250% compared with the corresponding bulk values in BaTiO₃ [4]. In addition to such a thin film strain engineering technique, chemical substitutions have also been used to explore new materials with enhanced tetragonality in PbTiO₃ and related compounds, resulting in the discovery of the high tetragonality of $c/a = 1.11$ in $PbTiO_3$–$Bi(Zn_{1/2}Ti_{1/2})O_3$ and a great enhancement of the ferroelectric Curie temperature in comparison to the host material PbTiO₃ [8, 9]. Here, we report on the control of tetragonality in the BaTiO₃-based system $Ba_{1-x}Ca_xTiO_3$
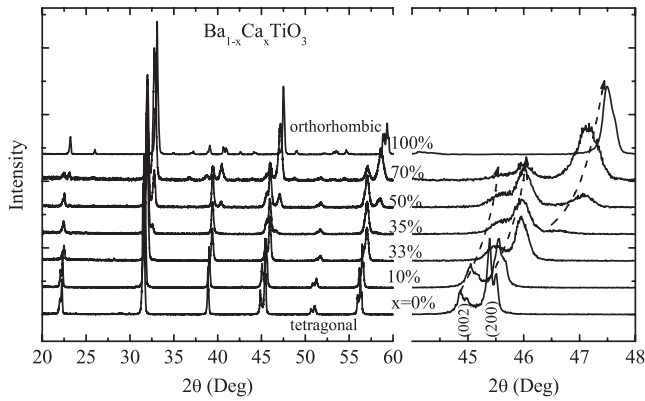
Figure 1. Phase evolution in the BaTiO$_3$–CaTiO$_3$ system viewed from the powder x-ray diffractions at room temperature. The right panel shows an enlarged view of the variation of the diffractions in the 2θ range of 44°–48°.

Table 1. Lattice parameters of Ba$_{1-x}$Ca$_x$TiO$_3$ at room temperature.

x (mol%)	a (Å)	c (Å)	c/a	V (Å^3)
0	3.993 31(11)	4.036 94(15)	1.0109	64.375
2	3.994 32(1)	4.027 75(3)	1.0084	64.261
3	3.993 02(12)	4.027 31(30)	1.0086	64.212
4	3.994 79(14)	4.027 10(31)	1.0081	64.266
5	3.992 39(1)	4.027 24(7)	1.0087	64.191
6	3.992 56(8)	4.027 66(11)	1.0088	64.203
10	3.979 61(5)	4.022 96(22)	1.0109	63.713
15	3.975 99(11)	4.014 71(9)	1.0097	63.467
23	3.963 19(13)	4.000 11(27)	1.0093	62.829
33	3.948 82(10)	3.983 71(8)	1.0088	62.119

(BCTO), which shows an anomalous evolution of its lattice strain and polarization: the lattice strain c/a and the saturation polarization remain nearly unchanged within the limit of the solid solution.

Investigations on BCTO ceramics obtained by a solid-state reaction can be tracked back to the early efforts to improve the dielectric, piezoelectric and ferroelectric properties of BaTiO$_3$ [10, 11]. It was found that the ferroelectric Curie temperature of BCTO is almost insensitive to the Ca substitution for composition $x \leqslant x_c$ ($x_c \simeq 22$ mol% for a conventional solid-state reaction process); this is in sharp contrast to substitutions with other elements, which generally result in a decease in the ferroelectric Curie temperature of BaTiO$_3$ [10]. In our recent investigations on the single crystals of this system [12, 13] in addition to such a unique characteristic we found many interesting phenomena including the significant effects of the quantum fluctuation on the ferroelectric phase transition at low temperature, the very large electric-field-induced strain, and the large piezoelectric effects at room temperature. These exotic properties of BCTO are closely related to the cooperation of the dipole moments due to the displacements of Ti with the dipole moments derived by the off-center displacements of the smaller Ca ions in the bulky Ba-site. These findings are of great significance from the viewpoint of either fundamental studies or technological applications for piezoelectric devices or the temperature-robust devices [12–18]. In this study, we examined the variations of lattice strain and polarization with composition, and found anomalous behaviors for this system. The present results will facilitate an understanding of the underlying physics in this interesting system.

Single crystals obtained by the floating-zone method were used as starting materials to prepare the powder and ceramic samples in this study. The detailed growth process for single crystals was reported in a previous paper [13]. Direct growth of crystals from the melt by the floating-zone technique allowed us to prepare BCTO samples with a limit of solid solution higher than that obtained by the conventional solid-state reaction ($x_c \simeq 22$ mol%). Powder x-ray diffraction with a Cu Kα radiation source was used to observe the

structural evolution in the BaTiO$_3$–CaTiO$_3$ system. Because of the difficulty of obtaining a mono-domain single crystal, we used the ceramic sample to investigate the compositional dependence of polarization in BCTO. Powders prepared from zone-melt crystal were milled and pressed in a 10 mm steel die with a pressure of 10 MPa to form a pellet, which was then sintered at 1773 K for 6 h in O$_2$. The pellet was polished to a thickness of about 500 μm and coated with Au electrodes for the polarization measurements. Electrical-displacement– electric-field (D–E) loops were measured at room temperature with a ferroelectric measurement system of an aixACC TF Analyzer 2000 with a high-voltage source of 10 kV. To prevent possible air breakdown at a high field, samples were immersed in silicon oil during measurements.

Figure 1 shows the structural evolution of the BaTiO$_3$– CaTiO$_3$ system. At room temperature, the BCTO solid solution shows diffraction patterns similar to those of BaTiO$_3$, indicating that it adopts the tetragonal structure of the BaTiO$_3$. However, when the Ca substitution is greater than a limit of $x_c \simeq 34\%$, the BCTO pure phase with a tetragonal structure is unavailable. As clearly shown in the right panel of figure 1, a new phase with an orthorhombic structure of the quantum-paraelectric CaTiO$_3$ occurs and coexists with the ferroelectric tetragonal phase for compositions $x \geqslant x_c$. The limit of solid solution obtained with the zone-melt method is much larger than the value of $\approx$22% reported for the conventional solid-state reaction [11]. In addition, it can be seen that the {200}-reflections (at 45°–46°) associated with the tetragonality show unique splitting, in which the interval between the (200) and (002) reflections remains nearly constant, indicating unique structural characteristics of the BCTO system.

The high-angle (60°–130°) diffractions were then measured to exactly determine the lattice constant at room temperature. The lattice constants evaluated with a careful calibration using Si as an internal standard are given in table 1 and figure 2. Several distinctive changes can be seen immediately in the structural evolution. (a) The lattice constants decrease with increasing Ca substitution as expected because the perovskite cell volume of CaTiO$_3$ ($V = 55.935$ Å^3) is smaller than that of BaTiO$_3$ ($V = 64.375$ Å^3). However, the variation in the lattice constant does not follow the famous Vegard law, which predicts a linear variation in the lattice constant of solid solution between the values of its two-end numbers [19, 20]. This is evident from the deviation of the measured perovskite parameter $(a^2c)^{1/3}$ from the predicted one (dashed line), as shown
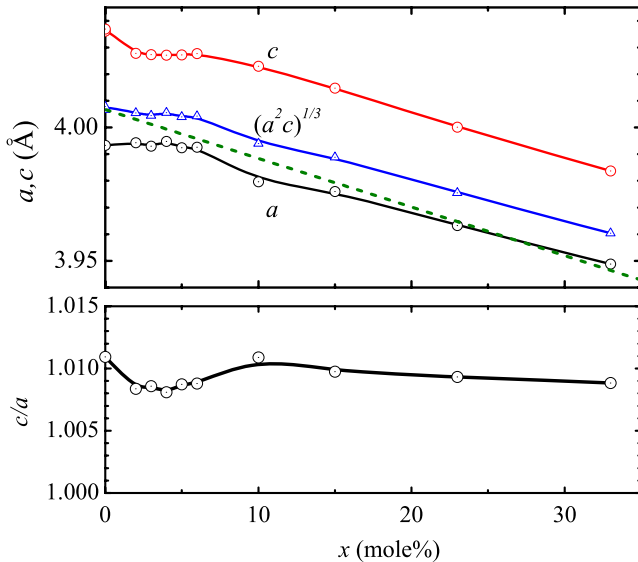
Figure 2. Compositional dependence of the lattice constant (upper panel) and tetragonality (lower panel) in $Ba_{1-x}Ca_xTiO_3$. The triangles show the variation of observed perovskite parameters $(a^2c)^{1/2}$ in comparison with that predicted by Vegard's law (dashed line).

Figure 3. Typical $D–E$ loops observed at room temperature for the ceramic samples of $Ba_{1-x}Ca_xTiO_3$.

Figure 4. Compositional dependence of the saturation polarization of $Ba_{1-x}Ca_xTiO_3$ ceramic samples.

in figure 2. (b) For a low Ca concentration of the substitution ($x \leqslant 6\%$), the variation in the lattice constant is extremely small. (c) When x is larger than 6%, both c and a decrease remarkably with increasing Ca concentration. (d) Surprisingly, despite a large decrease in the lattice constant, the tetragonality c/a remains nearly unchanged within the limit of solid solution. This characteristic is in sharp contrast to that observed for other solid solutions, which generally show a suppression or enhancement of c/a.

In ABO_3 ferroelectric oxides, the lattice strain is always associated with the ionic displacement that gives rise to the ferroelectricity in the structure. Therefore, the magnitude of the lattice strain can be used to evaluate the ferroelectricity of the material. For the case of a ferroelectric with tetragonal structure in particular, both experimental observations and theoretical calculations indicate that the increase of the tetragonality associated with the increase of the atomic displacements enhances the ferroelectric Curie temperature and spontaneous polarization [3, 8, 9]. Consequently, it is reasonable to expect that the invariant tetragonality will lead to a constant ferroelectric Curie temperature and spontaneous polarization in the system. Indeed, we found that the ferroelectric Curie temperature has a value that is very close to that of $BaTiO_3$ ($T_c \simeq 393$ K) and remains nearly unchanged in the BCTO system [12]. Here, we will show that the observed saturation polarization is also nearly independent of the Ca substitution within the limit of solid solution.

Figure 3 shows the typical $D–E$ hysteresis loops obtained at the same electric field at room temperature for pure $BaTiO_3$ and several BCTO ceramics. With the exception of the large relaxation of polarization in a pure $BaTiO_3$ sample when the electric field is removed, all observed $D–E$ hysteresis loops are basically similar. Such a large polarization relaxation
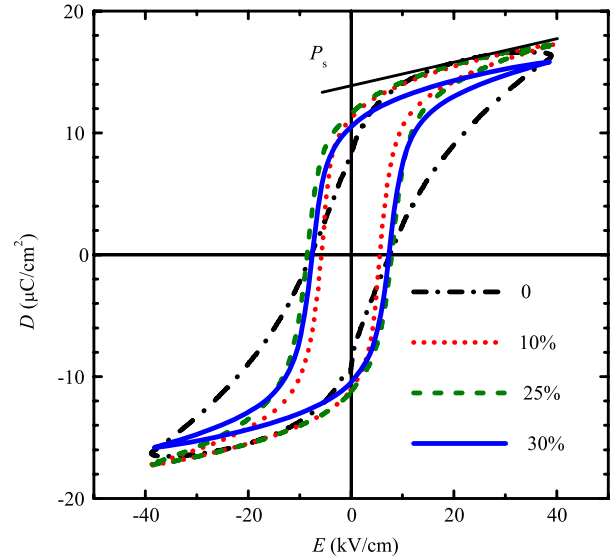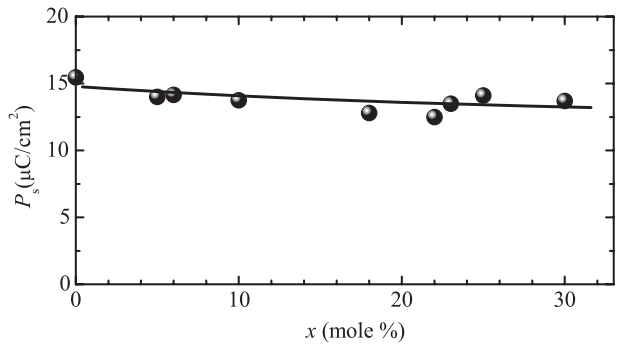
in $BaTiO_3$, which results in a smaller remnant polarization in comparison with a BCTO sample, is basically due to the existence of a tetragonal–orthorhombic phase transition around room temperature in $BaTiO_3$ [10, 12]. This phase transition gives rise to the instability of ferroelectric domains in the materials. In contrast to $BaTiO_3$, the tetragonal–orthorhombic phase transition has been strongly suppressed to a lower temperature with Ca substitution [12]. In particular, for $x \geqslant 23.3\%$, this phase transition disappears [12]. Therefore, it can be expected that the ferroelectric domains in BCTO are more stable than those in pure $BaTiO_3$ at room temperature. This characteristic property of BCTO is very useful for the applications of spontaneous polarization, such as in ferroelectric memory. The saturation polarization (P_s) calculated from the $D–E$ loop is given in figure 4. The variation of the saturation polarization with Ca substitution is very similar to that observed for the ferroelectric Curie temperature reported in [12]. Within the limit of solid solution, we may say that the spontaneous polarization is nearly insensitive to the Ca substitution, which supports the suggestion mentioned above.

In summary, we report the anomalous evolution of tetragonality with Ca substitution in the $(Ba, Ca)TiO_3$ system. We found that the tetragonality remains nearly unchanged within the limit of solid solution. It is reasonable to consider that such invariant tetragonality associated with the atomic displacements in the structure is responsible for the nearly compositional independence of the ferroelectric Curie temperature and spontaneous polarization in the system. Further theoretical or experimental investigations may provide new insight into the understanding of the exact origin of such anomalous behaviors. Moreover, the large and stable spontaneous polarization of this system may be interesting for some technological applications, for example in ferroelectric memory.

References

[1] Cohen R E 1992 *Nature* **358** 136
[2] Tinte S, Rabe K M and Vanderbilt D 2003 *Phys. Rev.* B **68** 144105
[3] Neaton J B, Hsueh C L and Rabe K M 2002 arXiv:condmat/0204511
[4] Choi K J *et al* 2004 *Science* **306** 1005
[5] Haeni J H *et al* 2004 *Nature* **430** 758
[6] Schlom D G *et al* 2007 *Annu. Rev. Mater. Res.* **37** 589
[7] Jang H W *et al* 2008 *Phys. Rev. Lett.* **101** 107602
[8] Stein D M, Suchomel M R and Davies P K 2006 *Appl. Phys. Lett.* **89** 132907
[9] Zhang X D, Kwon D and Kim B G 2008 *Appl. Phys. Lett.* **92** 082906
[10] Jaffe B, Cook W R Jr and Jaffe H 1971 *Piezoelectric Ceramics* (London: Academic)
[11] Mitsui T and Westphal W B 1961 *Phys. Rev.* **124** 1354
[12] Fu D, Itoh M, Koshihara S, Kosugi T and Tsuneyuki S 2008 *Phys. Rev. Lett.* **100** 227601
[13] Fu D, Itoh M and Koshihara S 2008 *Appl. Phys. Lett.* **93** 012904
[14] Fu D, Endo M, Taniguchi H, Taniyama T and Itoh M 2007 *Appl. Phys. Lett.* **90** 252907
[15] Fu D, Endo M, Taniguchi H, Taniyama T, Koshihara S and Itoh M 2008 *Appl. Phys. Lett.* **92** 172905
[16] Fu D, Itoh M and Koshihara S 2009 *J. Appl. Phys.* **106** 104104
[17] Tazaki R, Fu D, Itoh M, Daimon M and Koshihara S 2009 *J. Phys.: Condens. Matter* **21** 215903
[18] Cross E 2004 *Nature* **432** 24
[19] Vegard L 1921 *Z. Phys.* **5** 17
[20] Zen E-A 1956 *Am. Mineral.* **41** 523