Invariant lattice strain and polarization in BaTiO3-CaTiO3 ferroelectric alloys

著者	Fu Desheng, Itoh Mitsuru, Koshihara Shin-ya
journal or publication title	Journal of physics. Condensed matter
volume	22
number	5
page range	052204
year	2010-02-10
出版者	IOP science
権利	(C) 2010 IOP Publishing Ltd Printed in the UK
URL	http://hdl.handle.net/10297/6143

doi: 10.1088/0953-8984/22/5/052204

FAST TRACK COMMUNICATION

Invariant lattice strain and polarization in $BaTiO_3$-$CaTiO_3$ solid solution

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 & 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 $BaTiO_3$-$CaTiO_3$ solid solution. We found that the lattice strain evaluated by the tetragonality of the tetragonal phase at room temperature is nearly independent on 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 $BaTiO_3$ is very interesting for technological applications, such as in ferroelectric memory.

PACS numbers: 77.80.e,77.84.Dy

Submitted to: *J. Phys.: Condens. Matter*

The lattice strain in ferroelectrics plays a critical role in controlling the structure, ferroelectric phase transition, polarization and dielectric properties of the materials.[1, 2, 3, 4, 5, 7, 6, 8, 9] Recent first-principle 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 $BaTiO_3$, which possess a smaller lattice strain ($c/a = 1.01$) and thus exhibit a ground ferroelectric state of the rhombohedral phase.[1] Theoretical calculations also indicate that an increase in the lattice strain will lead to a more stable ferroelectric structure and the 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, 5, 6, 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 of the ferroelectric Curie temperature by nearly 500 °C and the remnant polarization by 250 % compared with the corresponding bulk values in $BaTiO_3$.[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 $PbTiO_3$ 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 $PbTiO_3$.[8, 9] Here, we report on control of the tetragonality in the $BaTiO_3$-based system $Ba_{1-x}Ca_xTiO_3$ (BCTO), which shows an anomalous evolution in the lattice strain and polarization: the lattice strain c/a and the saturation polarization remains 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 for the improvement of 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 $x \leq x_c$ ($x_c \simeq 22$ mole % 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 natures 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, 13, 14, 15, 16, 17, 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 the 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 process to grow single crystals was reported in a previous report.[13] The direct growth of crystal 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 ($x_c \simeq 22$ mole %). Powder X-ray diffraction with a Cu $K\alpha$ radiation source was used to observe the structure evolution in the $BaTiO_3$-$CaTiO_3$ system. Because of the difficulty in 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 equipment 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 Fig. 1, a new phase with an orthorhombic structure of the quantum-paraelectric $CaTiO_3$ occurs and coexists with the ferroelectric tetragonal phase for compositions $x \geq x_c$. The limit of solid solution obtained by the zone-melt method is greatly larger than the value of ≈ 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 a 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 by using Si as an internal standard are given in Table 1 and Fig. 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 $CaTiO_3$ ($V = 55.935\mathring{A}^3$) is smaller than that of $BaTiO_3$ ($V = 64.375\mathring{A}^3$). However, the variation in the lattice constant does not follow the famous Vergard's 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 in Fig. 2. (b) For a low Ca-concentration of the substitution ($x \leq 6$ %), the variation in the lattice constant is extremely small. (c) When x is larger than 6 %, both c and a remarkably decrease 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. Particularly, for the case of a ferroelectric with tetragonal structure, 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 $BaTiO_3$ ($T_c \simeq 393K$) 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 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 $x \geq 23.3$ %, 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 the ferroelectric memory. The saturation polarization (P_s) calculated from the $D - E$ loop was given in Fig. 4. The variation of the saturation polarization with Ca-substitution is very similar to that observed for the ferroelectric Curie temperature reported in Ref.[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 the 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. Furthermore, its stable polarization will be very useful for technological applications, such as in ferroelectric memory.

[1] Cohen R E 1992 Nature (London) **358** 136
[2] Tinte S, Rabe K M andVanderbilt D 2003 Phys. Rev. B **68** 144105
[3] Neaton J B, Hsueh C L and Rabe K M, arXiv:condmat/ 0204511.
[4] Choi K J et al. 2004 Science **306** 1005
[5] Haeni J H et al. 2004 Nature (London) **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** 012903
[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-An 1956 Am. Mineral. **41**, 523

Table 1. Lattice parameters of $Ba_{1-x}Ca_xTiO_3$ at room temperature.

x/mol%	$a/\AA$	$c/\AA$	c/a	$V/\AA^3$
0	3.99331(11)	4.03694(15)	1.0109	64.375
2	3.99432(1)	4.02775(3)	1.0084	64.261
3	3.99302(12)	4.02731(30)	1.0086	64.212
4	3.99479(14)	4.02710(31)	1.0081	64.266
5	3.99239(1)	4.02724(7)	1.0087	64.191
6	3.99256(8)	4.02766(11)	1.0088	64.203
10	3.97961(5)	4.02296(22)	1.0109	63.713
15	3.97599(11)	4.01471(9)	1.0097	63.467
23	3.96319(13)	4.00011(27)	1.0093	62.829
33	3.94882(10)	3.98371(8)	1.0088	62.119

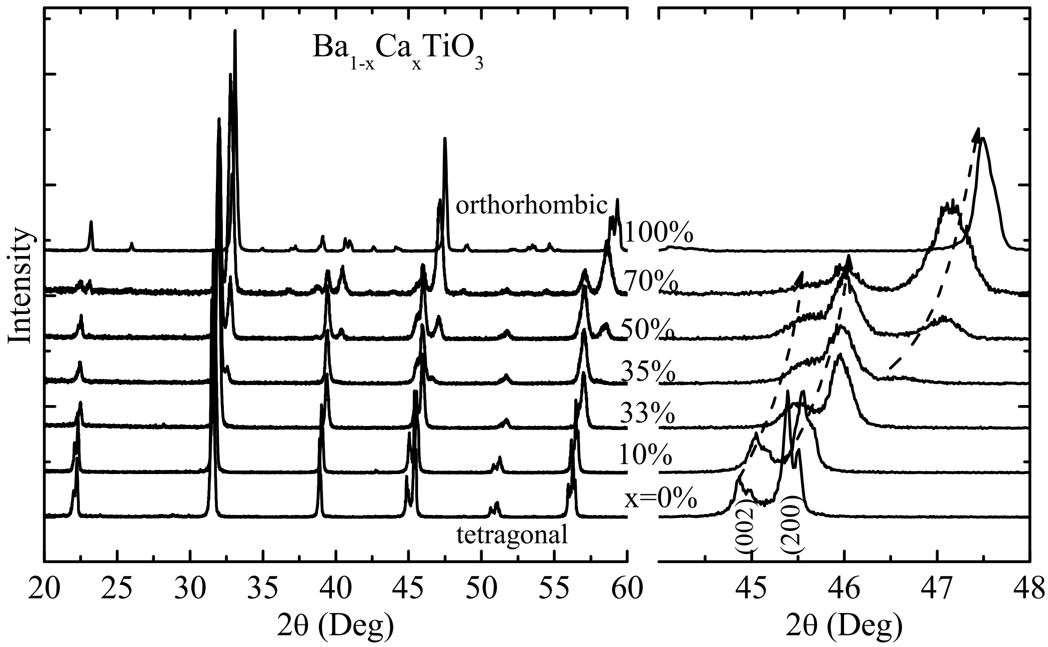

Figure 1. Phase evolution in the $BaTiO_3$-$CaTiO_3$ system viewed from the powder X-ray diffractions at room temperature. The right panel shows an enlarged view of the variation of the diffractions in the 2θ range of $44 - 48°$.

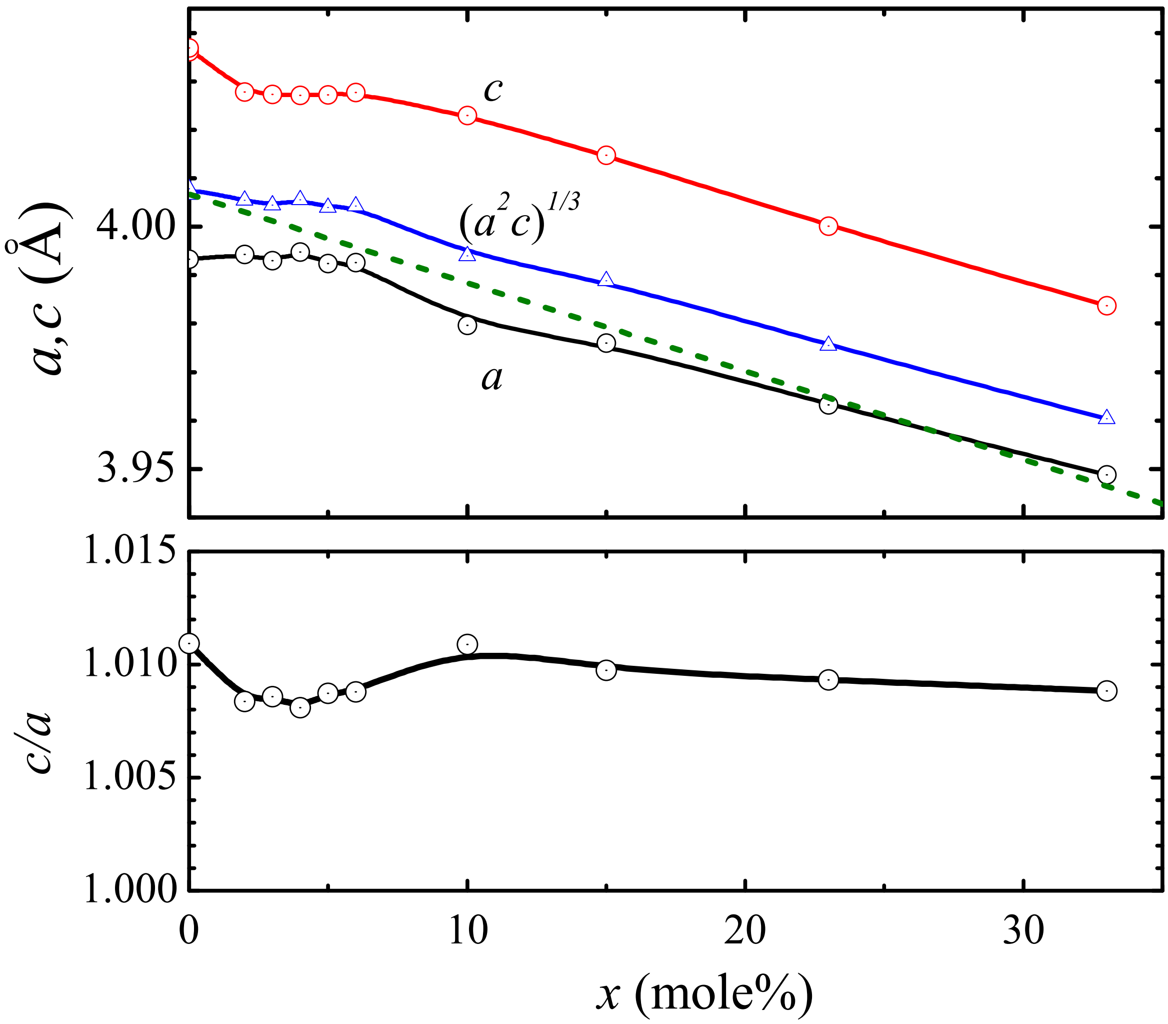

Figure 2. (Color Online) Compositional dependence of the lattice constant (upper panel) and tetragonality (lower panel) in $Ba_{1-x}Ca_xTiO_3$. The triangles show the variation of observed perovskite parameters $(a^2c)^{1/2}$ in comparison with that predicted by the Vergard's law (dashed line).

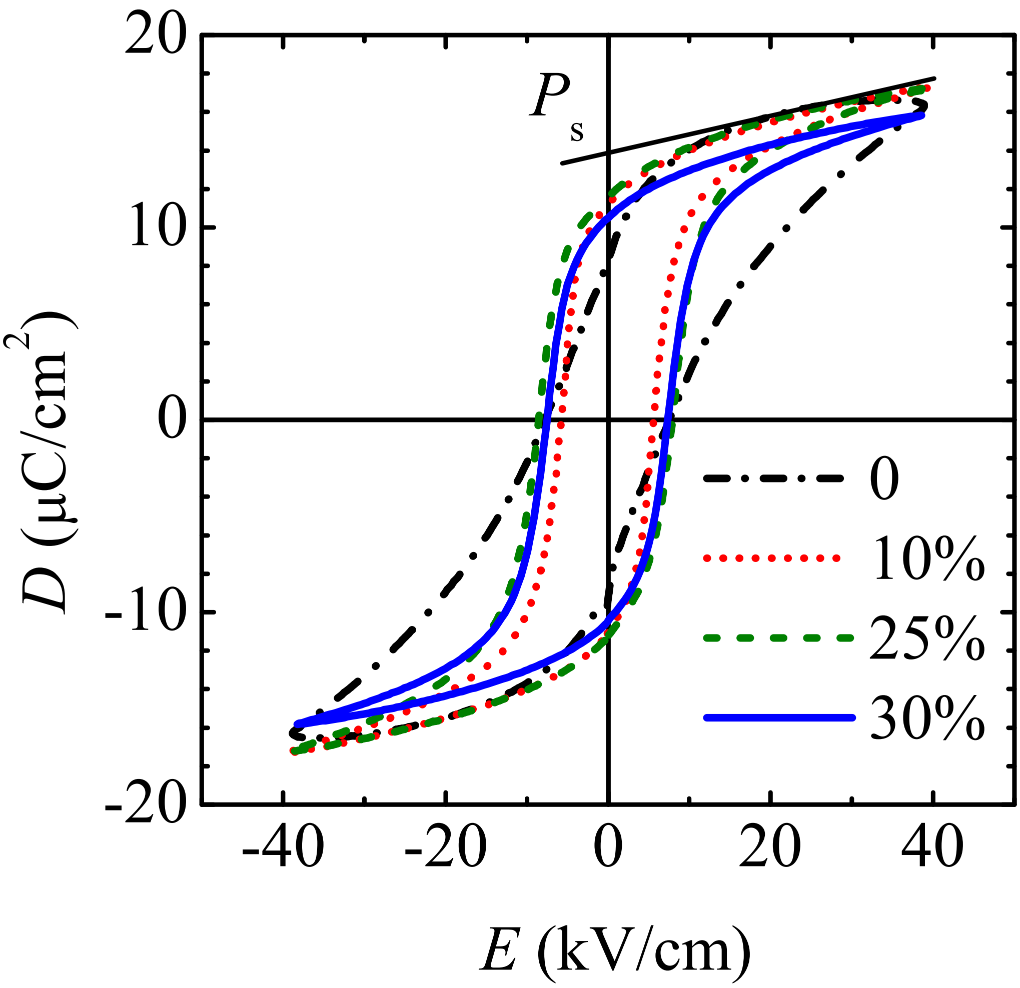

Figure 3. (Color Online) Typical $D-E$ loops observed at room temperature for the ceramic samples of $Ba_{1-x}Ca_xTiO_3$.

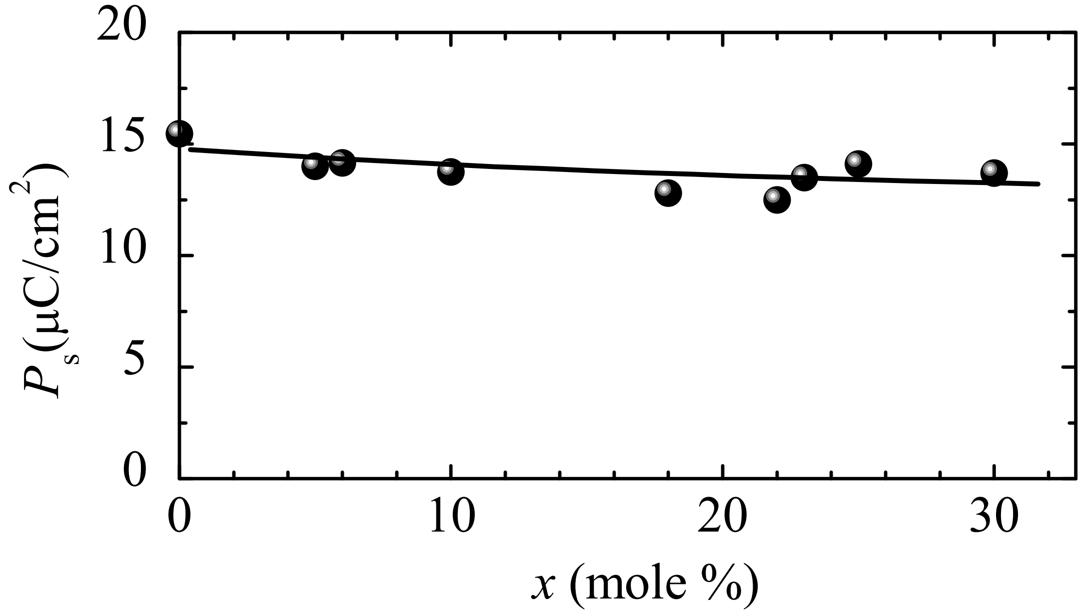

Figure 4. Compositional dependence of the saturation polarization of $Ba_{1-x}Ca_xTiO_3$ ceramic samples.