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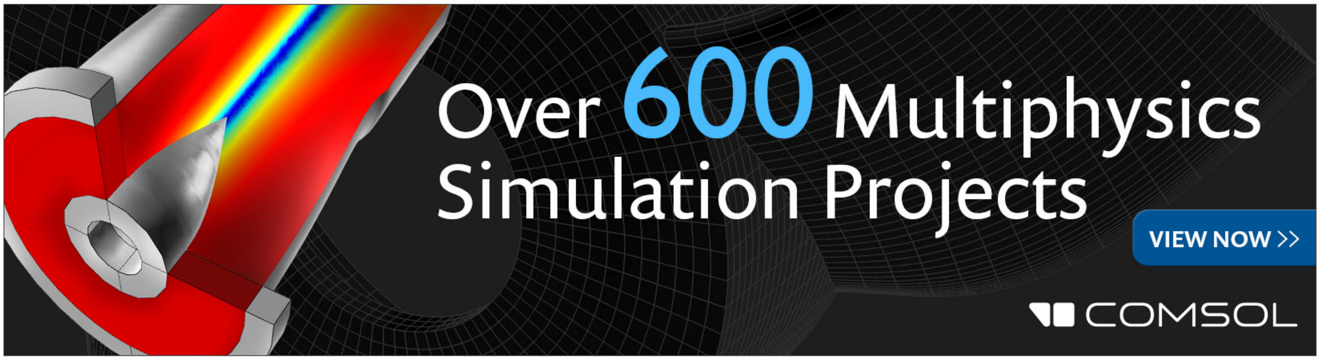

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Large electrostriction near the solubility limit in $BaTiO_3-CaTiO_3$ ceramics

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This study prepared $(1-x)BaTiO_3-xCaTiO_3$ $(x=0.20-1.0)$ ceramics. Their structural and electric properties were analyzed. High electrostrictive strain of 0.22%, higher by 157% as compared to $BaTiO_3$ ceramic, was obtained near the solubility limit in the side of composite $(x=0.23)$, which is a diphasic ceramic composed of a ferroelectric tetragonal $Ba_{0.8}Ca_{0.2}TiO_3$ solid solution and a normal dielectric orthorhombic $Ba_{0.07}Ca_{0.93}TiO_3$ solid solution. This enhanced electrostriction resulted from the coupling of the large ionic polarization in $Ba_{0.07}Ca_{0.93}TiO_3$ with the non-180° domains in $Ba_{0.8}Ca_{0.2}TiO_3$ during the external electric field exertion. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1850598]

Piezoelectric/electrostrictive materials and actuators are widely used in optics, astronomy, fluid control, and precision machining due to their high generative force, accurate displacement, and rapid response.[1] Practical materials with large piezoelectric/electrostrictive strain are mainly lead-based relaxor ferroelectric single crystals and ceramics.[1–3] With the recent growing demand of global environmental protection, lead-free materials have attracted much attention. Barium titanate $(BaTiO_3)$ based materials showed promising piezoelectric/electrostrictive properties. $BaTiO_3$ single crystals show large strain of around 1% despite their remarkable hysteresis;[4–6] and some doped $BaTiO_3$ solid solutions also exhibit interesting piezoelectric/electrostrictive properties.[7–9]

$BaTiO_3$ was the first perovskite-type ferroelectric and piezoelectric material developed and intensively studied ever since its discovery 60 years ago.[10] Early reports[10–12] revealed that in the $BaTiO_3-CaTiO_3$ system, Ca^{2+} replaces Ba^{2+} in $BaTiO_3$ to form $Ba_{1-x}Ca_xTiO_3$ solid solutions with x up to 0.21 and causes a negligible change of the Curie point (cubic paraelectric–tetragonal ferroelectric transition temperature) but strongly lowers the tetragonal–orthorhombic transition temperature, which is of great value in improving the temperature stability of piezoelectric/electrostrictive properties for many practical applications. Above the solubility limit $(x=0.21)$, an insolubility region extends to 90 mol % of $CaTiO_3$, and further $CaTiO_3$ added $(>90\text{ mol }\%)$, orthorhombic $CaTiO_3$-based solid solutions were formed. No detailed structural and electrical studies have been reported for composite materials in the insolubility region $(0.21<x<0.90)$. On the other hand, composite and diphasic materials have been known to possess the potential for performance far beyond those of constituent materials.[13,1] In fact, the lead-based ultrahigh electrostriction materials[1–3] like $Pb(Zn_{1/3}Nb_{2/3})TiO_3-PbTiO_3$ (PZN–PT) and $Pb(Mg_{1/3}Nb_{2/3})TiO_3-PbTiO_3$ (PMN–PT) are compositionally near the morphotropic phase boundary. Their high strain is thought to result from the coupling between two equivalent energy states, i.e., the tetragonal and rhombohedral phases. This letter reports our results for dielectric, ferroelectric, and electrostrictive properties in $BaTiO_3-CaTiO_3$ ceramics. Large electrostrictive strain was obtained near the solubility limit in the composite ceramics.

Our experiments prepared $(1-x)BaTiO_3-xCaTiO_3$ $(x=0.2, 0.23, 0.25, 0.30, 0.40, 0.5, 0.70, 0.90, 0.93, 0.95,$ and $1.0)$ ceramics using conventional solid-state reaction technique. Raw materials of $BaCO_3$ (99.95%), $CaCO_3$ (99.99%), and TiO_2 (99.9%) (all supplied by Kojundo Chemical Lab. Co.) were mixed with addition of alcohol, then dried and heated at 900 °C for 4 h in air. Thereafter, they were remixed and pressed into 10-mm-diam pellets and sintered at 1400 °C for 4 h in oxygen atmosphere. All samples had densities that were greater than 95% of their theoretical values. The sample crystallization behavior was examined using an x-ray diffractometer (XRD, Rint2000; Rigaku Corp.) and a scanning electron microscopy (SEM, S-4300; Hitachi Ltd.). The sintered pellets were polished to 0.6 mm thickness. Silver electrodes were fired on both surfaces of the specimens for electric measurement. Dielectric, ferroelectric, and electrostrictive properties were characterized using an impedance/gain-phase analyzer (HP4194A; Hewlett-Packard Co.), an LCR tester (Hioki3522; Hioki E. E. Corp.), and a ferroelectric analyzer (TF2000; aixACCT systems GmbH).

Using measured powder XRD patterns, the structures of $(1-x)BaTiO_3-xCaTiO_3$ ceramics were determined to be a pure tetragonal phase for $x=0.20$, tetragonal and orthorhombic phase coexistence for $x=0.23-0.90$, and a pure orthorhombic phase for $x=0.93-1.0$, respectively. Results of Ba-rich extreme $(x=0.20)$ and Ca-rich extreme $(x=0.93-1.0)$ are similar to reported ones,[10–12] but a decrease is reported in the solubility limit both for Ca addition in $BaTiO_3$ and Ba addition in $CaTiO_3$, which is possibly attributable to the high purity of raw chemicals in our experiment. We have tried a small amount (around 0.2%) of praseodymium substitution in the ceramics and obtained an increase in solubility limit to $x=0.23$ for tetragonal $Ba_{1-x}Ca_xTiO_3$ solid solution and to $x=0.90$ for orthorhombic $Ba_{1-x}Ca_xTiO_3$ solid solution. Figure 1 shows refined XRD patterns for the tetragonal strongest peak (110) [denoted as T(110)] and orthorhombic strongest peak (121) [denoted as O(121)], and the related composition dependence of interplanar distance as well. It shows that the tetragonal (110) and orthorhombic (121) peaks for all samples in the diphasic region $(x=0.23-0.90)$ almost coincide, respectively, with those of tetragonal $Ba_{0.8}Ca_{0.2}TiO_3$ $(x=0.20)$ and orthorhombic $Ba_{0.07}Ca_{0.93}TiO_3$ $(x=0.93)$ solid

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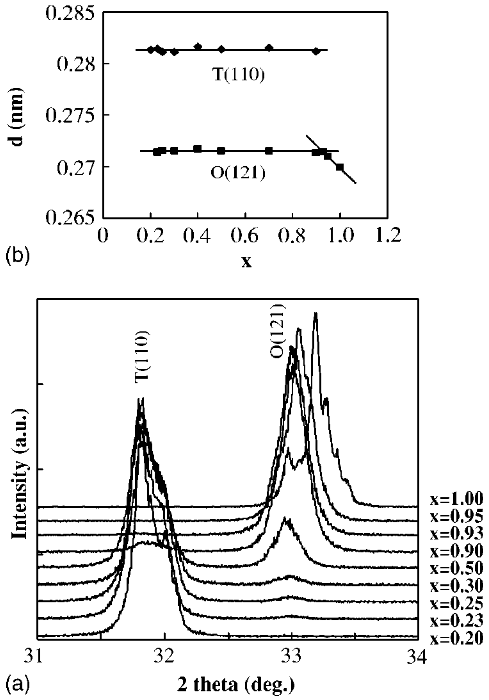
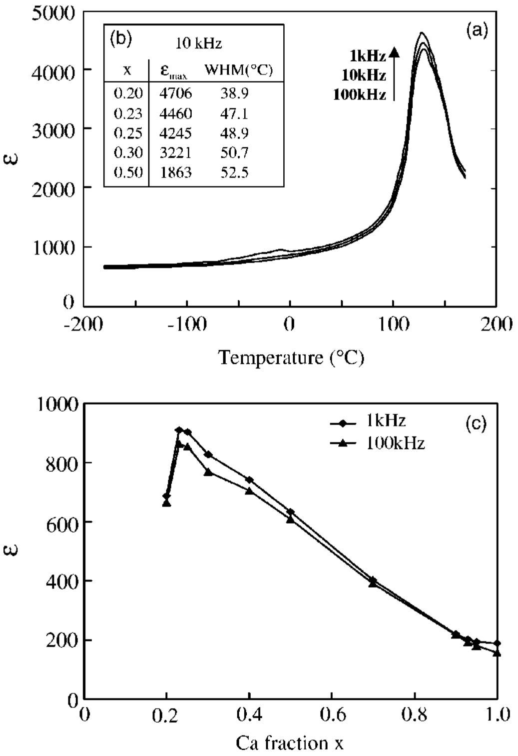


FIG. 1. Refined XRD patterns of $(1-x)BaTiO_3-xCaTiO_3$ ceramics near the tetragonal strongest peak (110) and orthorhombic strongest peak (121) (a), and related interplanar distance d (b).



x	ε_{max}	WHM(°C)
0.20	4706	38.9
0.23	4460	47.1
0.25	4245	48.9
0.30	3221	50.7
0.50	1863	52.5

FIG. 2. Temperature and composition dependence of dielectric constant ε for the $(1-x)BaTiO_3-xCaTiO_3$ ceramics. (a) ε vs temperature for the $x=0.23$ sample at different frequency, (b) the peak value ε_{max} and width at half-maximum (WHM) vs Ca fraction x, and (c) ε vs Ca fraction x at room temperature.

solutions. From the above-mentioned result we can infer that the ceramics, by present firing procedure and in compositional range of $0.23 \leqslant x < 0.93$, are in diphasic coexistence and composed of tetragonal $Ba_{0.8}Ca_{0.2}TiO_3$ solid solution and orthorhombic $Ba_{0.07}Ca_{0.93}TiO_3$ solid solution. The backscattered scanning electron microscopy and energy-dispersive x-ray spectrometry observations showed that small (submicron) $Ba_{0.07}Ca_{0.93}TiO_3$ grains dispersed among the larger $Ba_{0.8}Ca_{0.2}TiO_3$ grain matrix.

Dielectric, ferroelectric, and electrostrictive properties were measured with metal/ceramic/metal capacitors. Those measurements are shown in Figs. 2–4. Figure 2 shows the temperature and composition dependence of the dielectric constant. Samples from $x=0.20$ to 0.50 have a similar temperature dependence trend; for that reason, the dielectric constant versus temperature plot is given only for sample $x=0.23$ [Fig. 2(a)]. We found that Ca addition causes a negligible change in the Curie point, lying around 120 °C, but a decrease in peak height and an increase in width [Fig. 2(b)]. This fact implies that samples have relaxor features, which is also implied by the peak shift with frequency in Fig. 2(a). The dielectric constant in the composite phase $(x=0.23-0.40)$ is higher than that in the pure ferroelectric $Ba_{0.8}Ca_{0.2}TiO_3$ $(x=0.20)$ phase [Fig. 2(c)], unlike the simple mixture of two phases where the dielectric constant of the composite lies between those of the individual phases.[13] This fact indicates that some interaction exists between the two phases. Figures 3 and 4 show the polarization-electric field hysteresis loops and electrostrictive displacement-electric field butterfly curves for various compositional samples $(x=0.20-0.50)$. The remnant polarization (P_r) and electrostrictive strain (S: displacement divided by sample thickness) show the largest values in the composite ceramic of $x=0.23$, in which the strain (0.22% at 50 kV/cm) is 157% higher than that in pure $BaTiO_3$ ceramic (~0.14% at 50 kV/cm),[8] again supporting the conjecture of interaction between the two phases in the composite ceramics. With increase of added Ca, the remnant polarization and electrostrictive strain decreased and retained quite large values to $x=0.50$, which are reasonable for the composite of ferroelectric and normal dielectric materials but did not decrease greatly as did other similar composite materials.[14] Figure 5 shows a comparison of the composition dependence of field-induced strain (S), remnant polarization (P_r), and piezoelec-

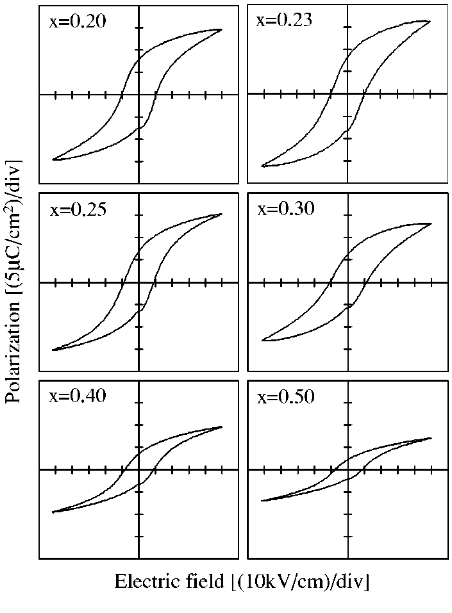


FIG. 3. Polarization vs electric field for various Ca fraction samples at room temperature.

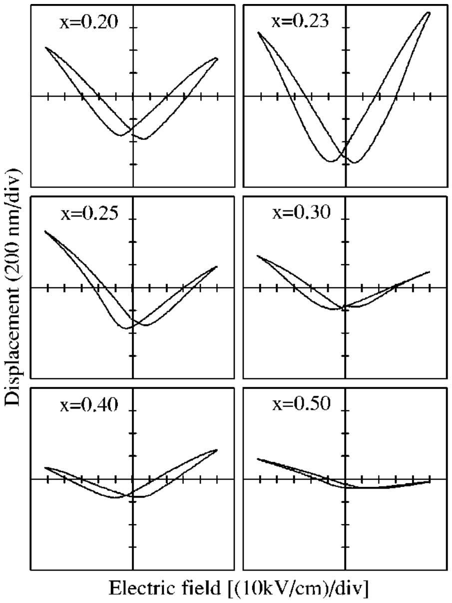


FIG. 4. Field-induced displacement for various Ca fraction samples with ±50 kV/cm, 1 Hz driving field at room temperature (sample thickness is 0.6 mm).

tric coefficient (d_{33}), where the latter parameter is an intrinsic physical parameter of the material and calculated by $d_{33} = 2Q\varepsilon\varepsilon_0 P_s$. Here $Q = S/P^2$ is the electrostrictive coefficient; ε and ε_0 are the relative and vacuum dielectric constants; P and P_s are the polarization and spontaneous polarization.

The above-mentioned result can be explained as follows. In the $(1-x)\mathrm{BaTiO_3}$–$x\mathrm{CaTiO_3}$ ($x = 0.20$–0.90) ceramics, the structure is a diphasic composite of the tetragonal $\mathrm{Ba_{0.8}Ca_{0.2}TiO_3}$ solid solution and orthorhombic $\mathrm{Ba_{0.07}Ca_{0.93}TiO_3}$ solid solution for $x \geqslant 0.23$, the former is a ferroelectric, while the latter is a normal dielectric in a large range of temperatures, including our investigated temperature range (−180–120 °C). Large electrostrictive strain is believed to originate from the non-180° domain rotation driven by an external electric field.[1–3,6] On the point of microscopic view, a domain and its motion in a ceramic grain are affected by surrounding domains, domain walls, and defects, which are finally exhibited in the form of an internal field. This local internal field overlaps on the external field and improved or depressed the piezoelectric and electrostrictive properties depending on whether there is a plus or minus interaction. In the present case, $\mathrm{CaTiO_3}$ is known as an incipient ferroelectric and showed ferroelectric-like features.[15–17] $\mathrm{CaTiO_3}$ and its solid solution $\mathrm{Ba_{0.07}Ca_{0.93}TiO_3}$ have large ionic polarization, thereby producing large dielectric constants of about 160 and 200, respectively [Fig. 2(c)]. In the composite ceramics ($x = 0.23$–0.50), $\mathrm{Ba_{0.07}Ca_{0.93}TiO_3}$ grains disperse among the ceramics; their ionic polarization couples with the non-180° domains in surrounding ferroelectric $\mathrm{Ba_{0.8}Ca_{0.2}TiO_3}$ grains. The polarization enhances the polarizability and domain rotation ability of the ceramics during the external electric field exertion. Therefore, the related parameters like dielectric constant, remnant polarization, electrostrictive strain, and piezoelectric coefficient of the ceramics increase. On the other hand, the ferroelectric properties of the composite are degraded by non-ferroelectric addition. Behaviors of the physical parameters in Fig. 2(c) and Fig. 5 are a result of a compromise between these two effects.

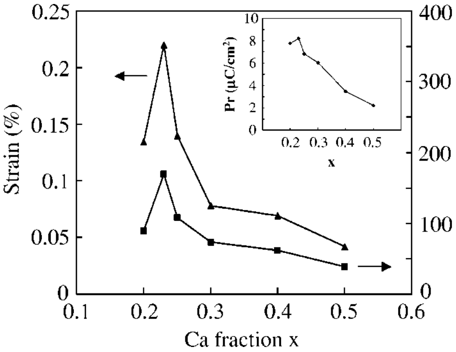


FIG. 5. Composition dependence of strain and piezoelectric coefficient in a ±50 kV/cm driving field.

In summary, high dielectric, ferroelectric, piezoelectric/electrostrictive properties were obtained in the composite of $(1-x)\mathrm{BaTiO_3}$–$x\mathrm{CaTiO_3}$ ceramics near the solubility limit. In the diphasic region ($x \geqslant 0.23$), the coupling of the large ionic polarization in $\mathrm{Ba_{0.07}Ca_{0.93}TiO_3}$ with the non-180° domains in $\mathrm{Ba_{0.8}Ca_{0.2}TiO_3}$ seems to act as an important factor in improving ceramic properties. Our material is similar to the high-strain MBP material to some extent, but ours is a composite of ferroelectric and nonferroelectric materials, implying a route to develop new high-strain materials in a wide range of different material families.

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