Piezoelectric and electrostrictive strain behavior of Ce-doped $BaTiO_3$ ceramics

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The ferroelectric and strain behavior of the $Ba(Ti_{1-y}Ce_y)O_3$ solid solutions was studied. Three phase transition temperatures were shifted with increasing Ce concentration, and pinched at $y=0.06$. The samples could be structurally indexed by x-ray diffraction in a tetragonal symmetry at $y\leqslant0.06$; and in a pseudo-cubic symmetry at $y>0.06$. The strain levels in the range of 0.15–0.19% at ~60 kV/cm with small hysteresis were obtained for the samples with low content Ce. With increasing Ce concentration, the tetragonality decreases, the strain level decreases, and becomes less hysteretic. The physical mechanism of the electrostrictive, piezoelectric, and ferroelectric-relaxor behavior is briefly discussed. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1473871]

Very high piezoelectric and electrostrictive properties have been achieved in a series of lead based perovskite-type relaxor ferroelectric single crystals[1,2] for a certain orientation. It is believed that in these systems the high strain is engendered by phase switching from low to high spontaneously deformed states and that the usual hysteresis in such a process is moderated by an induced monoclinicity which permits almost continuous rotation of the polarization vector. Unfortunately, lead compounds are toxic so there is an increasing desire to develop lead-free materials with high strain capability. Among several groups of lead free candidates barium titanate $BaTiO_3$ (denoted as BTO) is quite promising.[3] The high strain at high electric field is ~1% and is engendered by ferroelastic domain switching in the initial *c* domain single crystal. Unfortunately, it has large hysteresis, which restricts practical application.[3] Barium titanate compositions modified by Sn,[4] Hf,[5] Ce,[6,7] Y,[8] and Zr[9] have been extensively studied for dielectric application and all exhibit a crossover from typical ferroelectric to ferroelectric-relaxor behavior at higher concentrations of substitution. In fact, through Zr incorporation in BTO it has been reported that almost hysteresis-free high strain can be realized.[10,11] Thus it is logical to explore others in this sequence of modifiers for their piezoelectric and electrostrictive behavior.

Some of the present authors have recently studied the phase assemblage and ferroelectric behavior induced by Ce incorporation in BTO ceramics.[7] Obvious "pinch off" of the tetragonal, orthorhombic, and rhombohedral ferroelectric phases was observed together with the onset of ferroelectric-relaxor behavior at high Ce levels. Similarity to the BTO doped with Zr situation suggests that the Ce modified compositions may be promising as lead free actuator materials. In this letter we focus on the strain behavior in the Ce-doped BTO ceramics.

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Ceramics with the nominal composition $Ba(Ti_{1-y}Ce_y)O_3$ ($y=0$, 0.02, 0.04, 0.06, 0.08, 0.1, 0.13, 0.16, 0.2, 0.25, 0.3 and 0.33) were synthesized by the mixed oxide method. The dielectric properties were measured with an HP4284A meter in the temperature range 12–500 K. The hysteresis loop and strain were measured at room temperature by a modified Sawyer–Tower circuit, and a linear variable displacement transducer driven by a lock-in amplifier, respectively. The processing and electrical measurement details were described in the earlier work.[7,10]

The temperature dependence of the dielectric constant (ϵ) at 10 kHz for some $Ba(Ti_{1-y}Ce_y)O_3$ samples with $0\leqslant y\leqslant0.3$ is shown in Fig. 1. For undoped BTO ($y=0$), sharp phase transitions are observed at 398, 285, and 196 K, corresponding to the phase transitions of paraelectric (cubic)-ferroelectric (tetragonal) (at T_c), tetragonal-orthorhombic (T_1), and orthorhombic-rhombohedral (T_2), respectively. In the sample with $y=0.02$, similar to that of pure BTO, the three phase transitions are observed however the phase tran-

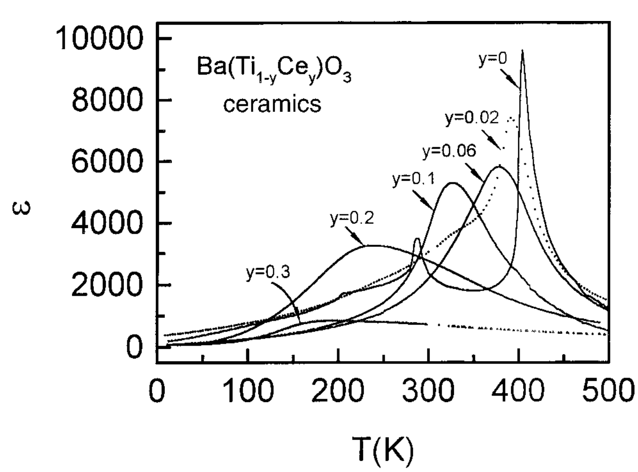

FIG. 1. Temperature dependence of the dielectric constant (ϵ) of the $Ba(Ti_{1-y}Ce_y)O_3$ ceramics with $y=0$, 0.02, 0.06, 0.1, 0.2, and 0.3 at 10 kHz.

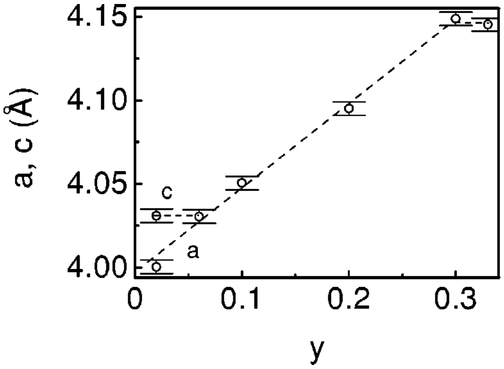

FIG. 2. The variation of the lattice parameters of the $Ba(Ti_{1-y}Ce_y)O_3$ ceramics as a function of Ce concentration *y*.

sition temperatures are shifted: T_c to lower temperatures, and T_1 and T_2 to higher temperatures. When the Ce content is greater than 0.06, only one rounded ε peak is observed, and the samples show typical ferroelectric relaxor behavior.[7]

The variation of the lattice parameters as a function of the Ce content is shown in Fig. 2. In the present work, the sample with $y=0.02$ can be well indexed with a tetragonal symmetry. However, the samples with $y \geqslant 0.06$ are better indexed by a pseudo-cubic symmetry, which corresponds to the Ce concentration at which the three phase transitions are pinched together. The lattice parameters of the samples with $y \geqslant 0.06$ increase monotonically with increasing Ce content in the range $0.06 \leqslant y \leqslant 0.3$, but are almost constant for $y \geqslant 0.3$, which confirms that the limit of the solid solubility of Ce^{4+} in BTO is about $y=0.3$.[7]

The conventional hysteresis loops at room temperature were measured, and some typical results are shown in Fig. 3. At room temperature, the saturation polarization is 15 $\mu C/cm^2$ for $y=0.02$, and 10 $\mu C/cm^2$ for $y=0.1$.

The unipolar strain (*S*) versus electric field (*E*) behavior for $Ba(Ti_{1-y}Ce_y)O_3$ ceramics measured at room temperature (~295 K) and 0.2 Hz is shown in Fig. 4. For the samples with low concentration Ce ($y \leqslant 0.08$), the strain level is in the range of 0.14–0.19%. This is a reasonably high level for ceramic samples, compared with lead containing materials, such as $Pb(Zr,Ti)O_3$ ceramics,[2] and electrostrictive ceramics $Pb(Mg,Nb)O_3-PbTiO_3$.[2] For the sample with $y=0.02$, which is tetragonal at room temperature, a hysteretic strain is

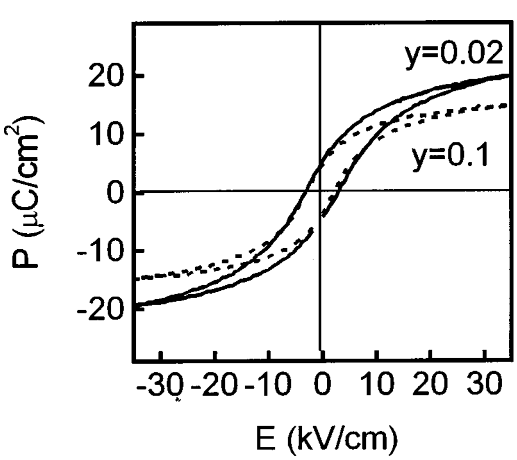

FIG. 3. The hysteresis loops of the $Ba(Ti_{1-y}Ce_y)O_3$ ($y=0.02$ and 0.1) ceramics measured at room temperature and 0.2 Hz.

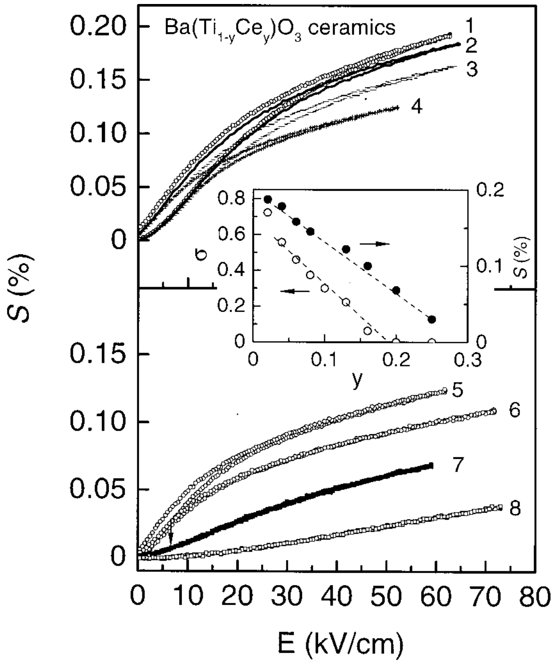

FIG. 4. The strain (*S*) vs electric field (*E*) of the $Ba(Ti_{1-y}Ce_y)O_3$ ceramics measured at room temperature and 0.2 Hz, 1–8: $y=0.02$, 0.04, 0.06, 0.1, 0.13, 0.16, 0.2, and 0.25. Inset: the composition dependence of *S* at 60 kV/cm and the hysteresis area (σ) of unipolar strain vs *E* profile.

observed below 45 kV/cm. As usually observed in the relaxor-based "soft" piezoelectric materials, the hysteresis at low fields is attributed to domain motions.[2] In the present work, the hysteresis could also be associated with the domain reorientation, which is prominent for a sample with a multidomain state. Above 45 kV/cm, the hysteresis-free strain is observed, implying a poling state free of domain wall motions induced by the high external electric fields. At ~60 kV/cm, the highest electric field in the work, the strain is 0.19%.

At the pinched point $y=0.06$, similar behavior of strain is observed, but the strain level slightly decreases, and a value of 0.16% was obtained. With increasing Ce doping concentration, the strain level gradually decreases, as shown in the inset of Fig. 4. In addition, for the samples with $y \leqslant 0.13$, the strain was measured in the ferroelectric-relaxor state (T_c or T_{ϵ_m} is higher than 300 K) and is mainly originated from the piezoelectric effect. However, for $y \geqslant 0.2$, the strain was measured in the paraelectric state (T_c or $T_{\epsilon_m} < 290$ K), the strain is attributed to the electrostrictive effect. Indeed, from Fig. 4, it can be seen that the profiles of the strain versus electric fields for the samples with $y \geqslant 0.2$ are parabolic-like (marked by an arrow), different from those observed in the samples with low Ce concentrations.

Correspondingly, the composition dependence of piezoelectric coefficient d_{33} was observed. For $y=0.02$, $d_{33} = 116$ pC/N, this value is reasonable as compared with the d_{33} value (~125–295 pC/N) reported for BTO single crystals.[3] With increasing Ce doping concentration, d_{33} decreases continuously.

The strain hysteresis versus Ce doping concentration is shown in the inset of Fig. 4, which is calculated from the area of unipolar strain hysteresis loop when the maximum electric field is 60 kV/cm. It can be seen that the hysteresis decreases with increasing Ce doping concentration. This is an important factor for a high strain application.

The three phase transitions of BTO are pinched by Ce doping at $y = 0.06$. In ceramic samples, unlike the single crystal materials, the randomly axed ensemble of individual grains (crystallites) makes it more difficult to exploit directly the concept of low to high spontaneously deformed states switching. It is clear, however, that approaching the pinch off point in the phase diagram, the energy differences between tetragonal (T), orthorhombic (O), and rhombohedral (R) states must become small so that at higher electric fields the system may exploit the 6 (T)+12(O)+8(R), i.e., 26 polarization orientation states of the three phases and in spite of the randomly axed state became quasi homogeneous. In the Ce modified compositions this process will be further aided by the random fields that give rise to relaxor character at the higher Ce concentrations. This breakup of macrodomains into micropolar regions that persist in compositions above pinch-off point will further ''smooth'' the macroscopic polarization behavior.

What is then to be expected, at low Ce concentration, where the system is in the tetragonal or orthorhombic phases at zero E field, is that both the spontaneous polarization and the associated strain will be larger; but switching between states is more hysteretic as is evidenced for samples with $y = 0.02$ and 0.04 in Fig. 4. At higher Ce concentration switching becomes easier, the behavior less hysteretic; but the magnitude of switchable strain and of polarization decreases as the temperature from the onset of polarization decreases. In addition, the smoothing effect of the onset of ferroelectric-relaxor behavior is evident from the continuous changes in the hysteresis and high field strain as a function of Ce concentrations evident in the inset of Fig. 4. There is no abrupt change on passing the composition of the pinch off point for, as it is well known in ferroelectric-relaxor systems, orientable micropolar regions persist to temperatures well above the dielectric maximum temperature in these systems.

In the Ce-modified BTO ceramic system it is evident that by varying composition a number of potentially useful nonlead electrostrictive actuator characteristics can be achieved with workable compromises between high strain and low hysteresis behavior.

In conclusion, the ferroelectric and strain behavior of the $Ba(Ti_{1-y}Ce_y)O_3$ ceramics indicates that the three phase transitions are pinched with increasing Ce concentration, and around $y = 0.06$. The strain level is in the range of 0.14–0.19% with a small hysteresis under 60 kV/cm for $0.02 \leqslant y \leqslant 0.08$, which is a high strain level in a lead-free ceramic form. With increasing Ce concentration, the strain level decreases, and the strain hysteresis further decreases. This indicates that the system might be a promising lead-free material for the high strain and low hysteresis applications near room temperature or at low temperatures. Growth of Ce doped BTO single crystals will be interesting to explore piezoelectric and strain properties in this system.

[1] J. Kuwata, K. Uchino, and S. Nomura, Jpn. J. Appl. Phys., Part 1 **21**, 1298 (1982).
[2] S. E. Park and T. R. Shrout, J. Appl. Phys. **82**, 1804 (1997).
[3] S. Wada, S. Suzuki, T. Noma, T. Suzuki, M. Osada, M. Kakihana, S. E. Park, L. E. Cross, and T. R. Shrout, Jpn. J. Appl. Phys., Part 1 **38**, 5505 (1999); E. Brucsu, G. Ravichandran, and K. Bhattacharya, Appl. Phys. Lett. **77**, 1698 (2000).
[4] N. S. Novosil'tsev and A. L. Khodakov, Zh. Tekh. Fiz. **26**, 310 (1956); Sov. Phys. Tech. Phys. **1**, 306 (1956); G. A. Smolenski, J. Phys. Soc. Jpn. **28**, 26 (1970).
[5] W. H. Payne and V. J. Tennery, J. Am. Ceram. Soc. **48**, 413 (1965).
[6] D. Hennings, B. Schreinemacher, and H. Schreinemacher, J. Eur. Ceram. Soc. **13**, 81 (1994); D. Makovec, Z. Samardaija, and D. Kolar, J. Am. Ceram. Soc. **80**, 45 (1997).
[7] Z. Jing, Dissertation, University of Aveiro, 2000, Portugal (in English); C. Ang, Z. Yu, Z. Jing, P. M. Vilarinho, and J. L. Baptista, J. Eur. Ceram. Soc. **17**, 1217 (1997); Z. Yu, C. Ang, Z. Jing, P. M. Vilarinho, and J. L. Baptista, J. Phys.: Condens. Matter **9**, 3081 (1997); C. Ang, Z. Yu, and Z. Jing, Phys. Rev. B **61**, 957 (2000).
[8] Z. Jing, C. Ang, Z. Yu, P. M. Vilarinho, and J. L. Baptista, J. Appl. Phys. **84**, 983 (1998).
[9] J. Ravez and A. Simon, Eur. J. Solid State Inorg. Chem. **34**, 1199 (1997); S. M. Neirman, J. Mater. Sci. **23**, 3973 (1988); D. Hennings and A. Schnell, J. Am. Ceram. Soc. **65**, 539 (1982).
[10] Z. Yu, R. Guo, and A. S. Bhalla, Appl. Phys. Lett. **77**, 1535 (2000).
[11] P. W. Rherig, S. E. Park, S. T. McKinstry, G. L. Messing, B. Jones, and T. M. Shrout, J. Appl. Phys. **86**, 1657 (1999).