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Short communication

In-situ diffuse phase transition at the Curie point of $BaTiO_3$ induced by amphoteric Ce^{3+}/Ce^{4+} ions

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Abstract

Nominal $(Ba_{1-x}Ce_x)(Ti_{0.95-x/4}Ce_{0.05})O_3$ ceramics were prepared by a solid state reaction method. A complete solid solution called BC3TC5 was formed only at $x=0.03$, with a single-phase perovskite structure. The structural and dielectric properties of BC3TC5 were investigated by X-ray diffraction, scanning electron microscopy, Raman spectroscopy, electron paramagnetic resonance, and dielectric measurements. BC3TC5 exhibited a cubic structure and a non-uniform microstructure. Ti-vacancy defects exist in BC3TC5, which has a feature of mixed valence of Ba-site Ce^{3+} and Ti-site Ce^{4+}. The amphoteric Ce^{3+}/Ce^{4+} ions can induce an *in-situ* diffuse phase transition at the Curie point of $BaTiO_3$ ($T_C=125$ °C). BC3TC5 exhibits a high-*k* behavior ($\varepsilon'_m=9470$) and low dielectric loss ($\tan\delta<0.025$).

Keywords: A. Powders: solid state reaction and sintering; B. Defects; C. Dielectric properties; D. $BaTiO_3$ and titanates

1. Introduction

As a candidate for capacitor applications, a Y5V-type $Ba(Ti_{1-y}Ce_y)O_3$ ceramic occurred at $y=0.2$ and showed a low rare-earth efficiency and dielectric permittivity ($\varepsilon'_m=\sim 2100$) [1]. In terms of La doping in $Ba(Ti_{1-y}Ce_y)O_3$, a high-*k* 'Y5V' ceramic $(Ba_{1-x}La_x)(Ti_{1-y-x/4}Ce_y)O_3$ ($x=0.03$, $y=0.05$) with room-temperature permittivity of $\varepsilon'_{RT}>10000$ can be achieved and the rare-earth efficiency can be raised significantly [2]. It is obvious that La doping at Ba sites plays an important role in a rapid peak shift toward low temperature and a rise in ε'_{RT}. $(Ba_{1-x}La_x)(Ti_{1-y-x/4}Ce_y)O_3$ can be considered as a solid solution of $(Ba_{1-x}La_x)Ti_{1-x/4}O_3$ and $Ba(Ti_{1-y}Ce_y)O_3$. The former contributes to the high-*k* behavior, while the latter can induce a strong diffuse phase transition (DPT) in the vicinity of room temperature. Since both $(Ba_{1-x}La_x)Ti_{1-x/4}O_3$ and $(Ba_{1-x}Ce_x)Ti_{1-x/4}O_3$ ($x\leq 0.05$) show a common feature of high-*k* first-order phase transition (FPT) [3–6], one holds certain expectations about a new high-*k* solid solution $(Ba_{1-x}Ce_x)(Ti_{1-y-x/4}Ce_y)O_3$ by means of the formation of solid solution of $(Ba_{1-x}Ce_x)Ti_{1-x/4}O_3$ and $Ba(Ti_{1-y}Ce_y)O_3$, i.e., an amphoteric feature of Ce^{3+} at Ba sites (Ce^{3+}_{Ba}) and Ce^{4+} at Ti sites (Ce^{4+}_{Ti}) is reflected in the Ce doping behavior. It was reported that the solid solubility of Ce in $BaTiO_3$ is 8% for Ba-site Ce^{3+} incorporation, whereas it is 35% for Ti-site Ce^{4+} incorporation [1,7]. The preference difference in the site occupation will hinder the formation of a single-phase ceramic. It seems surprising that Ce ions play a role in both high-*k* and DPT behaviors. This will inevitably cause the separation of other phases such as CeO_2, $BaCeO_3$ [1], or Ce-rich $Ba(Ti,Ce)O_3$ phases [8] in the main perovskite phase.

On the other hand, we are very curious about the dielectric response caused by the amphoteric $Ce^{3+}_{Ba}-Ce^{4+}_{Ti}$ ions in $BaTiO_3$ because the dielectric properties associated with the $R^{3+}_{Ba}-R^{4+}_{Ti}$ (where R is any element) double substitution in $BaTiO_3$ has never been reported to date.

In this work, the nominal $(Ba_{1-x}Ce_x)(Ti_{0.95-x/4}Ce_{0.05})O_3$ ceramics were prepared to seek a critical balance of the mixed valence of Ce^{3+}/Ce^{4+}. Fortunately, a single-phase ceramic can be formed only at $x=0.03$. The present communication reports

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the structural and dielectric properties of this ceramic. It was found that an *in-situ* high-*k* diffuse phase transition occurred at the Curie point of $BaTiO_3$.

2. Experimental procedure

The starting materials were reagent-grade $BaCO_3$ (99.4%), TiO_2 (99.5%), and CeO_2 (99.9%). The ceramics were prepared according to the nominal formula $(Ba_{1-x}Ce_x)(Ti_{0.95-x/4}Ce_{0.05})O_3$ ($x=0.01$–0.05) using a mixed oxide method described elsewhere [2]. The final sintering conditions were chosen as 1450 °C for 24 h. Powder X-ray diffraction (XRD) measurements were made using a DX-2700 X-ray diffractometer (Dandong Haoyuan Inc.). Lattice parameters and unit cell volume were calculated by MS Modeling (Accelrys Inc.) using Cu Kα1 radiation ($\lambda=1.540562$ Å).

For single-phase $(Ba_{1-x}Ce_x)(Ti_{0.95-x/4}Ce_{0.05})O_3$ ($x=0.03$) ceramic (abbreviated BC3TC5), scanning electric microscope (SEM) images were obtained using a JSM-6490 SEM (JEOL) operated at 25 kV. Temperature dependences of the dielectric permittivity and loss were measured at 1 kHz using an RCL meter (Fluke PM6306). Raman spectra of ceramic powders were measured using a LabRAM XploRA Raman spectrometer (Horiba Jobin Yvon), with a 532 nm laser. A Linkam-600 heating and cooling stage was equipped for temperature-dependent Raman measurements. The electron paramagnetic resonance (EPR) spectrum was measured at an X band frequency of 9.84 GHz and at room temperature in the sweep range of 1500–5500 G using an EMX Plus spectrometer (Bruker). The gyromagnetic value (g) was calculated by the relationship $h\nu_0=g\beta H$.

3. Results and discussion

XRD patterns of the nominal $(Ba_{1-x}Ce_x)(Ti_{0.95-x/4}Ce_{0.05})O_3$ ceramics are shown in Fig. 1(a). The main perovskite phase for all the samples has been formed, showing a pseudo-cubic structure. A small amount of CeO_2 and $BaCeO_3$ was separated out from the main perovskite phase when $x\leq0.02$, as clearly seen in Fig. 1(b) and (c). The Ce-rich perovskite phase of Ba $(Ti_{0.81}Ce_{0.19})O_3$ [8] appeared when $x\geq0.04$. A complete solid solution called BC3TC5 was found to be formed at $x=0.03$. With an increase in x, the unit-cell volume (V_0) of the main perovskite phase increases linearly up to $x=0.03$ (Fig. 1 inset), indicating a consecutive incorporation of Ce^{4+} ions into Ti sites on the basis of an ionic size comparison (12-CN Ba^{2+}: 1.61 Å, Ce^{3+}: 1.34 Å; 6-CN Ti^{4+}: 0.605 Å, Ce^{4+}: 0.87 Å [9]). The maximum value of V_0 appeared at $x=0.03$. Subsequently, a slower decrease in V_0 for $x\geq0.03$ implies a decrease in the solubility of Ce^{4+} at Ti sites. Hence, the formula of $(Ba_{1-x}Ce_x)(Ti_{0.95-x/4}Ce_{0.05})O_3$ is tenable just for $x=0.03$. Makovec et al. suggested that cerium is incorporated into the $BaTiO_3$ lattice at Ba sites as Ce^{3+} and at Ti sites as Ce^{4+} in the ratio of 4:3 when pure CeO_2 is added to $BaTiO_3$ [7]. The ratio of our single-phase sample with $x=0.03$ is 3:5. The difference between the two results arises from the differences in the Ba/Ti ratio and in the sintering temperature.

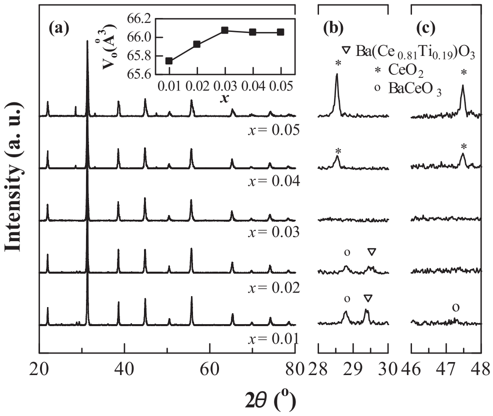

Fig. 1. XRD patterns of nominal $(Ba_{1-x}Ce_x)(Ti_{0.95-x/4}Ce_{0.05})O_3$ ceramics (a). The inset depicts variation in unit cell volume (V_0), as a function of x. (b,c) Enlarged XRD peaks in the vicinity of 29° and 47°, respectively for observation of the formation of a single-phase ceramic (BC3TC5).

The V_0 value of BC3TC5 (66.08 Å^3) is less than that of Ba $(Ti_{0.95}Ce_{0.05})O_3$ (66.37 Å^3) [2], but greater than that of the cubic $BaTiO_3$ (65.50 Å^3) (JCPDS Cards no. 31-174). This fact gives an evidence for the existence of the mixed valence of Ba-site Ce^{3+} and Ti-site Ce^{4+} in BC3TC5, i.e., the formation of $Ce^{3+}_{Ba}-Ce^{4+}_{Ti}$ complexes.

Temperature-dependent Raman spectra of BC3TC5 are shown in Fig. 2. The two broad bands at 260 and 525 cm^{-1}, which persisted till 180 °C, are attributed to intrinsic disorder in the cubic phase of BC3TC5 [10]. The rapid attenuation of the 720 cm^{-1} band at 180 °C implies an increase in cubicity. As with the Raman spectrum observed in $(Ba_{1-x}La_x)(Ti_{0.95-x/4}Ce_{0.05})O_3$ ($x=0.03$) ceramics (BL3TC5) [10], a weak 824 cm^{-1} band, which was generally caused by trivalent rare-earth ions (La^{3+}, Nd^{3+}, Eu^{3+}) at Ba^{2+} sites in the $BaTiO_3$ lattice [11–13], also gives evidence for Ce^{3+} entering Ba sites in BC3TC5. However, the 824 cm^{-1} band of BC3TC5 is much weaker

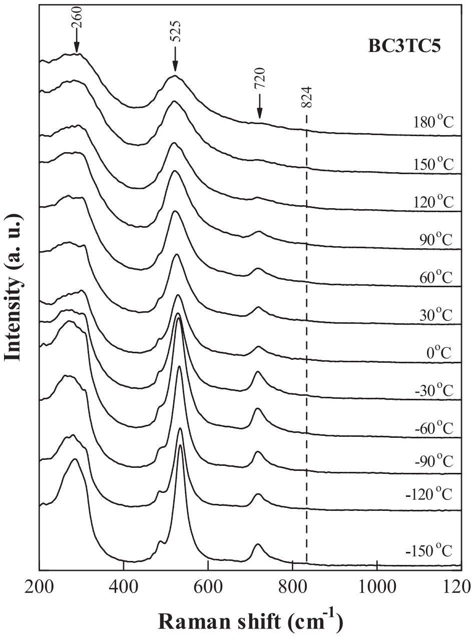

Fig. 2. Temperature-dependent Raman spectra of BC3TC5.

compared to BL3TC5 [10], which suggests that the Raman activity induced by Ba-site Ce^{3+} due to the formation of $Ce_{Ba}^{3+}-Ce_{Ti}^{4+}$ complexes is dramatically reduced.

EPR spectrum of BC3TC5 is shown in Fig. 3. A signal at $g=2.003$ was assigned to ionized Ti-vacancy defects (V_{Ti}) [10,14], which was caused by the substitution of Ce^{3+} at Ba^{2+} sites, in good agreement with the Raman scattering observations.

SEM image of BC3TC5 is shown in Fig. 4. BC3TC5 exhibited a non-homogeneous but denser microstructure consisting of coarse grains (3–6 μm) and fine grains (~1 μm). The average grain size is 2.7 μm. The morphology of the other four samples with $x \neq 0.03$ is the same as BC3TC5 (not presented here). The secondary phase that grew between three or four coarse grains boundaries can be observed when $x \geq 0.04$.

Temperature dependence of the dielectric permittivity (ε') and loss ($\tan\delta$) for BC3TC5 is shown in Fig. 5. The ε'–T curves of BL3TC5 and $BaTiO_3$ are depicted in this figure for comparison [2]. $BaTiO_3$ showed a first-order phase transition and a sharp-peak feature at its Curie point ($T_C \approx 125$ °C). For BL3TC5, the so-called Curie temperature (T_C) at which the maximum dielectric permittivity (ε'_m) occurred decreased rapidly at a dramatic rate of −30 °C/at% La [2]; therefore the dielectric peak of BL3TC5 could approach room temperature ($T_C=38$ °C) when x was increased to 0.03. Similar to BL3TC5, BC3TC5 also exhibited a strong high-*k* diffuse phase transition (DPT) behavior ($\varepsilon'_m=9470$), which demonstrates that Ba-site Ce^{3+} ions in BC3TC5 are responsible for raising the dielectric permittivity and Ti-site Ce^{4+} ions play a predominant role in the DPT behavior [2].

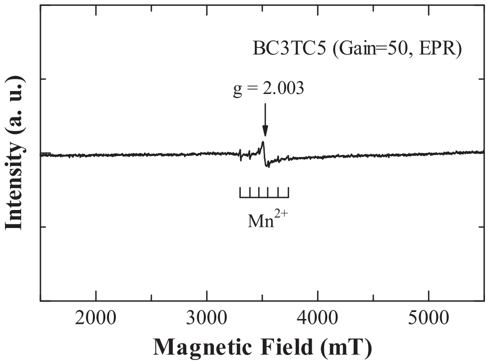

Fig. 3. EPR spectrum of BC3TC5.

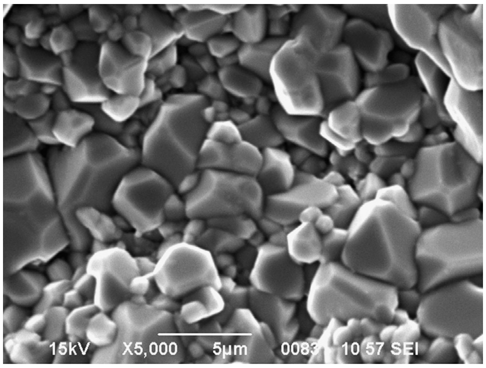

Fig. 4. SEM morphology of BC3TC5.

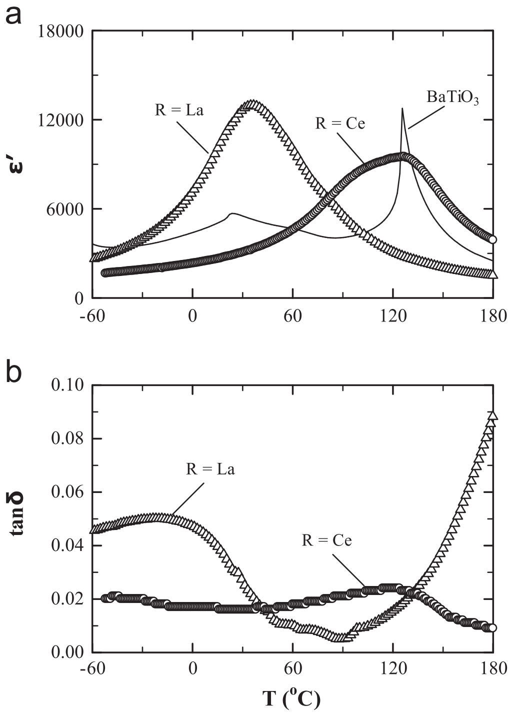

Fig. 5. Temperature dependence of (a) the dielectric permittivity (ε') and (b) the dielectric loss ($\tan\delta$) for BC3TC5 and BL3TC5. The data of BL3TC5 and $BaTiO_3$ are from Ref. [2].

However, the T_C of BC3TC5 occurred at 125 °C. This fact indicates that the amphoteric Ce^{3+}/Ce^{4+} ions make no contribution to a peak shift toward low temperature, and only induce an *in-situ* diffuse phase transition at the Curie point of $BaTiO_3$. The other four samples with $x \neq 0.03$ also exhibited high-*k* DPT behavior ($\varepsilon'_m > 9000$) and their T_C occurred at 123–127 °C (not presented here). Thus, *in-situ* DPT is the common property of this series of ceramics.

At room temperature, BC3TC5 exhibits a cubic structure, which is not in contradiction with T_C observed at 125 °C. Because of the nature of DPT, BC3TC5 can retain an average cubic structure at lower temperatures far from T_C, as observed for $(Ba_{1-x}La_x)(Ti_{0.95-x/4}Ce_{0.05})O_3$ ($x=0.02$) ($T_C=64$ °C) [2]. As far as phase structure is concerned, BC3TC5 with DPT is different from $BaTiO_3$ with first-order phase transition (FPT). The latter shows a very sharp dielectric peak at its T_C, accompanied by a clear cubic–tetragonal phase transition. whereas the dielectric peak of the former (BC3TC5) becomes vague. In the case of DPT, the so-called T_C, strictly speaking, cannot represent the cubic–tetragonal phase transition point, i.e., the Curie temperature. At present, T_C is often represented by the dielectric-peak temperature (T_m).

A type of ions that can split into the two sites in $BaTiO_3$ occurs in very few cases. This type of ions is usually trivalent. They form a self-compensation (donor–acceptor) mode of $R_{Ba}^{3+}-R_{Ti}^{3+}$ in $(Ba_{1-x}R_x)(Ti_{1-x}R_x)O_3$ such as trivalent rare-earth ions R = Nd [15], Eu [13], and Er [16,17]. All of this type of ions can induce strong DPT, accompanied by a peak shift toward low temperature

[13,15,16]. The dual character of Ce^{3+}/Ce^{4+} in $BaTiO_3$ is the sole case of the $R^{3+}_{Ba}-R^{4+}_{Ti}$ (R is any element) double substitution to date. The mechanism of *in-situ* DPT of BC3TC5 is not known.

BC3TC5 exhibited lower dielectric loss ($\tan\delta < 0.025$). A stronger Mn^{2+} ($3d^5$) sextet signal was observed (Fig. 3), which indicates that a large number of Mn^{4+} or Mn^{3+} impurities in BC3TC5 were reduced into Mn^{2+}. There is almost no Mn^{2+} signal in the EPR spectrum of BL3TC5 [10]. Thus, the lower dielectric loss of BC3TC5 is attributed to the role of trapping electrons by Mn impurities.

4. Conclusions

The sole single-phase solid solution (BC3TC5) with $x = 0.03$ can be prepared using a solid state reaction method according to the formula $(Ba_{1-x}Ce_x)(Ti_{0.95-x/4}Ce_{0.05})O_3$. BC3TC5 exhibits a cubic structure and a non-uniform microstructure. BC3TC5 with Ti-vacancy defects has a feature of mixed valence of Ba-site Ce^{3+} and Ti-site Ce^{4+} in the ratio of 3:5. A strong diffuse phase transition due to the amphoteric Ce^{3+}/Ce^{4+} occurs at the Curie point of $BaTiO_3$ ($T_C = 125$ °C). BC3TC5 shows a high-*k* behavior ($\varepsilon'_m = 9470$) and low dielectric loss ($\tan\delta < 0.025$). The ability of trapping electrons by Mn impurities is responsible for the lower $\tan\delta$ of BC3TC5.

Acknowledgments

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