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Diffuse phase transition and ferroelectric study of (Ba, Bi)(Ti, Cr)O_3 ceramics

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Abstract

Lead-free perovskite type $(Ba_{0.94}Bi_{0.06})(Ti_{0.94}Cr_{0.06})O_3$ (BBTC) ceramics have been prepared by the conventional mixed oxide method. The XRD results showed that BBTC ceramics have single phase tetragonal symmetry with space group *P4mm*. Dielectric studies exhibited a diffuse phase transition characterized by a strong temperature and frequency dispersion of permittivity. The quantitative characterization based on empirical parameters (ΔT_m, γ, ΔT_{relax}, and ΔT_{dif}) confirmed its relaxor nature. The origin of relax ferroelectric behavior is caused by the polar nanoclusters, which were arose due to the heterovalent substitutions of Bi^{3+} and Cr^{3+} at Ba^{2+} and Ti^{4+} sites. The *P–E* loops obtained at the temperature quite above T_m supported the diffuse phase transition behavior of the samples.
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Keywords: $BaTiO_3$; Dielectric properties; Co-doping; Diffusion

1. Introduction

Since the relaxors were discovered by Smolensky and co-workers in 1954 [1], they have attracted continued interest due to their unusual properties for capacitors and actuators. Most relaxor ferroelectrics belong to a family of complex lead-based perovskite oxides, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) which is often considered as a model system [2]. The $BaTiO_3$–$BaSnO_3$ was the first system in which relaxor properties were discovered. A crossover to the relaxor state was observed in $BaTiO_3$ by both heterovalent and isovalent ionic substitutions. In the first case, the relaxor behavior is induced by substitutions either on A- or B- or on both A- and B-sites of the perovskite lattice ABO_3. In the second case, the relaxor behavior appears in compounds with substituted B-site cations, such as $BaTiO_3$–$BaSnO_3$ or $BaTiO_3$–$BaZrO_3$ [3]. Several theories had been proposed to explain the behavior of the relaxor ferroelectrics, a common point of these models is based on the local order–disorder of the crystal structure, giving rise to polar clusters embedded in the matrix. The $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$ ceramics showed broad peak of dielectric constant and small dielectric loss due to the effect of Cr-doping [4]. Bahri and Simon [5] have found that the substitution of Ba^{2+} site with Bi^{3+} can trigger the relaxor behavior in $BaTiO_3$. A large mismatch in the ionic radius created by Bi^{3+}addition at the A site and a local heterogeneity with valence fluctuations created by Al^{3+} addition at the B site induced the transformation from normal ferroelectric to relaxors.

The aim of the present work is to obtain a relaxor with T_m near the room temperature by adding Bi^{3+} at the Ba^{2+} site and Cr^{3+} at the Ti^{4+} site simultaneously. The details of relaxor behavior and ferroelectric properties of the $(Ba_{0.94}Bi_{0.06})(Ti_{0.94}Cr_{0.06})O_3$ (BBTC) ceramics were investigated. A possible mechanism was also discussed in which the heterovalent substitutions of Bi^{3+} and Cr^{3+} at Ba^{2+} and Ti^{4+} sites caused these abnormal dielectric and ferroelectric behaviors' observations.

2. Experimental procedure

$BaCO_3$ and TiO_2 powders with a purity of 99.99% were thoroughly mixed according to the formula of $BaTiO_3$ and calcined at 1220 °C for 2 h so as to obtain a pure $BaTiO_3$ phase. The samples with the formula $(Ba_{0.94}Bi_{0.06})(Ti_{0.94}Cr_{0.06})O_3$ were prepared. The synthesized $BaTiO_3$, Cr_2O_3

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and Bi_2O_3 powders were weighed and mixed together with deionized water by ball milling (using ZrO_2 beads) for 4 h. After drying and granulating with polyvinyl alcohol (PVA, 5 wt%), the well-mixed powders were pressed into a disk (Φ $12 \times 1.6\,mm^2$) at 120 MPa and sintered at a temperature range of 1300–1350 °C in air for 2 h.

The crystal structure of the samples was identified using an X-ray diffractometer (XRD; Model D-MAX 2200 pc, Rigaku Co., Tokyo, Japan), in conjunction with Cu $K\alpha$ radiation, operated at 50 kV, 100 mA, and a scanning rate of 3°/min within the range of 2θ from 10° to 70°. The microstructure of the sintered samples was studied on polished and then on thermally etched surfaces using a scanning electron microscope (SEM; Model JSM-6390A, Tokyo, Japan). For dielectric measurements, Ag electrodes were screen printed with Ag paste on both sides of the pellets and heat treated at 600 °C for 20 min. The temperature dependence of the dielectric properties was measured using a precision LCR Meter (Model E4980A, Agilent Tech., CA, US) over a temperature range from room temperature to 300 °C. The different temperature hysteresis loop as a function of electric field was measured using a computer controlled modified Sawyer–Tower circuit. The electric field signal was triangular wave.

3. Results and discussion

Fig. 1 shows the XRD patterns of as synthesized $BaTiO_3$ and BBTC ceramics. The pattern showed that the compositions were of single phase tetragonal perovskite structure without the evidence of any additional phase. According to the Bragg law for the tetragonal system, the lattice parameters of BBTC ceramics have been refined as $a=3.9936$ Å, $c=4.0109$ Å which were lower than that of pure $BaTiO_3$ ceramics (JCPDS 76-0744, $a=3.9945$ Å, $c=4.038$ Å). This was because the ionic radius of Bi^{3+} (0.96 Å) was smaller than that of Ba^{2+} (1.60 Å), while the ionic radius of Cr^{3+} (0.62 Å) was close to Ti^{4+} (0.61 Å). It also demonstrated that Bi^{3+} substituted for Ba^{2+} site as a donor and Cr^{3+} substituted for Ti^{4+} site as an acceptor for $BaTiO_3$-based ceramics.

The SEM micrographs of BBTC and $BaTiO_3$ ceramics are shown in Fig. 2. All sintered ceramic samples showed a compact microstructure, and the grain size of $BaTiO_3$ ceramics decreased with the introduction of Cr_2O_3 and Bi_2O_3. These results revealed that Cr_2O_3 and Bi_2O_3 acted as grain growth inhibitor and transformed the grain into more spherulitic in nature.

It can be seen that there was no dispersion for a pure $BaTiO_3$ ceramic in Fig. 3. However, the BBTC ceramics showed strong frequency dispersion around the permittivity peaks. The temperature T_m corresponding to the maximum value of the dielectric constant was shifted to higher temperatures with increasing frequency. This phenomenon indicated that the BBTC ceramics showed a

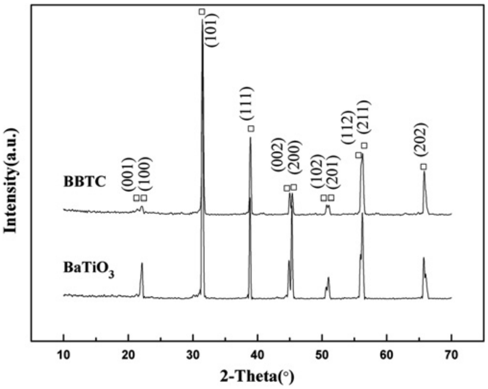

Fig. 1. XRD patterns of pure $BaTiO_3$ and BBTC ceramics.

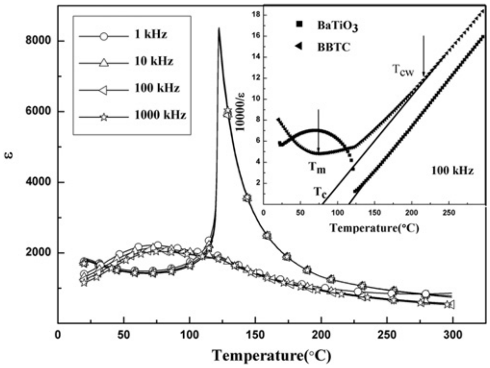

Fig. 3. The temperature dependence of the dielectric permittivity of $BaTiO_3$ and BBTC ceramics at different frequencies. Inset shows the plots of the inverse dielectric constant vs. temperature at 100 kHz for $BaTiO_3$ and BBTC. (Symbols: experimental data; the solid line: fitting to Eq. (1).)

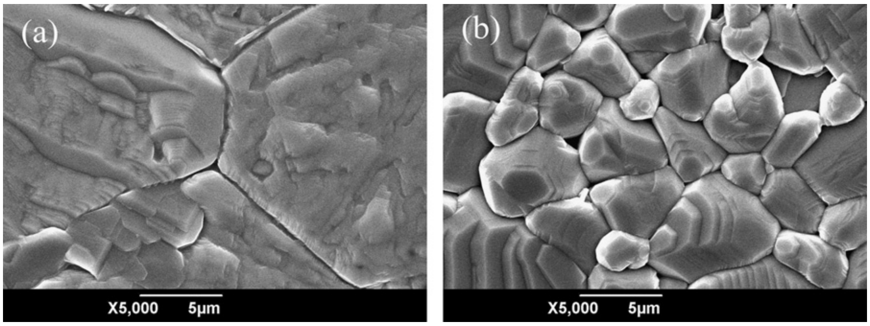

Fig. 2. SEM micrographs of (a) $BaTiO_3$ and (b) BBTC ceramics.

typical relaxor behavior which was usually observed in Pb-based relaxors [3].

It is well known that the dielectric permittivity of a normal ferroelectric above the Curie temperature follows Curie–Weiss law:

$$\frac{1}{\varepsilon} = \frac{(T - T_C)}{C}, \quad (T > T_C) \tag{1}$$

where T_c is the Curie temperature and C is the Curie–Weiss constant.

Inset of Fig. 3 shows the plot of inverse dielectric constant versus temperature for the pure $BaTiO_3$ and BBTC at 100 kHz. It can be seen that the dielectric constant of BBTC ceramics followed the Curie–Weiss law at a temperature much higher than T_m. The parameter ΔT_m, which describes the degree of the deviation from the Curie–Weiss law, is defined as $\Delta T_m = T_{cw} - T_m$, where T_{cw} denotes the temperature from which the permittivity starts to deviate from the Curie–Weiss law and T_m represents the temperature of the dielectric maximum. The experimental data were fitted by Eq. (1) using a linear fitting method. The fitting parameters were summarized in Table 1.

The diffuse characteristics of ferroelectric–paraelectric phase transition are known to deviate from the typical Curie–Weiss behavior and can be described by a modified Curie–Weiss relationship [3]:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^{\gamma}}{C}, \quad (1 \le \gamma \le 2) \tag{2}$$

where ε_m is the maximum value of dielectric constant, ε is the dielectric constant at temperature T, T_m is the temperature at the peak of the dielectric constant, C is the Curie constant, and γ is the indicator of the degree of diffuseness, giving information on the character of the phase transition: for $\gamma = 1$, a normal Curie–Weiss law is obtained, $\gamma = 2$ describes a complete diffuse phase transition. Thus the value of γ can also be used to characterize the relaxor behavior.

The plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ for the pure $BaTiO_3$ and BBTC ceramics at 100 kHz is shown in Fig. 4 by fitting with Eq. (2) to calculate the γ value. It can be seen that the value of γ at 100 kHz was found to be 1.67, which showed that the material was highly disordered. The diffuse phase transition and deviation from Curie–Weiss type may be assumed due to disordering [6].

The diffuseness of the phase transition can also be described by an empirical parameter ΔT_{dif}, which is defined as $\Delta T_{dif} = T_{0.9\varepsilon_m(100\ \mathrm{Hz})} - T_{\varepsilon_m(100\ \mathrm{Hz})}$, where $T_{\varepsilon_m(100Hz)}$ denotes the temperature of the dielectric maximum and $T_{0.9\varepsilon_m(100Hz)}$ represents the higher temperature of 90% of the dielectric maximum at 100 Hz. Yet another parameter, which is used to characterize the degree of relaxation behavior in the frequency range of 100 Hz–100 kHz, is described as $\Delta T_{relax} = T_{m(100\ \mathrm{kHz})} - T_{m(100\ \mathrm{Hz})}$. Based on the experimental data, the values of $\Delta T_{dif(100\mathrm{Hz})}$ and ΔT_{relax} were calculated to be 47.4 and 6.06 °C respectively. To recapitulate, the above empirical characterization with the Curie–Weiss law (ΔT_m) and the parameter (ΔT_{relax}, ΔT_{dif} and γ) showed that the BBTC was indeed a relaxor with DPT and frequency dispersion.

The replacements of Ba^{2+} by Bi^{3+} ions lead to the formation of dipolar impurities and defects that have a profound influence on the static and dynamic properties of this material. It was suggested that Bi ions with the $6s^2$ lone pair had the largest stereochemical activity, similar to the neighbor element of Pb^{2+}, and were located at an off-centered position of the A-site [7]. Considering the stereochemical activity of the Bi lone pair and the large difference of ionic radii between host Ba^{2+} ion and added Bi^{3+} ion, Bi impurity along $<111>$ drives the large displacement at the off-centered A position, resulting in the formation of the polar clusters (Fig. 5). The relaxation of these small clusters resulted in the dispersion of the dielectric permittivity and relaxor behavior of the system. As previously mentioned Ti was ferroelectrically active and off-centered in the octahedral site giving rise to a local dipolar moment, and the resulted dipole moment was balanced by the displacement of A-site cations along the opposite direction. However, Cr ions were at a central position with no displacement, which affected the Ti off-center symmetries among the $Ti\text{-}O_6$ octahedral and impeded a perfect alignment of all Ti displacements as in ferroelectric $BaTiO_3$ with temperature increasing.

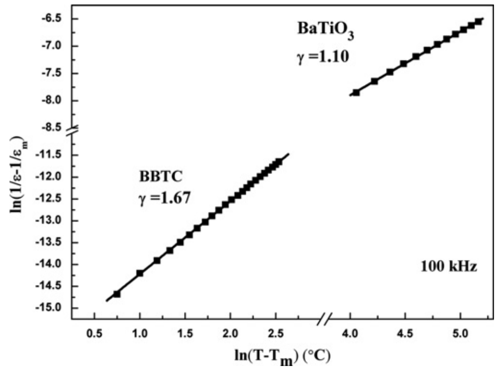

Fig. 4. $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ at 100 kHz for $BaTiO_3$ and BBTC ceramics. (Symbols: experimental data; the solid line: fitting to Eq. (2).)

Table 1
The temperature of the maximum dielectric constant (T_m), Curie–Weiss temperature (T_c), the temperature above which the dielectric constant follows the Curie–Weiss law (T_{cw}), the maximum dielectric constant (ε_m), and the critical parameters γ, ΔT_{dif} and ΔT_{relax} for BBTC ceramics.

	T_m (°C)	T_c (°C)	T_{cw} (°C)	ΔT_m (°C)	ε_m	γ	ΔT_{dif} (°C)	ΔT_{relax} (°C)
$BaTiO_3$	124	116	128	4	8123	1.10	1.9	0
BBTC	75	81	217	142	2074	1.67	47.4	6.06

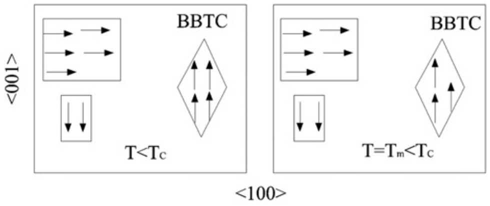

Fig. 5. Schematic diagram of polar nanoclusters for BBTC ceramics at different temperature. (Square islands stand for the polar nanoclusters caused by the replacements of Ba^{2+} by Bi^{3+} ions and rhombus islands stand for the polar nanoclusters caused by Cr^{3+}–Ti^{4+} heterovalent substitution.)

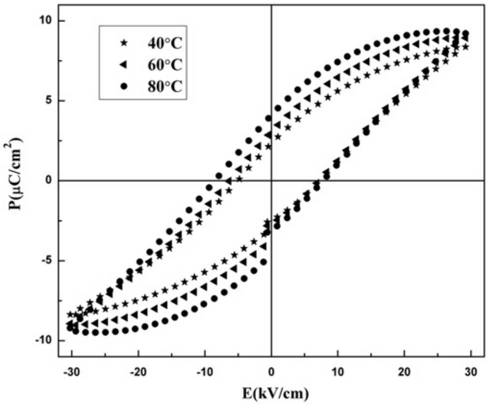

Fig. 6. The *P–E* loops for BBTC ceramics at different temperatures.

The broadened dielectric maximum and its deviation from the Curie–Weiss law may be assumed due to Cr^{3+}–Ti^{4+} heterovalent substitution. Moreover, in this case, Cr^{3+} compensated the charge imbalance arising from the substitution of the A-site by Bi^{3+}, which also contributed to the enhancement of the relaxor feature.

The polarization loops (*P–E*) of BBTC ceramics at 1 Hz at various temperatures are shown in Fig. 6. Coercive field and remanent polarization were estimated from the hysteresis curve. The value of coercivity and remanent polarization increased with increasing temperature. Presence of *P–E* loop at 80 °C confirmed that polar regions were present well above T_m (T_m=75 °C) which also means that the system would show relaxor behavior.

4. Conclusions

$(Ba_{0.94}Bi_{0.06})(Ti_{0.94}Cr_{0.06})O_3$ (BBTC) ceramic was fabricated by the conventional mixed oxide method. The perovskite type BBTC ceramics exhibited the typical characteristics of relaxor ferroelectrics, with broad and dispersive permittivity maxima, based on empirical parameters (ΔT_m, γ, ΔT_{relax}, and ΔT_{dif}). The nature of the relax ferroelectric behavior is caused by the polar nanoclusters, which arose from the heterovalent substitutions of Bi^{3+} and Cr^{3+} at Ba^{2+} and Ti^{4+} sites. The *P–E* loops obtained at the temperature quite above T_m supported the DPT behavior of the samples.

Acknowledgments

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