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Dielectric and piezoelectric properties of cerium modified $BaBi_4Ti_4O_{15}$ ceramics

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Abstract

Cerium modified barium bismuth titanate ceramics $BaBi_4Ti_4O_{15}$-$x$$CeO_2$ (wt%) were prepared by a solid-state reaction method. X-ray diffraction patterns showed that the ceramics have a four-layer Aurivillius-type structure with orthorhombic phase at room temperature. The plate-like morphology with average grain size about 2 μm was observed by scanning electron microscope (SEM). The effects of cerium modification on dielectric and piezoelectric properties of $BaBi_4Ti_4O_{15}$ ceramics were studied. The results showed that cerium modification enhanced the piezoelectric properties, decreased the temperature of the dielectric maximum (T_m) slightly from 413 °C to 406 °C and the dielectric loss, tan δ, as well. The modified Curie–Weiss law was used to describe the relaxor behavior of the ceramics and the degree of dielectric relaxation (γ) firstly increases then decreases with the cerium increasing. The relaxor nature was attributed to the A-site cationic disorder.

Keywords: C. Dielectric properties; $BaBi_4Ti_4O_{15}$ ceramics; Piezoelectric materials

1. Introduction

Bismuth layer-structured ferroelectrics (BLSFs), first described by Aurivillius, have attracted much attention for their potential applications in non-volatile random access memory (NVRAM) and high temperature piezoelectric devices [1–4]. The layered bismuth oxides $Bi_2A_{m-1}B_mO_{3m+3}$, is formed by the regular stacking of Bi_2O_2 slabs and perovskite-like blocks $A_{m-1}B_mO_{3m+1}$, as described in [5]. Various A and B cations are allowed, and m is the number of oxygen octahedra along c axis between two neighboring Bi_2O_2 layers. Its crystal structure and physical properties have been widely investigated for the past several decades. Unfortunately, the piezoelectric activity of BLSFs is relatively low, with values less than 20 pC/N found for many pure and modified BLSFs. Many efforts have been paid to improve the dielectric and piezoelectric properties of BLSFs, including A-site, B-site substitution and grain orientation techniques etc. [6–8]. Recently, a remarkable increase in the dielectric and piezoelectric properties was reported for cerium doped $K_{0.5}Bi_{4.5}Ti_4O_{15}$ ceramics [9].

$BaBi_4Ti_4O_{15}$ (abbreviated as BBT) is a well-known member of BLSFs, with $m=4$. Subbarao first reported BBT has a high Curie temperature of about 395 °C and low piezoelectric activity, with value of 12 pC/N [5]. Since BBT ceramics have the similar crystalline structure with $K_{0.5}Bi_{4.5}Ti_4O_{15}$, one can expect that cerium ions modification could also improve the dielectric and piezoelectric properties of BBT. To the author's knowledge, there have been no reports on the electrical properties of cerium ions doped $BaBi_4Ti_4O_{15}$ ceramics yet. In this work, the effects of cerium ions modification on the dielectric and piezoelectric properties of BBT are studied.

2. Experimental procedures

Polycrystalline samples of $BaBi_4Ti_4O_{15}$-$x$$CeO_2$ (wt%) ceramics ($x=0$, 0.25, 0.50, and 0.75; abbreviated as BBT-x) were prepared using high temperature solid-state reaction

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techniques. The stoichiometric mixtures of high purity powder $BaCO_3$, Bi_2O_3, TiO_2 and CeO_2 were mixed in a ball mill for 8 h, dried and calcined at 800 °C in an alumina crucible for 6 h. The calcined powder was pressed into disks, using polyvinyl alcohol as a binder. The pellets were sintered at 1070 °C for 4 h and cooled naturally. The phase identification and microstructure characterization were done using a Rigaku D/MAX-RB powder X-ray diffractometer (XRD) using CuK_α radiation and a field emission scanning electron microscopy (FE-SEM, JSM-7001F). Silver paste was applied to the circular surfaces of the samples as electrodes at 800 °C for 20 min. Temperature dependent dielectric properties was measured, using an Agilent 4294A precision impedance analyzer equipped with a thermostat. Samples were poled in silicone oil at about 150 °C under a DC electric field from 8 to 10 kV/mm for 20–30 min. The piezoelectric coefficient d_{33} was measured using a quasistatic d_{33} meter (Institute of Acoustics, Academia Sinica, ZJ-2). All measurements were performed at room temperature except for dielectric temperature spectrum.

3. Results and discussion

The XRD patterns of the calcined BBT-*x* powder are shown in Fig. 1. A single phase bismuth layer-structured phase structure with $m=4$ was present within the compositions studied herein. All diffraction peaks were indexed, and no impurity peaks corresponding to the reactant oxides or any other secondary phase were found in the XRD patterns, which confirm the monophasic nature of all the composition under investigation. The dominant diffraction peaks of BBT were in agreement with the orthorhombic (space group $A2_1am$) structure [10]. The highest intensity diffraction peak is the (119) reflection, in accordance with the fact that the most intense reflection of BLSFs is the type of $(112m+1)$. Although half of the bismuth atoms are located in the $(Bi_2O_2)^{2+}$ layers, the Ce^{4+} substitution should mainly occur in the perovskite A-site, since the Bi^{3+} site in the $(Bi_2O_2)^{2+}$ layers prefers cations with lone pair electrons.

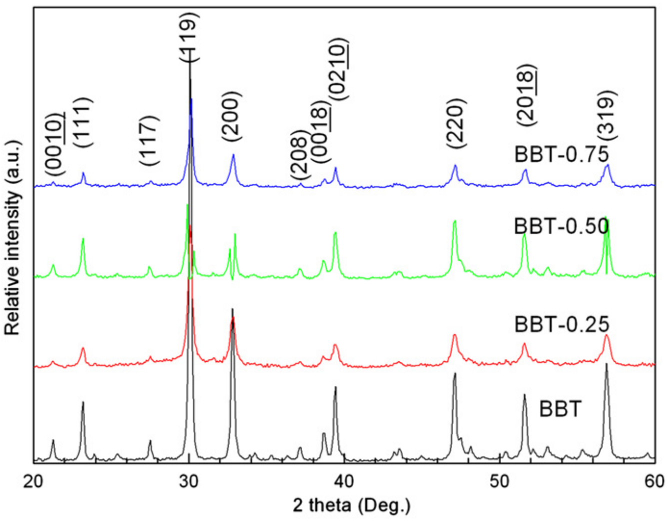

Fig. 1. XRD patterns of BBT-*x* ceramics.

The lattice parameters were refined from the XRD patterns as shown in Fig. 2. The lattice constant of *a* increases and that of *b* decreases when Ce^{4+} content is lower than 0.25; more Ce^{4+} content influences little on the values of *a* and *b*. The lattice parameter of the *c* axis shows an increase when $x \leq 0.50$ and decrease when $x > 0.50$. It is generally known that the piezoelectric properties of BLSFs are affected by the anisotropies of the *a* and *b* axes rather than that of *c* axis. Therefore, it is anticipated that BBT-0.50 ceramics have better piezoelectricity than that of other ceramics.

The SEM surface micrographs of the BBT and BBT-0.50 ceramics are indicated in Fig. 3. It is seen that the grain growth is structurally highly anisotropic with plate-like grains. The plate-like morphology of the grains is a characteristic feature of bismuth layer-structured compounds. Some researchers reported that the {001} planes possess lower surface energies which develops predominantly during sintering [8]. Accordingly, the grains of BBT-*x* grow in the *a*–*b* plane due to the high grain growth rate in the direction perpendicular to the *c* axis of the BLSF crystal and attain plate-like morphology in the process of sintering. The mixed different orientation plate-like grains were found to stack together. The even packed grain size is about 2 μm and grain morphology of BBT-*x* specimens becomes more homogeneous after cerium modification. Rare-earth ions are known to suppress the grain growth in perovskites which is attributed to their low diffusivity [11].

Fig. 4 presents the dielectric constant ε_r and dielectric loss tan δ measured at 1 MHz as a function of temperature for the BBT-*x* specimens. With increasing temperature, a broad peak of dielectric constant corresponding to ferroelectric–paraelectric phase transition was observed, meaning that BBT-*x* belongs to ferroelectric phase at room temperature [12]. It is indicated that the compounds exhibit diffused dielectric constant anomalies around the temperatures of dielectric constant maximum (T_m), and T_m decreases from 413 °C to 406 °C with cerium modification increasing up to 0.75 wt%, showing that cerium

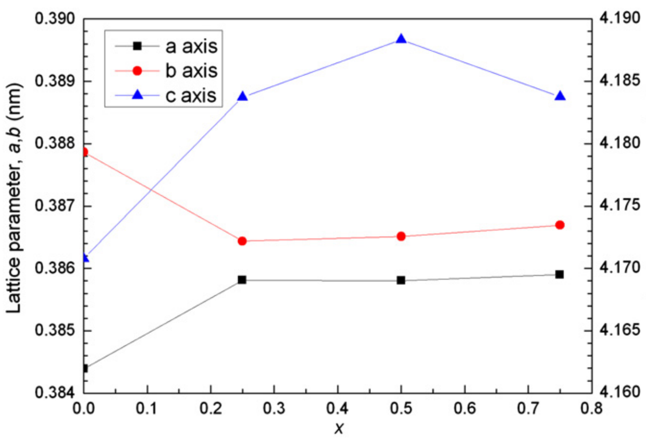

Fig. 2. Lattice parameter of BBT-*x* as a function of Ce^{4+} content.

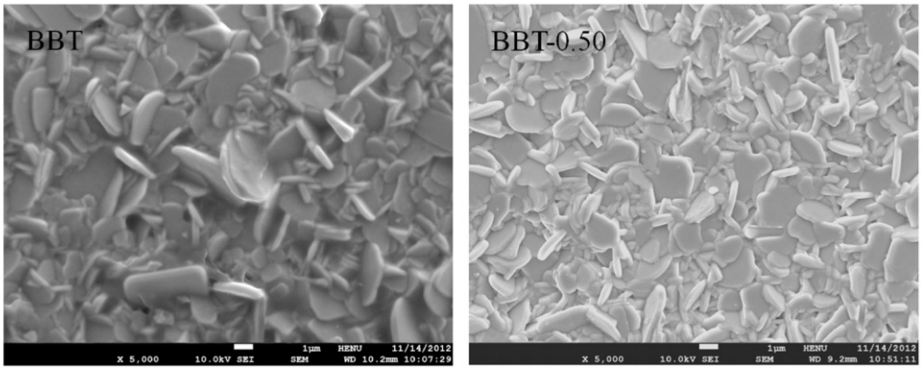

Fig. 3. SEM images of BBT and BBT-0.50 ceramics.

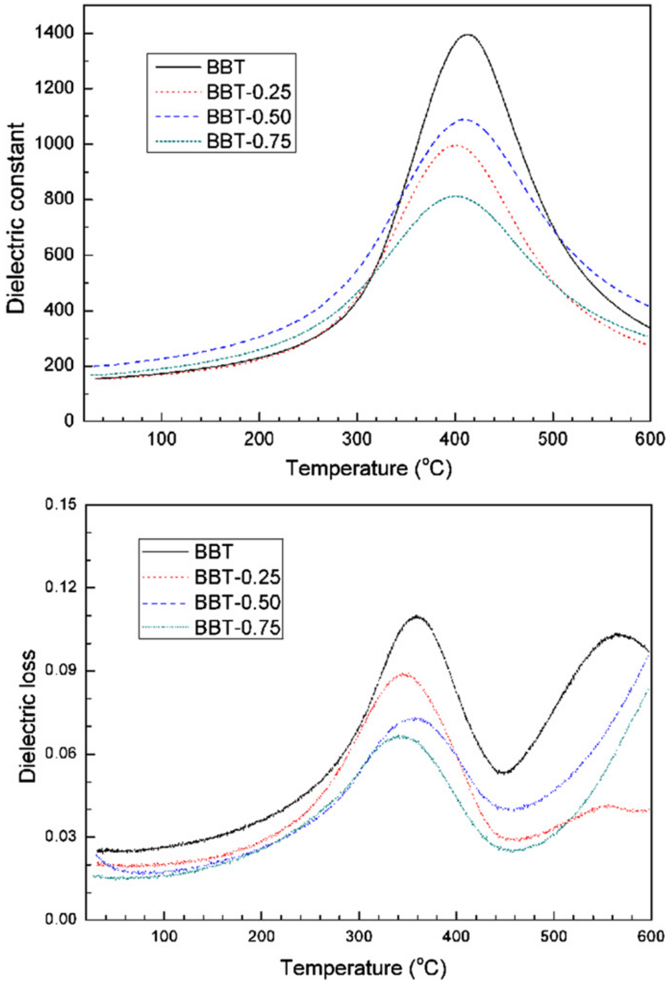

Fig. 4. The temperature dependence of dielectric constant and loss of BBT-x ceramics at 1 MHz.

modification decreases the Curie temperature. All samples exhibit a high dielectric constant around T_m due to the rapid slipping of nano-scaled polar clusters, which is suppressed after cerium substitution.

Due to the reduction of oxygen vacancies as space charge, the maximum of dielectric constant (ε_m) at T_m was found to be suppressed in cerium-doped BBT ceramics. The internal strain gradually becomes larger with the increase of cerium content and is predominant for $x=0.50$ cerium substitution. It has been reported that the ε rises with the increase of internal strain [13,14]. Similar mechanism was also applied to the case of BBT-0.50. When cerium content is 0.75, the strain releases owing to larger lattice distortion and the effect of oxygen vacancies on the suppression of ε_m becomes dominant; so the ε_m decreases. In BLSFs, ferroelectrics with Bi^{3+} at A-site often have the high Curie temperature for Bi^{3+} having lone pair of 6s electrons. Ce^{4+} substitution decreases the concentration of Bi^{3+} at A-site, and then decreases the Curie temperature.

Fig.4 also shows that the dielectric loss $\tan\delta$ is low; especially the temperature is lower than 250 °C. For all BBT-x ceramics, the dielectric loss values show a maximum at ~350 °C, which is attributed to the jump of oxygen vacancies during the sintering process [15]. The dielectric loss decreases after cerium modification, but more cerium modification does not decrease $\tan\delta$ further more. The dielectric loss of BLSFs is mainly caused by oxygen vacancies. Oxygen vacancies could be induced both at the titanium–oxygen octahedral and the $(Bi_2O_2)^{2+}$ layers. Ce^{4+} as a donor substituted for volatile Bi^{3+} which decreases the concentration of oxygen vacancies after cerium modification. But more cerium content could increase the defect concentration conducive to the increase of loss. The increase of $\tan\delta$ value at more than 450 °C might be attributed to the higher leakage loss.

For the relaxor ferroelectric, a modified Curie–Weiss (CW) law has been applied to describe the dielectric constant peak on the high temperature side and the diffuseness of the phase transition:

$\ln(1/\varepsilon - 1/\varepsilon_m) = \gamma \ln(T - T_m) + \text{Constant}$ [16]where ε_m is the maximum value of the dielectric constant at the transition temperature T_m, the value of γ is the expression of the degree of dielectric relaxation in a ferroelectric, and γ is between 1 and 2. $\gamma=1$, a normal ferroelectric–paraelectric phase transition, and $\gamma=2$ refers to ideal relaxors with a complete diffuse phase transition.

The obtained value of γ and the fitting curve is shown in Fig.5. It was found that the γ values are about 1.81, 1.82,

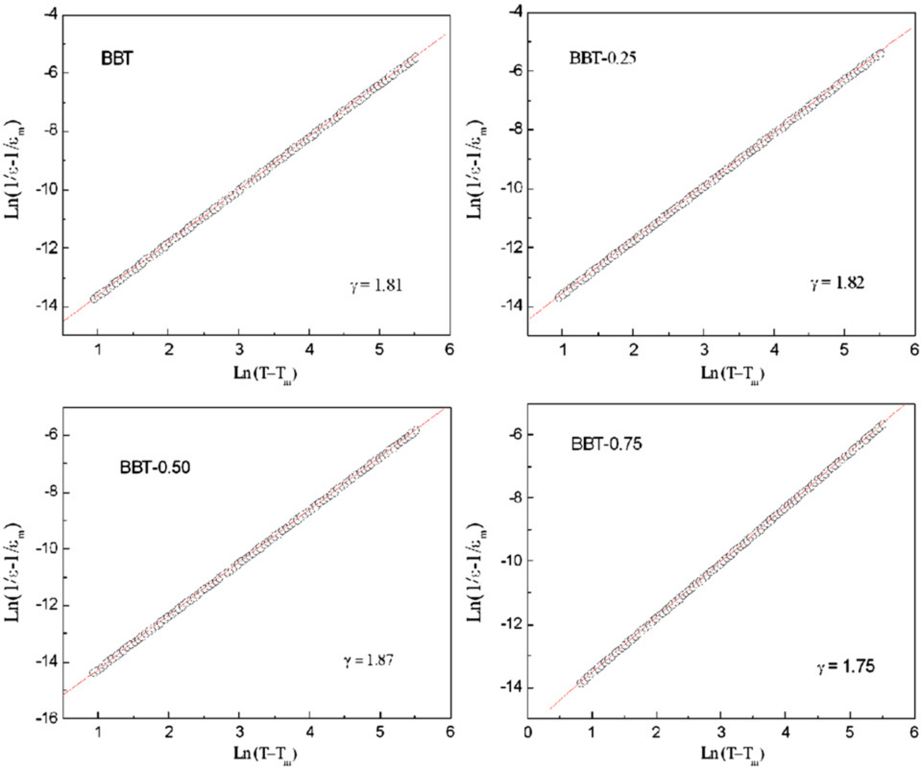

Fig. 5. Plot of ln $(1/\varepsilon - 1/\varepsilon_m)$ versus ln $(T - T_m)$ for BBT-x ceramics.

1.87 and 1.75 for BBT, BBT-0.25, BBT-0.50 and BBT-0.75 samples, respectively, which indicates that the diffuseness exponent of phase transition first increases, then decreases with the increase of cerium content, and confirms the diffuse phase transition and the disordered state of ions in the structure. In general, the relaxor behavior appears when at least two cations occupy the same crystallographic site, either A or B-site. The relaxor-like behavior of the Ba-based Aurivillius ceramics was attributed to the macroscopic disordering of Ba^{2+} and Bi^{3+} cations on A-sites of the lattice. The similar dielectric behavior was also observed in the other Ba-based Aurivillius relaxors such as $BaBi_{4-x}La_xTi_4O_{15}$ [17]. The observation of relaxor-like behavior in BBT ceramics confirms a cationic ordering on A-site. For cerium modified BBT, the dielectric relaxation behavior may be attributed to cation disorder, as Ce^{4+}, Bi^{3+} and Ba^{2+} ions are randomly distributed on A-site. The dispersion has a direct relation with cell volume, especially cell parameter c. The movement and redistribution of cations are easy in a loose structure with a large c value, which cause a short-range ordering and increase diffusion degree.

Table 1
Room temperature characterization of the BBT-x ceramics.

Material	ε_r	tan δ	T_m (°C)	d_{33} (pC/N)
BBT	154	0.025	413	19.2
BBT-0.25	153	0.021	411	20.7
BBT-0.50	199	0.023	407	24.2
BBT-0.75	166	0.015	406	17.7

The detailed properties of BBT-x piezoelectric ceramics at 1 MHz are listed in Table 1. The relative dielectric constant ε_r of BBT ceramics does not change significantly with cerium modification, varying between 150 and 200. The dielectric loss tan δ for the pure and cerium-modified BBT was found to be low, less than 0.025. The piezoelectric properties of the cerium modified BBT ceramics were found to be enhanced obviously compared with that of the pure BBT ceramics. The d_{33} of the BBT-0.50 was found to be 24.2 pC/N, the highest value among the cerium-modified BBT-based piezoelectric ceramics [5,7]. The enhancement of the piezoelectric activities can be attributed to the substitution of A-site Bi^{3+} ions by Ce^{4+} ions. Cerium probably plays two roles in the BBT-0.50 ceramics [18]. One is reduction in the volatilization of bismuth to densify the composite ceramics for Ce–O bond is stronger than Bi–O bond, thus higher electric field can be applied to make poling more sufficient. The other role of cerium is suggested to be a donor substitution based on the fact that the value of d_{33} can be greatly enhanced. The donor substitution leads to the constraint of maintaining the overall charge neutrality of the structure, cation vacancies are formed possibly at A-site. These cation vacancies generated in the structure effectively reduce the amount of oxygen vacancies and easy movement of domain walls [19]. When $x > 0.50$, cerium ions are easy to segregate and probably form second phase on the grain boundary, which decrease the suppression action of oxygen vacancies trace. Accordingly, the piezoelectric constant falls down while x is more than 0.50. The d_{33} and cell parameter *c* have the same change regularity with cerium content. The change in *c* axis value may play a major structural role in the polarization process, and the increase of *c* axis is beneficial to the domain wall movements and improves the piezoelectric properties.

4. Conclusions

BBT-*x* piezoelectric ceramics were synthesized with a solid-state reaction process. The samples possess polycrystalline phase with orthorhombic bismuth layer structure. The obtained ceramics have plate-like grains and the even grain size is about 2 μm. The dielectric properties were studied as a function of temperature. With increasing *x*, the temperature of the dielectric maximum of BBT-*x* was lowered and the peak of dielectric constant was significantly suppressed. The T_m and piezoelectric coefficient d_{33} for the ceramics modified with 0.50 wt% cerium are found to be 407 °C and 24.2 pC/N, respectively. The dielectric relaxoration coefficient (γ) was estimated with a curve fitting of modified Curie–Weiss(CW) law. The piezoelectric activity was improved by cerium modification. High Curie temperature and enhanced piezoelectric activity make the cerium modified BBT-based ceramics promising candidates for high temperature applications.

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