



Effect of samarium substitution on the dielectric and ferroelectric properties of $\text{BaBi}_{4-x}\text{Sm}_x\text{Ti}_4\text{O}_{15}$ ceramics

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Abstract

Sm-substituted barium bismuth titanate $\text{BaBi}_{4-x}\text{Sm}_x\text{Ti}_4\text{O}_{15}$ (BBST $_x$, $x=0, 0.4, 0.6, 0.8$) ceramics were prepared by a solid-state reaction method. X-ray diffraction patterns showed that the ceramics have a tetragonal structure with space group of $I4/mmm$ at room temperature. The plate-like morphology was observed by scanning electron microscope (SEM) and the average grain size decreases with the increase of Sm substitution. The dielectric, ferroelectric properties and complex impedance spectra of $\text{BaBi}_{4-x}\text{Sm}_x\text{Ti}_4\text{O}_{15}$ ceramics were studied. The results showed that Sm substitution decreased the temperature of the dielectric maximum (T_m) obviously from 390 °C to 241 °C. A modified Curie–Weiss law was used to describe the relaxor behavior of the ceramics. Through Arrhenius fitting, the activation energy was estimated to be 0.97–1.18 eV, which could be attributed to the thermal motion of oxygen vacancies. The remnant polarization (P_r) first increases, then decreases with increasing Sm substitution, and the maximum P_r was found to be 0.60 $\mu\text{C}/\text{cm}^2$ for BBST $_{0.6}$ ceramics.

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1. Introduction

Lead-based compounds are used widely for their fast switching polarization, high remanent polarization and large piezoelectric coefficients [1–3]. Unfortunately, lead is toxic to humans and environments. As an alternative lead-free material, bismuth layer-structured ferroelectrics (BLSFs) have attracted much attention for their promising applications in non-volatile random access memory (NVRAM) and high temperature piezoelectric devices in recent years [4–6]. The chemical formula of BLSFs is described by $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$, where various A and B cations are allowed and n is the number of pseudo-perovskite $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ layers [7]. Compared with lead-based materials, the remanent polarization and piezoelectric activities of BLSFs

are low. Many efforts have been done to improve their ferroelectric and piezoelectric properties. It was reported that the rotation of TiO_6 octahedron in the a - b plane accompanied by a tilt of the octahedral from the c axis is largely enhanced by lanthanide substitution of pseudo-perovskite A-site ions in BLSFs [8]. Therefore, it is possible to favor polarization by promoting rotational distortions through the replacement of some A-site ions with smaller lanthanides. Tomar et al. reported that Nd and Sm substitution improved the ferroelectric properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films [9].

$\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (BBT) is a member of BLSFs, with a Curie temperature of about 395 °C and low piezoelectric activity [10]. Since BBT and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ belong to the family of BLSFs, one can expect that samarium modification could also improve the ferroelectric and piezoelectric properties of BBT. Fang et al. reported the dielectric properties and relaxation of Sm-doped $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics [11]. However, there have been no reports on the ferroelectric properties of Sm modified

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BaBi₄Ti₄O₁₅ ceramics yet. In this work, the structure, dielectric and ferroelectric properties of samarium substitution on BBT ceramics have been investigated in detail.

2. Experimental procedures

BaBi_{4-x}Sm_xTi₄O₁₅ (BBST_x; $x=0, 0.4, 0.6, 0.8$) ceramics were prepared using high temperature solid-state reaction technique. High purity powders BaCO₃, Bi₂O₃, TiO₂ and Sm₂O₃ were weighed stoichiometrically and ball-milled for 24 h. After dried, the mixtures were calcined at 800 °C for 2 h. The calcined powder was remilled, dried and pressed into disks with a polyvinyl alcohol (PVA) binder. After burning out the PVA at 600 °C, the green pellets were placed in sealed Al₂O₃ crucibles and surrounded by matching composite powder. The samples were sintered at 1080 °C for 2 h.

The phase identification and microstructure characterization were done using a Rigaku D/MAX-RB powder X-ray diffractometer (XRD) with CuK α radiation and a field emission scanning electron microscopy (FE-SEM, JSM-7001F). Silver paste was applied to the surfaces of the samples and fired at 800 °C for 20 min as electrodes. Temperature dependent dielectric properties were measured, using an Agilent E4980A impedance analyzer equipped with a thermostat. The polarization–electric field (P – E) hysteresis loops were examined using a Radiant precision workstation (HVI0403-239) based on the Sawyer-Tower circuit at 10 Hz. All measurements were performed at room temperature except for dielectric temperature spectra.

3. Results and discussion

The XRD patterns of BBST_x ceramics are shown in Fig. 1a. All diffraction peaks match tetragonal BaBi₄Ti₄O₁₅ with space group $I4/mmm$ (JCPDS#35-0757) and no impurity peaks were found in these patterns, which means that all samples are a single phase bismuth layer-structured structure with $n=4$. The Fig. 1b represents the enlarged view of the (109) peaks. Compared with pure BBT sample, the position of (109) peak of Sm-substituted BBT

samples shifts to higher angle, indicating the decrease of lattice parameters. The result is consistent with the fact that the ionic radius of Sm (0.124 nm, C.N.=12) is smaller than that of bismuth (0.131 nm, C.N.=12) [12,13].

The SEM surface micrographs of BBST_x ceramics are shown in Fig. 2. It is seen that all samples are dense and the grains are anisotropic with plate-like shape. The plate-like morphology of the grains is a characteristic of BLSFs, which is due to the low surface energies of {001} planes and accordingly high grain growth rate in the direction perpendicular to the c -axis of the BLSF crystal during sintering [14]. The grain size of pure BBT ceramics is about 1–3 μ m. With the increase of Sm substitution, the average grain size decreases obviously. It was suggested that the rare earth ions could suppress the grain growth in perovskites owing to their low diffusivity [15].

Fig. 3 presents the dielectric properties of BBST_x ceramics as a function of temperature at 100 kHz. In Fig. 3a, a broad peak of dielectric constant corresponding to ferroelectric–paraelectric phase transition was observed, meaning that BBST_x belongs to ferroelectric phase at room temperature [16]. Due to the rapid slipping of nano-scaled polar clusters, the pure BBT sample exhibits a high dielectric constant around the temperature of dielectric constant maximum (T_m). After Sm substitution, a significant decrease of dielectric constant at T_m (ϵ_m), with a tendency toward the diffuse increase of phase transition, which was thought to be associated with the larger internal stress between smaller grains because of the higher concentration of grain boundaries [17,18]. When x increases from 0 to 0.8, T_m decreases from 390 °C to 241 °C, illustrating that Sm substitution decreases the Curie temperature obviously. BLSFs often have high Curie temperature for Bi³⁺ having lone pair of 6s electrons. Sm substitution reduces the concentration of Bi, consequently lowering T_c .

Fig. 3b shows that the dielectric loss is low, especially when the temperature is lower than 200 °C. All samples demonstrate a relaxation peak below T_m . At less than T_m , the compounds are ferroelectrics, where polar nano-regions (PNRs) exist. In an electric field, the movement of PNRs leads to the increase of loss and the relaxation peak appears. However, at the elevated

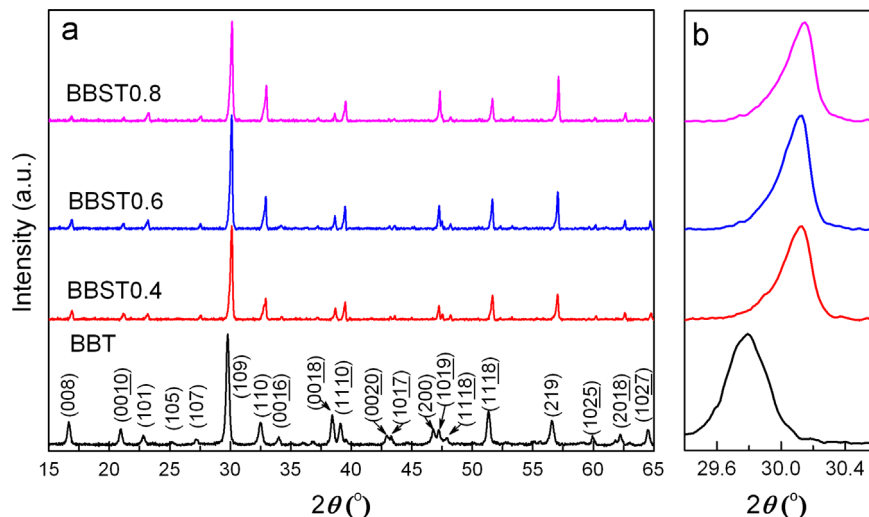


Fig. 1. XRD patterns of BBST_x ceramics.

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