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The microstructure and dielectric relaxor behavior of $BaBi_{4-x}La_xTi_4O_{15}$ ferroelectric ceramics

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ABSTRACT

Ferroelectric ceramics $BaBi_{4-x}La_xTi_4O_{15}$ (BBLT) were prepared with a solid-state reaction process. The obtained phases were confirmed as the Bi-layered perovskite phase with orthorhombic structure by the X-ray diffraction analysis (XRD). The dielectric relaxation was studied as a function of temperature and frequency. A dispersion of the maximum dielectric constant (ε_{max}) appears around the temperature of T_m, which shifts toward higher temperatures with the increase of frequency. The modified Curie–Weiss (CW) law was used to describe the relaxor behavior of BBLT ceramics. The relaxation indication coefficient (γ) was estimated with a quadratic fit of modified CW law. The coefficient firstly increases then decreases with the lanthanum increasing, which indicates that the BBT ceramics changes from relaxor-like ferroelectrics to relaxor ferroelectrics then to relaxor-like ferroelectrics with the lanthanum increasing. The relaxor nature of BBLT ceramics was attributed to the A site cationic disorder and the special relaxor behavior of BBLT ceramics was attributed to the high temperature phase transition by La^{3+} induced.

1. Introduction

Bismuth layer structured ferroelectrics (abbreviated as BLSFs) have attracted considerable interest for their potential applications in non-volatile random access memory (NVRAM) and high temperature piezoelectric devices [1–7]. The general chemical formula for BLSFs is $(Bi_2O_3)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A is mono-, di-, or trivalent cations (e.g., Ba^{2+}, Ca^{2+}, Pb^{2+}, Bi^{3+}, Na^+, or K^+), B is tetra-, penta-, or hexavalent cations of a transition metal (e.g., Ti^{4+}, Nb^{5+}, Ta^{5+}, or W^{6+}), and m is the number of perovskite-like layers (m = 1, 2, 3, 4, 5) [8,9]. The crystal structure of these compounds is composed of $(Bi_2O_2)^{2+}$ layers interleaved with perovskite-like blocks $(A_{m-1}B_mO_{3m+1})^{2-}$. This reflects the fact that there exists a good possibility for mutual dopings within these various elements or with some other ions to BLSFs. Generally, the doping could be in bismuth oxide layer and/or in perovskite-like units (A or B sites).

$BaBi_4Ti_4O_{15}$ (abbreviated as BBT), as the m = 4 member of the Aurivillius family has Ba and Bi ions at the A sites and Ti ions at the B sites of the perovskite $(A_{n-1}B_nO_{3n+3})^{2-}$ block ($(Bi_2O_2)^{2+}$ $((BaBi_2)Ti_4O_{13})^{2-}$). Since its discovery by Aurivillius in 1949 [10], BBT has attracted considerable attention duo to its high Curie temperature of about 417 °C [11] and excellent ferroelectric properties. Pribosic et al. [12] reported that the dielectric constant and Curie temperature of the BBT compound were increased insignificantly when Nb or Fe substitute for Ti and the BBT compound exhibits p-type electronic conductivity. Kumar and Varma [13] reported the influence of lanthanum doping on the dielectric, ferroelectric and relaxor behavior of barium bismuth titanate ceramics and found that La^{3+} doping did not affect the crystal structure of BBT. At the same time, the diffuseness increased with increasing lanthanum content and partial doping could enhance the ferroelectric properties of BBT ceramic. Rout et al. [14] reported the phase transition in $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) Aurivillius oxide prepared through a soft chemical route and found that the BBT ceramic showed a relaxor-like behavior near phase transition and the dielectric relaxation rate follows the Vogel–Fulcher relation with activation energy = 0.02 eV and freezing temperature = 362 °C. However, there have been few reports of the influence of lanthanum substituting bismuth in A site on the microstructure and dielectric relaxor behavior of BBT ferroelectric ceramics. In this work, we have investigated the dielectric relaxor behavior of $BaBi_{4-x}La_xTi_4O_{15}$ (BBLT, x equals to 0.0, 0.25, 0.50 and 0.75, abbreviated as BBT, BBLT25, BBLT50 and BBLT75, respectively) ceramics. An obvious relaxation transition from relaxor-like ferroelectrics to relaxor ferroelectrics, then to relaxor-like ferroelectrics was observed with the increase of lanthanum content.

2. Experimental procedures

The BBLT ceramics was prepared by the standard solid-state reaction method. Reagent-grade oxides and carbonate of Bi_2O_3, La_2O_3, TiO_2 and $BaCO_3$ were used as the starting materials. The powders of these raw materials were mixed and ball milled for 12 h using acetone as a medium, followed by calcination at 800 °C for 4 h, and the calcined powder was milled again for 24 h. The obtained powder was

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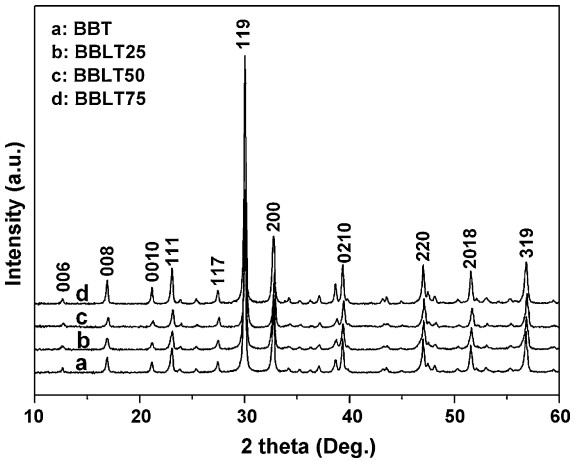

Fig. 1. The X-ray diffraction patterns of BBLT specimens.

pressed into pellets with 15 mm in diameter and ~1 mm in thickness by cold isostatic pressing method (~100 MPa). The final sintering was performed at temperature 1130 °C for BBT and BBLT25, 1150 °C for BBLT50 and BBLT75 for 1 h covered by alumina crucible followed by furnace cooling.

The crystal structure of each species was characterized by an automated diffractometer (XRD; X'Pert PRO MPD, Philips, Eindhoven, Netherlands) with Cu $K\alpha_1$ radiation. The morphology was characterized by the scanning electron microscopy (SEM, S-450, Hitachi). The pellets were polished to the thickness of about 1 mm, and then silver paste was painted on each sample face and fired as the electrodes at 850 °C for 30 min before dielectric properties measurement. Electrical properties measurements were taken with an applied voltage of 500 mV using an Agilent 4294A impedance analyzer over the frequency range of 100 Hz to 10 MHz.

3. Results and discussion

The XRD diffraction patterns of BBLT specimens measured at room temperature were shown in Fig. 1. The X-ray Bragg peaks in all these patterns could be indexed to a pure Bi-layered perovskite structure with $m = 4$. 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 compositions under investigation. Kennedy et al. [15] had studied the structural phase transitions in the layered bismuth oxide BBT at room temperature using powder neutron diffraction, and from 300 to 1000 K using synchrotron X-ray diffraction methods. The structure is orthorhombic (space group $A2_1am$) at 300 K and transforms to a tetragonal ($I4/mmm$) structure near 700 K. The dominant diffraction peaks of BBLT specimens were in excellent agreement with that reported on the orthorhombic BBT. So the obtained phase was indexed using an orthorhombic space group $A2_1am$.

The SEM images of cross-sectional surface for BBLT specimens are shown in Fig. 2. It is seen that all the specimens are composed of plate-like grains. This plate-like morphology of the grains is a characteristic feature of bismuth layer compounds. Some researchers had been reported that the {0 0 1} planes possess lower surface energies which develop predominantly during sintering [16]. Therefore, the grains of BBLT specimens grow in the a–b plane and attain disc/plate-like morphology in the process of sintering. Furthermore, the grain morphology of BBLT specimens becomes more homogeneous with the increase of lanthanum content. Rare-earth ions are known to suppress the grain growth in perovskites which is attributed to their lower diffusivity [17].

The temperature dependence of dielectric constant and dielectric loss of BBLT specimens at 100 kHz were shown in Fig. 3. It is indicated that the temperature of dielectric constant maximum (T_m) of BBLT specimens significantly decreases with the increase of lanthanum content. The changes of T_m are attributed to the changes of crystal structure for BBLT specimens, which indicated that the La^{3+} have entered into the lattice of BBT. At the same time, the phase transition temperature range around T_m for BBLT25 specimens becomes broader compared with that of BBT specimens. The same results can be observed in the patterns of the temperature dependence of the dielectric loss. This phenomenon is called diffuse phase transition, which is a typical characteristic of relaxor ferroelectrics. At the same time, the remarkable changes of the dielectric loss value for all specimens were observed beyond 420 °C.

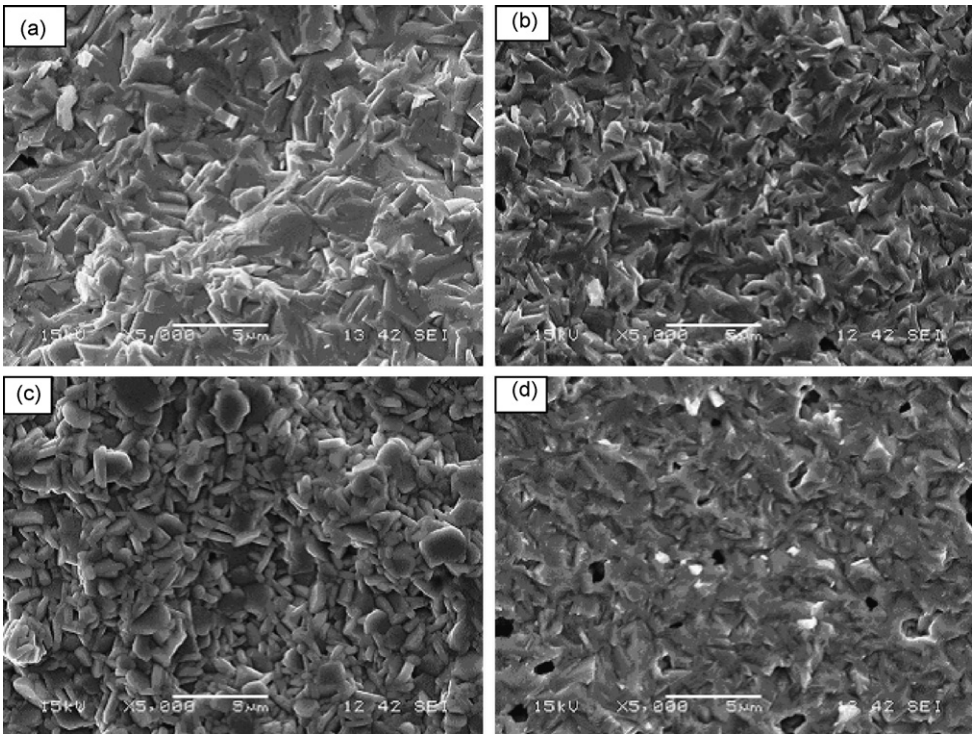

Fig. 2. The SEM images of cross-sectional surface for BBLT specimens: (a) BBT; (b) BBLT25; (c) BBLT50; (d) BBLT75.