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Short communication

Enhanced energy storage properties in $La(Mg_{1/2}Ti_{1/2})O_3$-modified $BiFeO_3$-$BaTiO_3$ lead-free relaxor ferroelectric ceramics within a wide temperature range

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ABSTRACT

A new ternary lead-free (0.67-x)$BiFeO_3$-0.33$BaTiO_3$-x$La(Mg_{1/2}Ti_{1/2})O_3$ ferroelectric ceramic exhibited an obvious evolution of dielectric relaxation behavior. A significantly enhanced energy-storage property was observed at room temperature, showing a good energy-storage density of 1.66 J/cm^3 at 13 kV/mm and a relatively high energy-storage efficiency of 82% at $x = 0.06$. This was basically ascribed to the formation of a slim polarization-electric field hysteresis loop, in which a high saturated polarization P_{max} and a rather small remnant polarization P_r were simultaneously obtained. Particularly, its energy storage properties were found to depend weakly on frequency (0.2 Hz–100 Hz), and also to exhibit a good stability against temperature (25 °C–180 °C). The achievement of these characteristics was attributed to both a rapid response of the electric field induced reversible ergodic relaxor to long-range ferroelectric phase transition and a typical diffuse phase transformation process in the dielectric maxima.

1. Introduction

Dielectric capacitors were believed to provide effective technical solutions for energy-storage applications because they can offer much higher power density based on extremely high discharge speeds. Compared with linear dielectric polymer materials, nonlinear dielectrics exhibit many advantages in terms of maximum working voltage, charge/discharge rate, output power, cycling life, leakage current and ease of the fabrication [1,2]. A normal ferroelectric material with large remnant polarization P_r should not be suitable for the energy-storage application because the charges cannot be effectively released. Relatively large energy loss from domain reorientation in ferroelectrics has restricted their practical applications. For antiferroelectric ceramics, the switching between the antiferroelectric and ferroelectric states occurs at low fields near room temperature, leading to smaller energy-storage density and temperature-sensitive energy-storage properties. In general, the energy-storage density (W) and efficiency (η) of a dielectric capacitor could be estimated according to a polarization-electric field (P-E) loop using the following formula:

$$W = \int_{P_r}^{P_{max}} EdP \quad \text{and} \quad W_{loss} = \int \text{PdE} \tag{1}$$

$$\eta = W/(W + W_{loss}) \tag{2}$$

where P_{max} is the saturated polarization, and W_{loss} is the area of hysteresis loops. Thereby, a large polarization difference $\Delta P = P_{max} - P_r$ would be definitely essential for achieving obviously enhanced energy-storage properties, apart from high dielectric breakdown strength allowing the application of an extremely high electric field. From this point of view, relaxor ferroelectrics might have large potentials against normal ferroelectrics and even antiferroelectrics for many energy-storage applications [3]. A couple of lead-based relaxor ferroelectric materials exhibited good potentials in the application of energy-storage capacitors [4–7]. However, widespread applications of lead-based materials would be restricted in future due to the toxicity of lead. Endeavors to develop lead-free alternatives have been made all over the world.

In recent years, extremely large W values were reported in $BiScO_3$-$BaTiO_3$ (BT) (15 J/cm^3) [8], $Bi(Mg_{1/2}Ti_{1/2})O_3$-BT (37 J/cm^3) [9] and $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT)-BT (154 J/cm^3) [10] lead-free thin films, but their limited thickness has restricted the overall stored energy. Some lead-free bulk ceramics have been also investigated,

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such as $Bi_{0.5}Na_{0.5}TiO_3$ (BNT)-based and BT-based systems with W values of rarely larger than 1 J/cm^3 [11–15]. $BiFeO_3$ (BF) has been recognized as a potential lead-free ferroelectric material owing to its excellent intrinsic polarization ($P > 100\ \mu C/cm^2$) [16], which offers the greatest scope for enhancing energy storage properties. BF-$SrTiO_3$ (ST) thin film was reported to have a good energy storage density of 18.6 J/cm^3 at 972 kV/cm [17]. Solid solutions of (1-x)BF–xBT exhibited a high P_{max} at a rhombohedral to pseudocubic structural phase boundary ($x = 0.33$) [18], but their W values were very limited because of large energy loss from an obvious hysteresis and a large P_r value.

$La(Mg_{1/2}Ti_{1/2})O_3$ (LMT) is a typical low-loss microwave dielectric material [19]. It is characterized by a distorted cubic perovskite structure and thus expected to be an appropriate end member to modify the dielectric relaxation and domain switching behavior of BF-BT binary system [20,21]. In this work, we reported a new (0.67-x)BF-0.33BT-xLMT lead-free relaxor ferroelectric ceramic for energy storage applications. The influence of the substitution of LMT for BF on the structure, dielectric, ferroelectric and energy storage properties was explored, clarifying the mechanism of generating good energy-storage properties. An excellent energy storage property ($W = \sim 1.66$ J/cm^3, $\eta = \sim 82\%$) was attained in the $x = 0.06$ sample together with a desirable temperature stability from 25 to 180 °C and a weak frequency dependence from 0.2 Hz to 100 Hz.

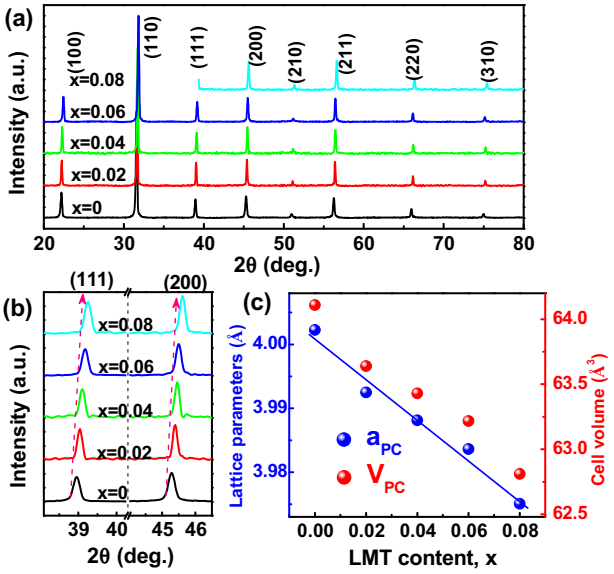

Fig. 1. (a) Powder XRD patterns of (0.67-x)BF-0.33BT-xLMT ceramics as indicated, (b) locally magnified (111) and (200) diffraction peaks and (c) lattice parameters and cell volume as a function of x.

2. Experimental

The (0.67-x)BF-0.33BT-xLMT ($x = 0$–0.08) ceramics were prepared by a conventional solid-state reaction method using high–purity oxides: Bi_2O_3 (≥99.0%), Fe_2O_3 (≥99.0%), $BaCO_3$ (≥99.0%), TiO_2 (≥99.0%), La_2O_3 (≥99.0%) and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ (≥99.0%) as raw materials. The powders were weighed at stoichiometric ratios and then ball-milled in ethanol using zirconia balls for 4 h. After calcination at 800 °C for 2 h, the mixture was ball-milled again for 6 h together with 0.5 wt% PVB as a binder. The granulated powder was uniaxially pressed into discs with a diameter of 10 mm and a thickness of 1 mm. The green sample discs were sintered in the temperature range of 990–1030 °C for 2 h. To minimize the vaporization of bismuth, all samples were buried in a sacrificial powder of the same composition during sintering. For electrical measurements, two major surfaces of the sample discs were completely covered with silver paste and then fired at 550 °C for 30 min.

The relative densities were evaluated by the Archimedes method. The crystal structure of crushed ceramics was determined using a powder X-ray diffractometer (XRD, D/Max-RB, Rigaku, Tokyo, Japan). The grain morphology was observed by using a filed-emission scanning electron microscope (FE-SEM, SU8020, JEOL, Tokyo, Japan). Before the SEM observation, the samples were polished and thermally etched at ~900 °C for 30 min. Dielectric properties of virgin samples were measured as a function of temperature (25–550 °C) and frequency (1–1000 kHz) using an LCR meter (Agilent E4980A, Santa Clara, CA). P-E hysteresis loops were measured using a ferroelectric measuring system (Precision multiferroelectric, Radiant Technologies Inc., Albuquerque, NM). For the P-E measurement, the thickness and diameter of the samples were diced into ~0.5 mm and ~8 mm, respectively.

3. Results and discussion

Fig. 1(a) shows XRD patterns of (0.67-x)BF-0.33BT-xLMT ceramics. Apparently, all compositions showed a single perovskite structure without trace of secondary phases. No splitting of both (111) and (200) diffraction peaks was identified regardless of the LMT content, indicating that all samples have a pseudocubic symmetry. Moreover, the (111) and (200) diffraction peaks were found to shift to higher angles (Fig. 1(b)), suggesting that there is a slight lattice shrinkage. It can be seen form Fig. 1(c) that the lattice parameter and the unit cell volume were found to become smaller with an increase of the LMT content. This is probably due to relatively small ionic radii of La^{3+} compared with Bi^{3+} at A sites (CN = 12, $R_{La}{}^{3+} = 1.22$ Å and $R_{Bi}{}^{3+} = 1.42$ Å), although the B-site average ionic radius of $((Mg_{1/2}Ti_{1/2})^{3+}$ (CN = 6, $R_{(Mg1/2Ti1/2)}{}^{3+} = 0.65$ Å) are slightly larger than that of Fe^{3+} (CN = 6, $R_{Fe}{}^{3+} = 0.645$ Å) [22].

Fig. 2 shows SEM micrographs of polished and thermally etched surfaces of (0.67-x)BF-0.33BT-xLMT ceramics sintered at optimum temperatures. It can be seen that all compositions have been well densified. Uniform grains with an average grain size of 2–3 μm were closely compacted, indicating a high relative density of >97% as confirmed by the Archimedes method. The substitution of LMT for BF was found to have little influence on the grain morphology.

The temperature and frequency dependence of dielectric permittivity (ε_r) of (0.67-x)BF-0.33BT-xLMT ceramics is shown in Fig. 3(a) using the x = 0, x = 0.03 and x = 0.06 samples as examples. It can be seen that the temperature (T_m) at the dielectric maxima (ε_m) decreased with increasing the LMT content. Moreover, the dielectric anomaly became more and more diffuse and more frequency-dependent. Similar phenomenon was also observed in some other perovskite relaxor ferroelectrics [23–25]. The observed relaxor characteristics of (0.67-x)BF-0.33BT-xLMT ceramics can be described by a modified Curie-Weiss law $1/\varepsilon\text{-}1/\varepsilon_m = (T\text{-}T_m)^\gamma/C$ at $T > T_m$, where γ is the indicator of the diffuseness degree [26]. In addition, the parameter ΔT_{relax} defined as the difference between two T_m values measured at 1 MHz and 1 kHz is a rough estimation of the relaxation degree. Both parameters (γ and ΔT_{relax}) were found to increase obviously with increasing the LMT content, as shown in Fig. 3(b). The enhancement of dielectric relaxation behavior would be ascribed to the increase of the random local fields as a result of the disordered distribution of different ions at A- and B-sites of ABO_3 lattices, accompanying a gradual increase of the dynamics of polar nanoregions (PNRs) as well as a decrease of the size of PNRs. As a result, the dielectric relaxation behavior of the samples should follow an empirical *Vogel-Fulcher* relation [27], which can be also employed to determine the value of the freezing temperature (T_f) of

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