Multiferroic properties of (1-x)BCZT-xLCMO laminated composites

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ABSTRACT

The electrical, ferromagnetic and magnetoelectric properties of the (1-x) $Ba_{0.85}Ca_{0.15}Zr_{0.10}Ti_{0.90}O_3$-$xLa_{0.67}Ca_{0.33}MnO_3$ [(1-x)BCZT-xLCMO] laminated composites were investigated. The ferroelectric and ferromagnetic characteristics demonstrated that the laminated composites are multiferroic in nature. Our results indicated that the performances of the laminated composites showed strong dependence on the thickness ratio between the ferroelectric BCZT layer and ferromagnetic LCMO layer. Enhanced dielectric properties were obtained for the laminated composites compared with that of the pure BCZT. The piezoelectric coefficient (d_{33}) and coercive electric fields (E_C) of the laminated composites declined with the increasing LCMO nonferroelectric layer, while the saturated magnetization (M_S) increased and the coercive magnetic field (M_C) kept constant. The 0.3BCZT-0.7LCMO composites obtained the largest magnetoelectric coefficient of α_{E31} = 1.66 mV/cm·Oe.

1. Introduction

In recent years, multiferroic magnetoelectric (ME) materials with coexistence of ferroelectric and ferromagnetic orders have been of considerable interest to scientist due to their fascinating multifunctional features and potential applications such as energy transducers, sensors, microwave devices, etc. The predominant feature of these materials is that they enable the simultaneous display of ferroelectric and ferromagnetic properties as well as the coupling effect between the magnetization and electric polarization. The coupling effect, namely the ME effect, which is defined as the coupling process that a spontaneous electric polarization induced by an external magnetic field or a magnetization induced by an applied electric field, is attracting more and more researchers' attention.

The intrinsic ME effect was first observed in single-phased compounds, such as $BiFeO_3$ [1] and Cr_2O_3 [2], but they are hardly utilized because of their low Curie or Neel temperatures and the weak ME effect at room temperature. Later, many attempts [3–7] have been made to develop artificially multi-phased composites consisting of ferroelectric components with large piezoelectric response and ferromagnetic ones with high magnetostrictive coefficient. They could potentially generate a strong extrinsic ME effect at room temperature, resulting from the elastic coupling interaction across piezoelectric-magnetostrictive (P-M) interfaces. The common combinations of ME composites can be roughly divided as: (1) 0–3 type particle-matrix composites where the ferromagnetic particles/fibers are embedded in the ferroelectric matrix, which makes the electric poling difficult and degrades the ME effect because of the high conductivity of the ferromagnetic phase. (2) 2-2 type laminated composites composed of alternating ferromagnetic and ferroelectric layers. Such 2-2 type laminated composites can separate the insulating ferroelectric phase and the conducting ferromagnetic phase, leading to the higher degree of polarization than the 0–3 type particle-matrix composites, and thereby exhibit better ME response and electric properties [8–10].

In the previous works, a series of $PbZr_xTi_{1-x}O_3$ (PZT)-based laminated ME composites, such as $PZT-CoFe_2O_4$ [11], $PZT-NiFe_2O_4$ [12] and $PZT-La_{0.7}Sr_{0.3}MnO_3$ [13] have been developed. Nevertheless, abandoning the use of lead-based piezoelectric materials is a global tendency in order to eliminate their toxicity to humans and environments. Thus, it is imperative to develop new environmentally-friendly lead-free ME composites. There have been some reports on lead-free multilayer ME composites such as $BaTiO_3/CoFe_2O_4$ [14] and $Ni_{0.5}Ti_{0.5}NbO_4-Ni_{0.8}Zn_{0.2}Fe_2O_4$ [15] in which multiferroicity are reported.

$Ba_{0.85}Ca_{0.15}Zr_{0.10}Ti_{0.90}O_3$ (BCZT) ceramic is found recently to be an attractive non-lead material with outstanding piezoelectric properties (d_{33} = 620 pC/N) [16] comparable to that of lead-based materials, making it a promising candidate for lead-free ME composites. However, as far as we know there are few reports on ME composites based on this compound.

On the other hand, lanthanum manganite $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) has attracted considerable attention too [17], which is well known for its metallic conductivity, double exchange mediated ferromagnetism and colossal magnetoresistance. Compared with the common ferrites,

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LCMO would be an appealing candidate as a ferromagnetic component for ME composites because of the large magnetostriction [18], lattice-matched parameters to perovskite ferroelectric materials [19] and additional freedom for functional devices [20], as reported in PZT/LCMO [21], $Ba_{0.6}Sr_{0.4}TiO_3$/LCMO [18] and $BiFeO_3$/LCMO [22] composites.

In the present study, a new 2-2 type laminated ME composite based on BCZT as a ferroelectric component and LCMO as a ferromagnetic component is then prepared. The detailed investigations of multiferroic properties on the (1-x)BCZT-xLCMO laminated composites are firstly reported.

2. Experimental

Laminated composites of (1-x)BCZT-xLCMO were prepared by Plasma Activated Sintering (PAS) and silver paste method, where x denotes the volume fraction of the LCMO layer. The BCZT ceramics preparation process can refer to our previous study [23]. For LCMO ceramics preparation process, stoichiometric of La_2O_3, $CaCO_3$, and $MnCO_3$ were ball milled using agate balls in ethanol for 24 h. The dry mixed powders were first calcined at 1300 °C for 15 h and then at 1350 °C for 25 h with intermediate grindings. The calcined LCMO powders were heated in a vacuum atmosphere at 975 °C under a pressure of 80 MPa for 10 min using a PAS device (ED-PAS-111, ELENIX). Finally, the samples were annealed at 900 °C for 10 h. BCZT and LCMO ceramic discs were first grinding and polishing in proper shape and thickness, and then were bonded with silver to obtain (1-x)BCZT-xLCMO laminated composites.

The microstructures of fracture surfaces of the composites were characterized by scanning electron microscopy (SEM, Quanta, FEG250). The piezoelectric constant (d_{33}) was measured using a quasi-static d_{33} meter (Institute of Acoustics, ZJ-3AN). The dielectric properties were measured as a function of temperature (25–200 °C) and frequency (20 Hz-1 MHz) using a LCR meter (Agilent, E4980A). P-E hysteresis loops at 10 Hz were obtained using a precision LC unit (Radiant, Premier II). Ferromagnetic hysteresis loops at 10 K were measured using a superconducting quantum interference device (SQUID, Quantum Design) magnetometer. The transverse magneto-electric effect (α_{E31}) at room temperature was measured as a function of dc magnetic field H_{dc} by a ME measurement system (SuperME, Quantum Design), and the magnetic field was perpendicular to the polarization direction.

3. Results and discussion

The cross-sectional SEM image and corresponding EDS analysis of the BCZT/Ag/LCMO interface are illustrated in Fig. 1. It is evident that no cracks or micro-pores are observed in each phase as well as the
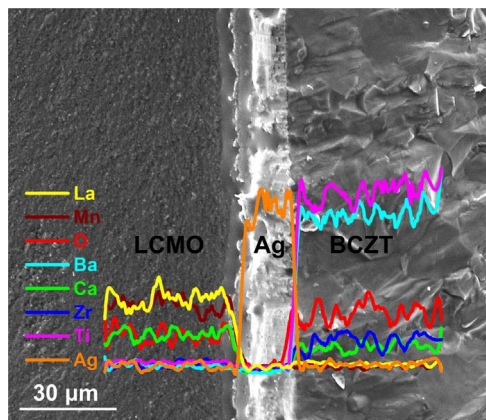

Fig. 1. Cross-sectional SEM image and corresponding EDS analysis of the BCZT/Ag/LCMO interface.

BCZT/Ag/LCMO interface, showing that the PAS-ed BCZT and LCMO ceramics are highly compact and a good bonding between the BCZT phase and LCMO phase is obtained by silver paste method. According to the corresponding EDS line analysis, all elements show sharp changes without any diffusion. This implies that the silver paste method could effectively hinder the elemental diffusions between the BCZT and LCMO phases.

Fig. 2 presents the room-temperature frequency-dependence of the (a) dielectric constant (ε_r) and (b) dielectric loss (tan δ) for (1-x)BCZT-xLCMO laminated composites. The curve variation of the (1-x)BCZT-xLCMO laminated composites at x = 0.3, 0.5 and 0.7 is similar to the pure BCZT. With increasing measuring frequency, a continuously decreasing in ε_r is observed whereas the tan δ first decreases and then increases. As the ferromagnetic LCMO content of the laminated composites increases, so does the ε_r and tan δ. Compared with the pure BCZT, all (1-x)BCZT-xLCMO (x = 0.3, 0.5 and 0.7) laminated composites exhibit enhanced ε_r. In our opinions, the enhanced ε_r should be contributed by the ferromagnetic LCMO and Maxwell-Wagner type interfacial polarization mechanism [24]. As shown in Fig. 2(a) and (b), the ferromagnetic LCMO ceramic exhibits high values in ε_r and tan δ at room-temperature ascribe to the peculiar phase-separated electronic state that arises above T_C [25]. According to phase-separated state, LCMO ($T_C \sim 268$ K) ceramic is supposed to be composed of a mixture of insulting nonmagnetic and metallic ferromagnetic regions, which will generate space-charge or interfacial polarization, and hence yield a dielectric response. Furthermore, the interface between the ferroelectric BCZT and ferromagnetic LCMO phases acts as a trap for the mobile charge carriers because of their very large difference in conductivities, which will lead to the formation of inner fields due to the uncompensated interface charges, and hence increases the dielectric losses, especially activates at low frequency [26].

Fig. 3 shows the temperature-dependence of ε_r and tan δ for the (1-x)BCZT-xLCMO laminated composites, measured at 1, 10, 100 and 1000 kHz. Similar to the pure BCZT, the (1-x)BCZT-xLCMO laminated composites show two obvious dielectric peaks, corresponding to the phase transition from rhombohedral to tetragonal and from tetragonal to cubic phase, respectively. In addition, the maximum dielectric constant (ε_m) reduces and the Curie temperature (T_C) moves towards to higher temperatures with increasing frequency, indicating a relaxor behavior characteristic of strong frequency dispersion and diffuse phase transition. The T_C at 1 kHz is about 80 °C for all samples, which means that the thickness ratio between the ferroelectric BCZT and ferromagnetic LCMO phases has no impact on T_C of the laminated composites. The values of ε_m at 1 kHz are found to be 13170, 14987, 20280 and 17616 for (1-x)BCZT-xLCMO laminated composites at x = 0.0, 0.3, 0.5 and 0.7, respectively, indicating that the dielectric constant of the laminated composites is strongly dependent on the thickness ratio between the ferroelectric BCZT and ferromagnetic LCMO phases. Interestingly, the ε_m of all laminated composites has been significantly increased compared with that of the pure BCZT. The dielectric constant of the laminated composites has not been diluted by the ferromagnetic LCMO phase, while the previous studies found that the dielectric properties degraded with increasing ferromagnetic phase of $Li_{0.058}(Na_{0.535}K_{0.48})_{0.942}NbO_3$-$Co_{0.6}Zn_{0.4}Fe_{1.7}Mn_{0.3}O_4$ [8], $Ba(Fe_{0.5}Nb_{0.5})O_3$-$Bi_{0.2}Y_{2.8}Fe_5O_{12}$ [9] and $(K_{0.45}Na_{0.55})_{0.98}Li_{0.02}(Nb_{0.77}Ta_{0.18}Sb_{0.05})O_3$-$Ni_{0.37}Cu_{0.20}Zn_{0.43}Fe_{1.92}O_{3.88}$ [27] composites. But similar results have also been reported by Yu et al. for $BaTiO_3$-$(Ni_{0.3}Zn_{0.7})Fe_{2.1}O_4$ composites and by Chen et al. for $Sr_{0.5}Ba_{0.5}Nb_2O_6$-$CoFe_2O_4$ composites [28], which were attributed to the Maxwell-Wagner polarization mechanism [29]. The difference in conductivities between the BCZT phase with higher resistivity and the LCMO phase with a much lower resistivity would cause the assembling of charge carriers at the BCZT-LCMO interface, and hence contribute to the dielectric polarization. The tan δ-T curves of all samples show two dielectric loss peaks at the rhombohedral-tetragonal temperature and the Curie temperature. With the increase of ferromagnetic LCMO content, the tan δ of the laminated composites slightly increase.

The piezoelectric coefficient (d_{33}) of the (1-x)BCZT-xLCMO