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Ferroelectric, Ferromagnetic, and Magnetoelectric Characteristics of $0.9(0.7BiFeO_3–0.3BaTiO_3)–0.1CoFe_2O_4$ Ceramic Composite

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A $0.9(0.7BiFeO_3–0.3BaTiO_3–0.3$ wt% $MnO_2)–0.1CoFe_2O_4$ (BF–BT–CF) multiferroic ceramic composite was prepared and characterized. The composite showed well-saturated polarization–electric field and magnetic hysteresis loops simultaneously at room temperature, with a remanent polarization of 15.7 $\mu C/cm^2$ and a coercive field of 27 kV/cm. Spontaneous and remanent magnetizations of the BF–BT–CF composite were 6.7 and 0.87 emu/g, respectively. Its magnetoelectric voltage coefficient dE/dH was measured as a function of applied magnetic field at different frequencies. This ceramic composite might be a promising candidate as multiferroic materials displaying ferroelectricity, ferromagnetism, and magnetoelectricity.

I. Introduction

There has been an increasing interest in multiferroic materials, which have two or more order parameters simultaneously such as ferromagnetic, ferroelectric, and/or ferroelastic ordering.[1,2] Coupling between magnetic and ferroelectric ordering leads to the magnetoelectric (ME) effect. The ME effect provides an additional degree of freedom in the design of new functional sensors, current devices, transducers, and multistate memory devices.[3,4] $BiFeO_3$ (BFO) is a promising candidate as a single-phase multiferroic material because it is antiferromagnetic with a relatively high Neel temperature ($T_N = 380°C$) and ferroelectric with a high Curie temperature ($T_c = 810°C$).[5] BFO and BFO-based single-phase multiferroics have been widely studied in both ceramic and film forms.[6–10] However, in spite of their excellent ferroelectric property, BFO-based single-phase multiferroics generally have weak macroscopic magnetic properties. Although relatively enhanced magnetization can be observed in highly constrained epitaxial films or chemically substituted films and ceramics, the enhancement is limited. This leads to weak ME effect in these materials. This problem prevents the application of BFO-based single-phase multiferroics because large ME effect is desirable for real applications. The reason for low magnetization of BFO-based single-phase multiferroics is the weak magnetization due to the intrinsic spatially modulated, incommensurate cycloidal spin structure and antiferroelectric nature in BFO.[11] Although chemical substitution and strain engineering are effective ways to suppress or destroy the spin cycloid and thus enhance magnetization and ME effect to some extent, they cannot change the intrinsic antiferroelectric nature of BFO-based single-phase multiferroics.[6–9]

One effective way of increasing the magnetism for the BFO-based multiferroics is to introduce suitable ferrites to form composites. Most of the studies in the past focused on $CoFe_2O_4$ (CFO),[8–10] which was used as a piezomagnetic constituent due to its large magnetostriction. Our previous work indicated that $0.7BiFeO_3–0.3BaTiO_3–0.3$ wt% MnO_2 (Mn–BF–BT) ceramics has good ferroelectric properties.[12] Therefore, we proposed to develop multiferroic materials by using $0.7BiFeO_3–0.3BaTiO_3–0.3$ wt% MnO_2 and $CoFe_2O_4$. In this work, we report on multiferroic properties of ceramic composite with a composition of $0.9(0.7BiFeO_3–0.3BaTiO_3–0.3$ wt% $MnO_2)–0.1CoFe_2O_4$.

II. Experimental Procedure

$CoFe_2O_4$ powders were synthesized by a combustion method with glycine as fuel. Analytical-grade metal nitrate $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and glycine in an appropriate ratio were dissolved in deionized water to obtain a precursor solution. The precursor solution was concentrated in a hot porcelain crucible until the excess water was evaporated, so that final spontaneous ignition occurred. Within a few seconds, the combustion reaction was completed resulting in black and porous ash filling the container. $CoFe_2O_4$ powder was obtained by annealing the resultant ash at 900°C for 2 h.

$0.7BiFeO_3–0.3BaTiO_3–0.3$ wt% MnO_2 powders were prepared by the conventional solid-state reaction method.[12] Finally, the CFO powders and Mn–BF–BT powders, with a composition of $0.9(0.7BiFeO_3–0.3BaTiO_3–0.3$ wt% $MnO_2)–0.1CoFe_2O_4$, were thoroughly mixed via ball milling for 24 h using ethanol as a medium. The slurries were dried, ground completely, and pressed into 10-mm-diameter and about 1-mm-thick disks, which were then sintered at 1010°C for 2 h.

Phase compositions of the specimens were characterized by using X-ray diffraction (XRD) (Rigaku D/MAX-2400, Cu$K\alpha$ radiation, Tokyo, Japan). Ferroelectric hysteresis loops were characterized by using a ferroelectric test system (TF Analyzer 2000, aixACCT, Aachen, Germany). Magnetic properties were measured by using a superconducting quantum interference device (SQUID, MPMS XL-7, Quantum Design, San Diego, CA) magnetometer. ME effect was measured by using a dynamic method. ME voltage coefficient ($\alpha_E = dE/dH$) is determined by the induced electric field E at a small ac magnetic field. An ac magnetic field H_{ac} was superimposed onto a dc magnetic bias H_{dc}, both of which were parallel to the thickness direction of the pellets. The induced electric field E was measured by using a lock-in amplifier (SR7280, SRS Inc., Oak Ridge, TN). Before measurement, the samples were polarized in the silicon oil at an electric field of about 2800 V/mm at room temperature (RT).

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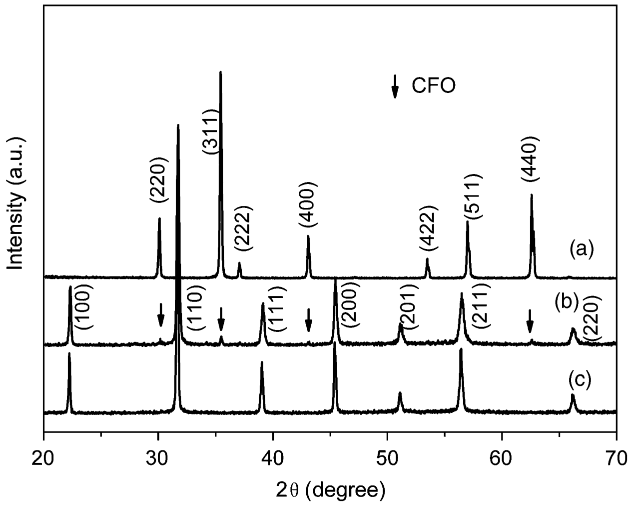

Fig. 1. X-ray diffraction patterns of CFO powder (a), BF–BT–CF composite (b), and Mn–BF–BT ceramics (c).

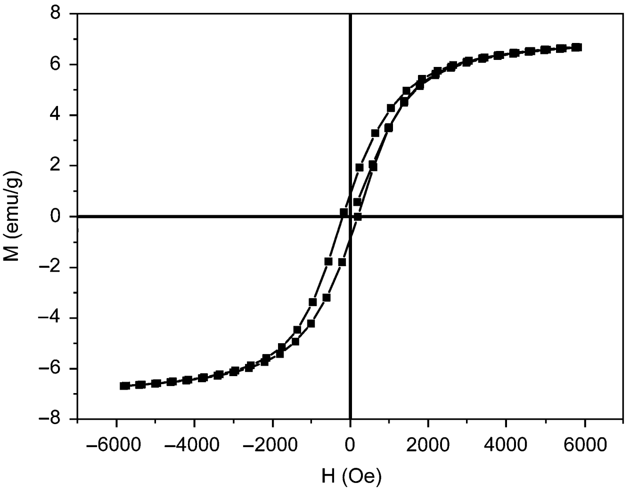

Fig. 3. *M–H* loop of the BF–BT–CF composite at room temperature.

III. Results and Discussion

Figure 1 shows the XRD patterns of the sintered CFO powder, BF–BT–CF composite, and Mn–BF–BT ceramics, respectively. Obviously, the CFO powder is of single phase with spinel structure. The sharp diffraction peaks confirm that CFO is well crystallized. For the composite, the peaks of perovskite Mn–BF–BT and spinel CFO can be clearly identified. No third phase can be observed. This means that there is no reaction between BF–BT and CFO.[13,14]

Ferroelectric polarization–electric field (*P–E*) loop (at 1 Hz) of the BF–BT–CF ceramic composite at RT is shown in Fig. 2. A well-saturated hysteresis loop is observed, indicating a typical ferroelectric behavior of the BF–BT–CF composite. Spontaneous polarization, remnant polarization, and coercive field of the samples are 17.5, 15.7 μC/cm^2, and 27 kV/cm, respectively. As compared with Mn–BF–BT,[12] the composite has a slightly lower P_r/P_s and larger E_c.

Magnetization–magnetic field (*M–H*) loop of the BF–BT–CF composite is shown in Fig. 3. A weak hysteresis is observed, with a remnant magnetization (M_r) of 0.87 emu/g. The low H_c (194 Oe) and M_r at RT indicate that the composite is in a superparamagnetic order, which is similar to nanostructured CFO.[15] Because M_r of Mn–BF–BT is only 0.1 emu/g,[12] the magnetic response of the composite is mainly contributed by CFO. To further investigate the magnetic properties of the composite, its temperature-dependent magnetization was studied, as shown in Fig. 4. From RT to 190 K, its magnetization increases, and this can be attributed to the temperature-dependent magnetization of ferromagnetics. With the further decrease in temperature, its magnetization decreases, this is the characteristic of antiferromagnetics. Because the Mn–BF–BT solid solution is basically antiferromagnetic with weak ferromagnetism, it is concluded that the antiferromagnetic-like magnetic response in Fig. 4 comes from Mn–BF–BT component and its coupling with CFO. However, as discussed above, the *M–H* loop has already indicated that the magnetization is mainly contributed by the CFO component and its coupling with Mn–BF–BT at RT, which appears inconsistent with Fig. 4. One possible explanation is that there is a coupling between Mn–BF–BT and CFO. As a result, the antiferromagnetic Mn–BF–BT dominates the tendency of temperature-dependent magnetization while ferrimagnetic CFO is responsible for the high magnetization value.

The coexistence of the ferromagnetism and ferroelectricity in the composite gives rise to promising ME effect. Variations of α_E with H_{dc} at various magnetic frequencies (f) are shown in Fig. 5. At $H_{dc} = 0$, the composite exhibits an initial high α_E value. It is found that α_E is slightly decreasing with H_{dc}, while increasing with an increasing frequency. A maximum α_E value of 67 mV/cm Oe is obtained at $f = 50$ kHz.

ME coupling mainly arises from the magnetic–mechanical–electric transform through the stress-mediated transfer at interfaces. A dynamic magnetoelastic coupling, which is caused by

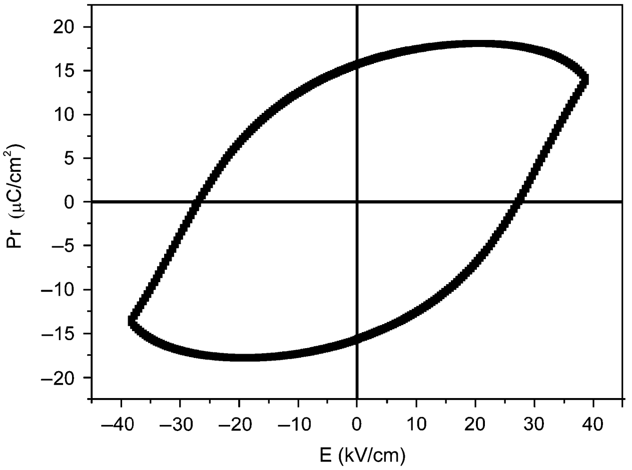

Fig. 2. Room temperature *P–E* loop of the BF–BT–CF composite.

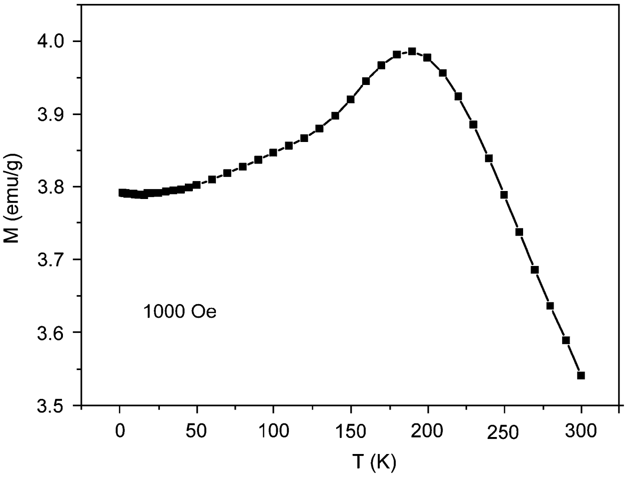

Fig. 4. Temperature-dependent magnetization of the BF–BT–CF composite.

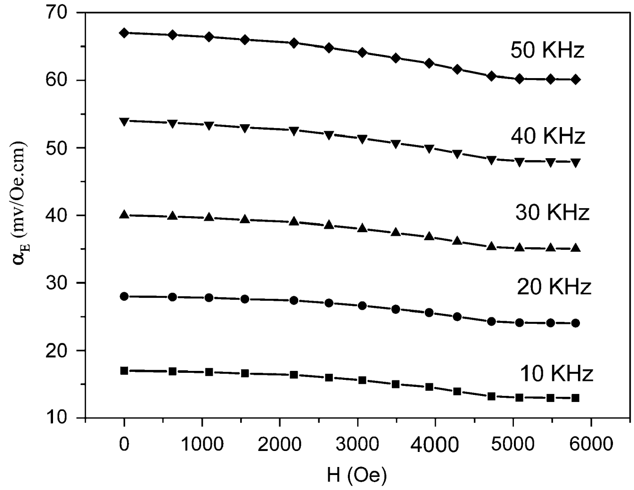

Fig. 5. Variation of α_E with H_{dc} at various magnetic frequencies for the BF–BT–CF composite.

magnetostriction of the $CoFe_2O_4$ phase, due to domain-wall motion and domain rotation, is involved in the ME effect. Therefore, a low coercivity and a high magnetostriction are advantageous for a strong ME effect.[16,17] In spinels, magnetostrictive coefficient reaches saturation concomitant with magnetization at a certain value of the magnetic field. Hence, the strain produced in the ferrite phase would produce a constant electric field in the piezoelectric phase, thereby decreasing the piezomagnetic coupling coefficient $q = \delta\lambda/\delta dH_{dc}$.[18] For most ferrites, once the magnetostriction attains saturation value, q decreases and the piezomagnetic coupling gradually becomes weak, resulting in a decrease in ME effect. The variation of α_E with f is most likely caused by the frequency dependence of dielectric constant of the individual phases and the piezoelectric coefficient of Mn–BF–BT.[19]

IV. Summary

In summary, 0.9(0.7BiFeO$_3$–0.3BaTiO$_3$–0.3 wt% MnO$_2$)–0.1Co Fe$_2$O$_4$ ceramic composite were found to show multiferroic behaviors. It had a well-saturated P–E ferroelectric loop with P_r of 15.7 μC/cm^2. At the same time, its magnetic response as the function of temperature and ME characteristic were investigated and discussed. These results might be useful to further understanding and designing new multiferroic composites.

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