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# Enhanced Curie temperature and magnetoelectric effects in the $BaTiO_3$-based piezoelectrics and $CoFe_2O_4$ laminate composites

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ABSTRACT

In the present work, the $0.65BaTiO_3–0.35Bi_{0.5}Na_{0.5}TiO_3/CoFe_2O_4$ laminate composites targeting lead-free magnetic field sensor, which can be used at high operating temperatures without depolarizing, were prepared by the conventional solid-state sintering method. Excellent dielectric, piezoelectric, magnetic and magnetoelectric properties can be observed in the $0.65BaTiO_3–0.35Bi_{0.5}Na_{0.5}TiO_3/CoFe_2O_4$ laminate composites compared with the $BaTiO_3/CoFe_2O_4$ laminate composites. The ME response is dependent on the relative mass ratio of $0.65BaTiO_3–0.35Bi_{0.5}Na_{0.5}TiO_3$ phase and $CoFe_2O_4$ phase and the dc magnetic field. The maximum ME coefficient of the $0.65BaTiO_3–0.35Bi_{0.5}Na_{0.5}TiO_3/CoFe_2O_4$ laminate composites reaches up to about 113 mV/cm Oe, which is larger than that of the $BaTiO_3/CoFe_2O_4$ laminate composites (86 mV/cm Oe).

## 1. Introduction

Magnetoelectric (ME) materials, which can produce a electric polarization in an external magnetic field, or a magnetization response in an applied electric field, have recently drawn ever-increasing interest due to their potential for applications as sensors, transducers and memory devices [1–4]. The ME effect in the single phase compounds is weak and commonly appears at low temperature, which limits their use in most of the application areas. Since its ME coefficient is typically three orders of magnitude higher than that of the particulate composites, ME multilayer composite material has attracted particular attention. In the previous studies, a series of laminated ME ceramic composites, such as PZT/Terfenol-D [5] and PZT/$CoFe_2O_4$ [6] have been developed. In view of environmental hazards, it is necessary to find materials for lead free applications.

Barium titanate (BTO) has become one of the most important electroceramics, which is often used as the ferroelectric constituent due to its excellent piezoelectric properties and lead free chemical composition, attracting more and more attention on the use for ME composites [7]. However, comparatively low Curie temperature (120 °C) of BTO leads to poor temperature stability of electrical properties. Hence, it is necessary to use BTO-based lead free piezoelectric ceramics to increase the Curie temperature. Among various lead-free materials, bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$) abbreviated as BNT is an A-site substituted distorted perovskite compound ($ABO_3$), which is rarer than the B-site one [8]. A and B sites are refered to center (1/2, 1/2, 1/2) and corner (0, 0, 0) in a normal perovskite structure, respectively. A site substitution of BNT with drastically different ionic radius elements may have a more radical effect. These substitutions can induce a chemical stress to the structure, change lattice constant, and can even affect electronic structure through changing angle [9]. It has high Curie temperature ($T_c = 320$ °C) with relatively large remnant polarization ($P_r = 38$ μC/cm$^2$) [10]. By the introduction of BNT we could increase the Curie temperature of BTO ceramics [11,12].

In the present work, $0.65BiTiO_3–0.35Bi_{0.5}Na_{0.5}TiO_3$ (BFO–BT) was chosen as piezoelectric phase and $CoFe_2O_4$ (CFO) as magnetostrictive phase to prepare the laminated BTO–BNT/CFO composites. It was sintered at a temperature of 1100 °C, which is potentially used for low-temperature cofired ceramic (LTCC) technology. The sintering temperature is below the melting point of Ni. The aim of the present paper is to find a BTO-based piezoelectric material, which simultaneously enhances Curie temperature and the ME effect.

## 2. Experimental

Magnetoelectric laminate composites of $(1-x)0.65BTO–0.35BNT/xCFO$ ($x = 0.1, 0.2, 0.3, 0.4$) were prepared by the conventional solid-state sintering method. Commercial $BaCO_3$, $TiO_2$,

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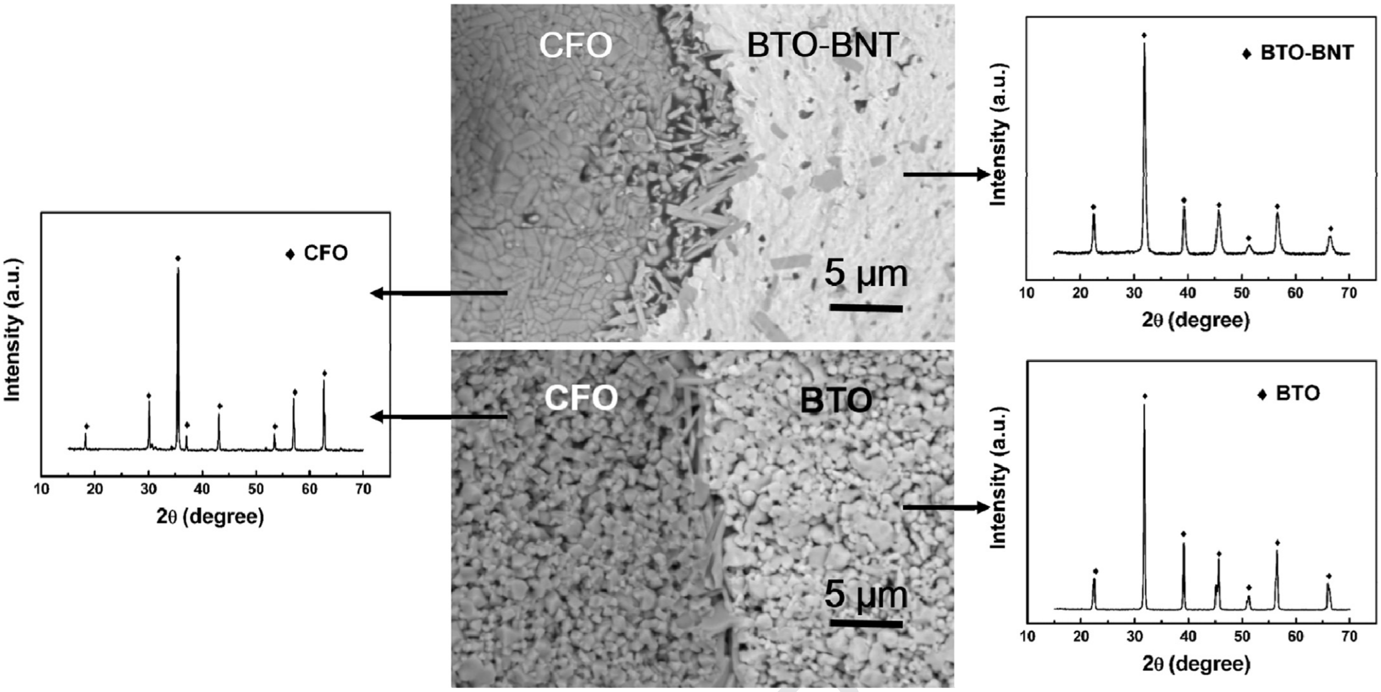

**Fig. 1.** SEM images of the 0.6BTO–BNT/0.4CFO laminate composite and 0.6BTO /0.4CFO laminate composite and the XRD patterns of each phase.

$Na_2CO_3$ and $Bi_2O_3$ were weighed, mixed thoroughly and calcined at 900 °C in air for 4 h to prepare BTO–BNT powder. Meanwhile, CFO was prepared from reagent-grade $Co_3O_4$ and $Fe_2O_3$, which were also weighed, mixed thoroughly and calcined at 1000 °C for 4 h. The purities of the above starting materials are all higher than 99%. The BTO–BNT powder and CFO powder were granulated after adding the same amount of PVA aqueous solution. According to different mass ratios, two fractions of granulated BTO–BNT powder and one fraction of granulated CFO powder were weighed and poured into the die in the sequence of BTO–BNT, CFO and BTO–BNT. The laminate sandwiched composite powders were preliminary pressed together in the die and then pressed at 200 MPa through the cold isostatic pressing method to ensure the same thickness of top and bottom BTO–BNT layers. In order to cofire the two phase together, the sintering temperature of the two phases should be consistent. The BTO/CFO laminate composites were also sintered at the same condition for comparison.

The phase composition of the BTO–BNT/CFO composites was analyzed using an X-ray diffractometer (D/max 2200pc, Rigaku, Tokyo, Japan). The microstructure of the BFO–BT/CFO composites was observed using a scanning electron microscopy (JEOL JSM-6390A JEOL Ltd., Tokyo). The dielectric properties and the impedance of the composites were measured using an impedance analyzer (E4980A, Agilent, Palo Alto, CA). The magnetic hysteresis loops of the composites were measured using a vibrating sample magnetometer 113 (Lake Shore 7410, Westerville, OH). The polarization hysteresis loop was characterized using a ferroelectric test system (Premier II, Radiant, USA). The piezoelectric coefficient ($d_{33}$) of the composite was measured using a quasi-state $d_{33}$ meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science). The ME measurements were done by varying the bias magnetic field (400 mT) under a superimposed ac magnetic field of 1 Oe ($f=1$ kHz) generated by Helmholtz coils. The

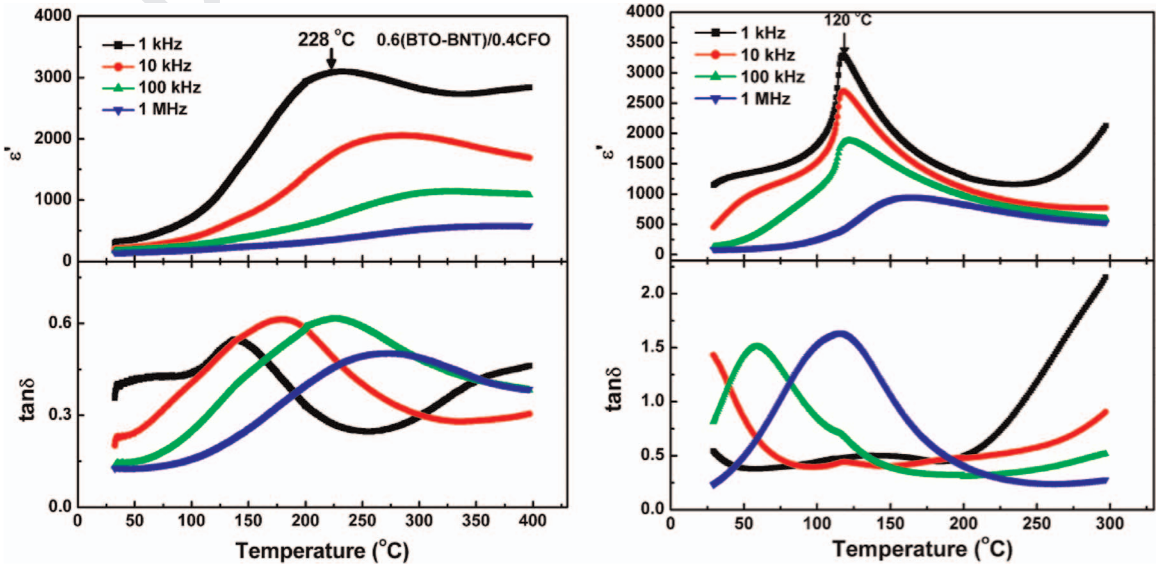

**Fig. 2.** Temperature dependence of the dielectric properties of the representative 0.6BTO–BNT/0.4CFO laminate composite and BTO/CFO laminate composites.

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