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# Size-dependent magnetoelectric response of $(Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3)$-$(Ni_{0.8}Zn_{0.2})Fe_2O_4$ particulate composites

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ABSTRACT

In this paper, we investigated the effect of magnetic grain size on magnetoelectric responses of particulate magnetoelectric $0.7(Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3)$-$0.3(Ni_{0.8}Zn_{0.2})Fe_2O_4$ (BNKT-NZFO) composites. The coexistence of two chemically separated phases was confirmed using x-ray diffraction analysis. The composites had homogeneous microstructure with controlled grain size. The magnetoelectric response of the BNKT-NZFO composites sensitively depended on the grain size of the NZFO phase and the magnetoelectric voltage coefficients presented a marked enhancement of 33% in the engineered grain size range. This result indicated that tailoring the magnetic grain size physically will provide a powerful mean of enhancing magnetoelectric coupling in a two-phase particulate composite, with large potential application in area of magnetic field sensor.

## 1. Introduction

Magnetic sensor is a system or device that can measure the creation or variation in magnetic fields of the surrounding environment without physical contact, which has been widely used in detection and imaging applications, such as microscopy imaging, navigation systems, non-destructive material testing, position and speed measurement and so on [1–3]. Multiferroic materials can be used to fabricate magnetic field sensors by utilizing the magnetically induced magnetoelectric (ME) effect, without the need of external power sources [4,5]. Compared to the traditional magnetic sensor, ME magnetic sensor has the advantages of self-power supply, miniature size, low detection limits, reliability and cost-effectiveness. The magnitude of ME conversion coefficient of multiferroic materials is a critical requirement in the realization of high-performance ME sensors. Considering the effective ME conversion, so far only bulk-sized ME composites that exhibit a large ME effect above room-temperature have the possibility to be implemented as current sensors [5,6]. However, the limited ME conversion coefficient is not enough to satisfy the practical usage in sensors. Therefore, the development of bulk ME composites with high ME response is technologically important. An ME composite can be physically labeled as particulate, fiber/rod and laminated structure, according to the geometrical connectivity of the magnetostrictive and piezoelectric phases. The bulk of particulate ME composites are distinguished by many advantages over a laminated or rod/fiber structure, including unlimited tailorability, superior mechanical strength and feasible preparation technology [7–9]. The ME effect of such attractive particulate composites not only lies strongly in intrinsic properties of the individual phase, but also in the strain-mediated magnetic-mechanical-electrical interaction at the interfaces through magnetostriction and electrostriction. A large number of investigations in recent years have reported on particulate composites to improve the ME effect, mainly focusing on constituent phase engineering, composition optimization and processing modification [7–11]. The available studies reporting on microstructure-related properties, such as the influence of grain size effect, size distribution and interface behavior on ME coupling, are rarely given mention. Specifically, while the proper content and phase connectivity in composites is designed to achieve the desirable ME coupling, the behavior of interface associated with particle size plays a crucial role in determining the strength of ME interactions. The presence of size difference in the two-phase isotropic microstructure of magnetostrictive/ferroelectric composite gives rise to local different contact area between two phases and affects the interfacial elastic coupling and ME voltage coefficient. Particularly, theoretical predictions highlighted that it is possible to significantly improve the ME coupling in particulate composites by manipulating the particles size of magnetic phase [12–14]. Motivated by this, we provide a systematic experimental investigation to understand the correlations between magnetic particle size and ME responses in particulate composites, aiming to increase ME conversion coefficient. Lead-free perovskite

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$Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$ (BNKT) exhibits high Curie temperature, large remnant polarization and an excellent piezoelectric coefficient, which is a favorable piezoelectric component for ME ceramics [15,16]. In parallel, the nickel-based ferrite shows attractive magnetic properties. The substitution of Zn in $NiFe_2O_4$ presents large saturation magnetization, high electrical resistivity and excellent low-field piezomagnetic coefficient, in favor of acquiring a high ME coefficient [17,18]. Therefore, in this work, a series of particulate composites constituted by $0.7(80Bi_{0.5}Na_{0.5}TiO_3$-$20Bi_{0.5}K_{0.5}TiO_3$-$0.3(Ni_{0.8}Zn_{0.2})Fe_2O_4$ (BNKT-NZFO) with NZFO particle size gradient were prepared and the effect of size on ferroelectric and magnetic properties, as well as ME response were investigated. The variation in NZFO particle/grain size of composites was achieved by ball-milling. ME measurements reveal that ME coefficient of particulate composites with two-phase microstructure can be effectively tailored by engineering the particle size of the magnetic phase.

## 2. Experimental method

The sol-gel technique was employed for fabrication of $0.8Bi_{0.5}Na_{0.5}TiO_3$-$0.2Bi_{0.5}K_{0.5}TiO_3$ (BNKT) and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZFO) powders. The starting raw materials were analytical reagent grade Bi $(NO_3)_3{\cdot}5H_2O$, $NaNO_3$, $KNO_3$, $Ti(OC_4H_9)_4$, $Ni(NO_3)_2{\cdot}6H_2O$, Zn $(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$. Ethylene diamine tetra acetic acid (EDTA) was used as complexing agent and deionized water served as a solvent. Initially the stoichiometric amount Bi-Na-K-Ti sol was heated up to 80 °C under stirring, adjusting the pH value to 7 by ammonia. The gelation of the sol was dried at 120 °C for 8 h first and then pre-sintered at 450 °C for 4 h. Subsequently, the mixture powder was ground and sintered at 1150 °C for 2 h in air to obtain BNKT powders. A similar process was performed in the synthesis of NZFO powder. Differently, the pre-sintered Ni-Zn-Fe powder was pelleted and sintered at 1000 °C for 4 h. Sequentially, to form the particle size gradient, the as-prepared NZFO pellets were pulverized and ball-milled with grinding zirconia media ($\Phi \times 3$ mm and $\Phi \times 7$ mm) in high-energy planetary ball-milling for different time (1–9 h). By increasing the milling time in the ball-milling process, however, the temperatures of the ball mill tank system and the NZFO particles will rise, and the material crystal structure may be changed. A circulatory cooling system was actually used in the ball-milling system to suppress the temperature rise, ensuring the controllability of the ball-milling process and the stability of the material properties. Then the obtained BNKT powders and the ball-milled NZFO particles were taken in a required molecular ratio of 7:3 and thoroughly mixed in acetone media for 8 h using a low-energy ball mill. The mixed powders were pelleted and finally sintered at 1070 °C for 2 h in air. The as-prepared pellets were electroded with silver on both the surfaces for further electric properties and ME measurements.

The crystalline phases of the samples were identified by X-ray diffraction (XRD, Philips X-Pert Pro). Microstructure and composition were studied by scanning electron microscope (SEM, TESCAN VEGA 3) and energy-dispersive spectroscopy (EDS). The bulk density of pellets was measured using Archimedes' method and grain size was determined by mean linear intercept. DC resistivity was measured using precision LCR meter (TH2829C). The piezoelectric coefficient $d_{33}$ was measured using the $d_{33}$ meter (ZJ-3AN). Dielectric characteristics were performed using a HP4284 LCR meter. A magnetodielectric effect was obtained by combining an LCR meter and a superconducting magnet. Ferroelectric hysteresis loops were measured using a ferroelectric tester based on Sawyer Tower circuit. Magnetic hysteresis loops were characterized using a vibrating samples magnetometer (Lakeshore 7404). The transverse magnetostriction measurement $\lambda_{11}$ (the direction of dc magnetic field parallel to the sample plane and strain gage) was measured with a standard strain gauge method. The electroded sample was polarized perpendicularly to the pellet plane in the field of 5 kV/cm prior to the ME measurements. The transverse ME measurements (the direction of magnetic field perpendicular to the direction of polarization) were carried out using the lock-in technique. A small alternating magnetic field H ($f$ = 1 kHz, $H_{ac}$ = 1.0 Oe) was generated using a solenoid that was superimposed onto a magnetic bias up to 3.5 kOe.

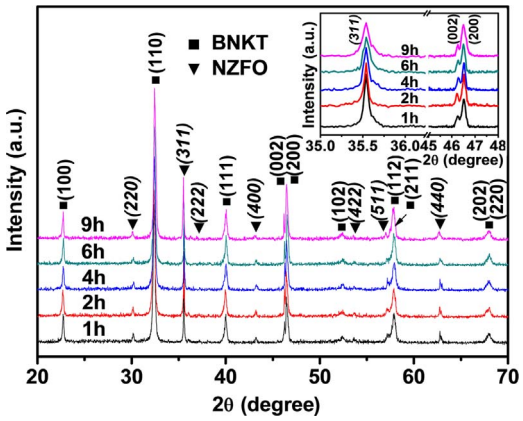


**Fig. 1.** XRD patterns of the BNKT-NZFO composites with different milling time (1 h, 2 h, 4 h, 6 h and 9 h) of NZFO. Inset shows the magnified XRD patterns in the angle range of 35–36° and 45–48°.

## 3. Results and discussion

Fig. 1 presents the XRD patterns of BNKT-NZFO composites with different milling time (1 h, 2 h, 4 h, 6 h and 9 h) of NZFO. The characteristic well-defined set of peaks confirms the formation of the individual perovskite structure BNKT phase and cubic spinel structure NZFO phase, respectively. No traces of impurity peaks are detected, indicating that no significant chemical reaction occurred at the phase interface. The widening of the peak (311) corresponding to the NZFO phase with the increase of milling time suggests the refinement crystallite size, shown in inset of Fig. 1. Concurrently, the splitting of (200) and (002) peaks are clearly found in the vicinity from 45° to 48° for samples, which reveals the coexistence of a rhombohedral and tetragonal structure in BNKT constituent [16]. Such a feature is indicative of the presence of the morphotropic phase boundary and helps to enhance piezoelectric response. Additionally, no peak shifting is observed in the XRD patterns, suggesting no structural changes occurred in BNKT-NZFO composites.

The micromorphology of the BNKT-NZFO particulate composites is presented in Fig. 2. Distinct and well-crystallized light and dark phase regions can be easily identified, which corresponds to BNKT and NZFO phases, respectively. The well-dispersed NZFO particles embedded in continuous BNKT matrix not only ensure effectively transfer of strain from each phase, but also avoid the formation of a leakage path caused by the assembly of the low resistance magnetic phase. Expectedly, the sintered homogeneous composites show the evident size gradient of magnetic phase and the average grain size ranges from 4.29 μm to 1.21 μm with increasing milling time, shown in inset of Figs. 2(a)–2(e). There was no significant variation in the size of the BNKT in composites. Furthermore, the composites exhibited well-packed microstructures without obvious micropores or cracks, in accordance with the relative high density of 91–93% (listed in Table 1). Also sintering with small particle sizes slightly increases densification of composite. Fig. 2(f) shows the grain size dependence of atomic ratios of Fe/Ti and Zn/K. The observed values of the Fe/Ti and Zn/K atomic ratio are in good agreement with the theoretical values of 0.907 and 1.301, respectively. Based on the analyses of the composition of two phases, the inter-diffusion between phases was minimized. This is an important result for investigating size effect, as it ensures that the difference in the electric, magnetic and ME responses of composites comes mainly from the size difference, but not from others aspects, such as impurity or inter-diffusion effects.