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Multiferroic properties of lead-free $Ni_{0.5}Zn_{0.5}Fe_{1.9}O_{4-\delta}-Na_{0.5}Bi_{0.5}TiO_3$ composites synthesized by spark plasma sintering

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Abstract

Multiferroic composites of x $Ni_{0.5}Zn_{0.5}Fe_{1.9}O_{4-\delta}-(1-x)$ $Na_{0.5}Bi_{0.5}TiO_3$ (x NZF$-(1-x)$ NBT, where $x=0.05$, 0.15 and 0.25 mol fraction) were synthesized by spark plasma sintering (SPS) in conjunction with high-energy ball milling. The presence of NZF and NBT phases in the composites was confirmed by X-ray diffraction. The dielectric constant was studied as a function of frequency (0.5 kHz to 1 MHz) and temperature (30–500 °C). It was found that the 0.25 NZF–0.75 NBT composite possessed the most promising dielectric properties with its dielectric constant being 5–10 times higher than those for the other two composites in the full range of frequency. The magnetic and ferroelectric properties were examined at room temperature and all composite samples exhibited both pronounced ferromagnetic and ferroelectric characteristics. A maximum ME voltage coefficient of ~870 μV/cm Oe was obtained at the magnetic field of ~1.25 kOe for the 0.25 NZF–0.75 NBT composite, which was well comparable with the ME output for the lead-containing NZF–PZT composites.

Keywords: B. Composites; C. Magnetic properties; C. Ferroelectric properties; C. Electrical properties; D. Ferrites

1. Introduction

Multiferroic magnetoelectric (ME) materials have been attracting considerable attention for their potential applications in memories, sensors and transducers [1]. Such materials can display not only ferroelectric and ferromagnetic ordering but also coupling ME effect, i.e., a dielectric polarization induced by an external magnetic field or a magnetization induced by an applied electric field [2]. However, proper room-temperature single phase multiferroic compounds are still sparse due to the mutual exclusion of ferromagnetism and ferroelectricity, although several families of compounds have been intensively investigated as multiferroics [3]. It is well-known that $PbZr_xTi_{1-x}O_3$ (PZT) ceramics are the most widely used piezoelectrics due to their superior piezoelectric properties. Nevertheless, they are not environment-friendly due to the lead oxide toxicity. Many researchers have focused on environment-friendly lead-free piezoelectrics such as (KNa)NbO_3-based, ($Na_{0.5}Bi_{0.5}$)TiO_3-based and $Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$ systems [4–6]. Among these, $Na_{0.5}Bi_{0.5}TiO_3$ ceramics are promising for their excellent ferroelectric properties as a new candidate for use in lead-free piezoelectric and pyroelectric ceramics. It is well-known that NBT possesses a Curie temperature (T_c) of 320 °C, a relatively large remanent polarization (P_r) of 38 μC/cm^2, and a coercive field (E_c) of 73 kV/cm at room temperature [7].

In recent studies on NBT-based composites, Praveena et al. [8] have investigated the ME properties of NBT–$MnFe_2O_4$ composites prepared by sol–gel technique followed by a conventional sintering method. Babu et al. have studied $Na_{0.5}Bi_{0.5}TiO_3$–$NiFe_2O_4$ [9], $Na_{0.5}Bi_{0.5}TiO_3$–$CoFe_2O_4$ [10], and $Na_{0.5}Bi_{0.5}TiO_3$–$Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_4$ [11] ME composites by a solid state conventional double sintering method. Ramana et al. [12] have studied $Na_{0.5}Bi_{0.5}TiO_3$–$BiFeO_3$ ME composites by a semi

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sol–gel method. The conventional solid state double sintering method invovles two-steps. Initially the powders are partially sintered (called the pre-sintering or calcination) at a lower temperature, and then they are milled again for a few hours followed by final sintering at a higher temperature. The semi sol–gel method is a citrate precursor method. In this method, the stoichiometric quantities of nitrates are mixed in a solution, followed by stirring to transform into an aqueous solution. The metal nitrates are converted to different citrates by addition of citric acid. The precursor solution is heated to form a sol and subsequently a gel by adding gelatin reagent, viz. ethylene glycol. The resulting gel is pulverized and calcined at an elevated temperature to obtain ceramic powders.

There are limited reports on the magnetic and ferroelectric properties of spark plasma sintered NBT-based ME composites. There are no reports of the influence of microstructure on the multiferroic properties of multiferroic composites. As far as the development of magnetoelectric ceramic composites is concerned, the properties of individual ferroelectric and ferromagnetic phases, the distribution of the two phases, and the volume fraction of ferromagnetic phase should be taken into consideration. The uniform distribution of ferrite particles in the ferroelectric matrix could be crucial to exhibit magnetoelectric coupling. When the ferrite particles are connected as chains, the electrical resistivity of the composite will reduce significantly due to the low resistivity of ferrite. Of course, additional phases created by chemical reactions between two constituting phases should be avoided.

In the preparation of multiferroic ceramic composites, the choice of ferroelectric and ferromagnetic components depends on their Curie transition temperatures, good piezoelectric properties of the piezoelectric phase, high piezomagnetic properties of the magnetostrictive phase, high electromechanical and magnetomechanical coupling coefficients and structural comparability. A highly piezomagnetic insulator should be chosen as the magnetostrictive component in the particulate composites. The resistivity of the magnetostrictive phase should also be as high as possible in order to avoid short circuit path for the ME voltage developed in the ME composite through the ferromagnetic phase. Recently [13], we investigated the mutiferroic properties of $Ni_{0.83}Co_{0.15}Cu_{0.02}Fe_{1.9}O_{4-\delta}$–$Na_{0.5}Bi_{0.5}TiO_3$ (NCCF–NBT). The results indicated an apparent magnetoelectric effect. Since the Cu-doped Ni-ferrite undergoes a structural phase transition accompanied by reduction in the crystal symmetry due to the co-operative Jahn–Teller effect [14], NCCF shows promising magnetic properties. The distortion of the ferrite lattice due to the Jahn–Teller ions (i.e. Ni^{2+} and Cu^{2+}) induces a stress in the nearby ferroelectric lattice, which may result in an improvement of electrical properties. Moreover, the Ni-ferrite doped with Co has high resistivity and magnetostriction under a low magnetic field [15]. In the present work, a highly magnetostrictive ferrite generally used for high-power ultrasonic applications, $Ni_{0.5}Zn_{0.5}Fe_{1.9}O_{4-\delta}$ (NZF) [16–18], was chosen as the ferrite component. In this ferrite, Fe deficiency could suppress the formation of Fe^{2+} and thus its resistivity could increase by orders of magnitude [19]. The selected ferroelectric component was NBT as used in our previous work [13]. The study was focused on electrical, magnetic and magnetoelectric properties of different NZF–NBT composites synthesized by spark plasma sintering (SPS) in conjunction with high-energy ball milling in order to determine a promising combination of NZF and NBT.

2. Experimental procedure

Lead-free multiferroic composites of x NZF–$(1-x)$ NBT (where $x=0.05$, 0.15 and 0.25 mol fraction) were synthesized by virtue of SPS in conjunction with high-energy ball milling. The piezomagnetic NZF was synthesized from the stoichiometric powders of NiO, ZnO and Fe_2O_3, and the ferroelectric NBT from the stoichiometric powders of $NaCO_3$, Bi_2O_3 and TiO_2. The precursor powders of NZF and NBT were prepared separately by high-energy ball milling. The milling was carried out in a high-energy ball mill at room temperature for 10 h. Wet milling was done in absolute ethanol media in tungsten carbide (WC) vials with 10 mm diameter WC balls at 400 rpm and 10:1 ball to powder weight ratio. After ball milling, the slurries were dried at 70 °C for 12 h. The dried NZF and NBT powders were blended in different mole ratios and ground thoroughly again for 3 h for subsequent SPS synthesis. High-energy ball milling has been used to prepare the precursor powders for synthesis of fine-grained ferroelectrics, ferrites, composites, and other metal alloys [20,21]. Compared with normal ball-milling processes, the high-energy ball milling is more efficient in strengthening the rate of reaction and modifying the particle morphology of materials [22]. The high-energy ball milling may increase the driving force of sintering, accelerate the sintering process, and lower the sintering temperature. There may be particle agglomeration after long-period milling. Our previous work [17] has indicated that the 10 h high-energy ball milling usually does not cause apparent particle agglomeration. The ball-milled powders were sintered in a spark plasma sintering furnace under a vacuum of 10^{-2} Pa. They were loaded into a graphite die to sinter disk-shaped pellets of 10 mm diameter. According to our previous work [13], the heating rate was chosen as 100 °C/min, and the sample was sintered at 950 °C for 5 min under a uniaxial pressure of 50 MPa. The SPS-consolidated samples were annealed at 850 °C for 2 h in air to ensure their full oxidation and possible graphite contamination removal. Details on the SPS can be seen elsewhere [23,24].

The phase purity and structure of the samples were evaluated by X-ray diffraction (XRD) using a Rigaku diffractometer with Cu-Kα radiation (D/max-RB, Rigaku Co., Tokyo, Japan). The parameters of XRD were: acceleration voltage=40 kV; beam current=200 mA; 2θ scanning step=0.02°, and 2θ scanning range=20°–80°. Optical microscopy was used to observe the overall morphologies of NZF and NBT phases with the polished samples, and scanning electron microscopy (S-4700 SEM) was used to examine the detailed microstructure of each phase with the samples thermally etched at 800°C. The samples were electroded with silver and then poled in an electric field (40 kV/cm) at 100 °C for dielectric, piezoelectric and ferroelectric measurements. The dielectric measurement was carried out by means of a Hioki 3535-50 LCR Meter. The piezoelectric coefficient (d_{33}) was measured using a quasi-static d_{33} meter. Ferroelectric measurements were performed by virtue of an automatic PE loop tracer