Research Article

Multiferroic Properties of Nanopowder-Synthesized Ferroelectric-Ferromagnetic 0.6BaTiO_3 - $0.4\text{NiFe}_2\text{O}_4$ Ceramic

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Multiferroic 0.6BaTiO_3 - $0.4\text{NiFe}_2\text{O}_4$ dense nanoceramic composites were synthesized via a powder-in-sol precursor hybrid chemical synthesis route and a ceramic sintering process. At the measured frequency range (1 kHz~1 MHz), the relative dielectric constant is 150~1670 and the dielectric loss is 0.05~0.70. The composite ceramic showed obvious coexistence of ferroelectric and ferromagnetic phases. With the increase of temperature, the saturation ferromagnetic magnetization decreases, while the ferroelectric polarization increases.

1. Introduction

Multiferroic materials have been formally defined as materials that exhibit more than one primary ferroic order parameter simultaneously and have stimulated much scientific and technological interest, owing not only to potential applications for devices taking advantage of the multiferroic coupling, but also to the interesting physics manifested by these materials [1]. It was first presumed to exist by Curie in 1894 based on the crystal symmetry considerations [2]. The multiferroic effect was first experimentally observed in Cr_2O_3 in 1961 [3, 4], and over the recent decades, a lot of monophase materials have been investigated [5]. However, due to low Neel temperature, it is difficult to use them in practical devices [3–5]. As a possible alternative, laminated ferromagnetic/ferroelectric composites have received much interest with regard to product properties [6, 7]. The multiferroic effect in a composite ceramic or laminated structure has a multiferroic coupling constant two or three orders higher than that in single phase structures [6, 7].

However, the laminated structure is limited by the feature size, miniaturizing difficulties, and brittleness. Composites ceramics are limited by their high dielectric loss, often higher than 1, which is not good for practical applications [7]. The high dielectric loss should be attributed to the interface reaction at high sintering temperature and the low resistance of the magnetic phase. Therefore, choosing the suitable ferroelectric and ferromagnetic phases and decreasing the sintering temperature to reduce the reactions at the phase interfaces, are crucial for the excellent multiferroic properties of ceramic composites.

In our research, we select the conventional barium titanate BaTiO_3 as the ferroelectric phase and use nickel ferrite NiFe_2O_4 as the ferromagnetic phase, due to its low anisotropy and high initial permeability. We also prepared nanopowders to synthesize BaTiO_3 (BT) phase and nickel ferrite phase in order to decrease the sintering temperature and reduce the interface reactions. A chemical method was developed to mix ferromagnetic and ferroelectric phases uniformly at the microscale, which also favors the multiferroic

coupling. The temperature dependence on the multiferroic properties of $0.6\text{BaTiO}_3\text{-}0.4\text{NiFe}_2\text{O}_4$ nanoceramic was presented in this paper. The combination of nickel ferrite and BaTiO_3 leads to a good multiferroic property.

2. Experimental Section

The $0.6\text{BaTiO}_3\text{-}0.4\text{NiFe}_2\text{O}_4$ composites were made of two individual phases. The nano- BaTiO_3 powders were synthesized via a hydrothermal method [8]. $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{C}_6\text{H}_8\text{O}_7\cdot \text{H}_2\text{O}$, and NH_4OH were used to synthesize NiFe_2O_4 ferrite. Highly dense microparticulate ceramics of the $0.6\text{BaTiO}_3\text{-}0.4\text{NiFe}_2\text{O}_4$ compound were synthesized via a chemical powder-in-sol precursor hybrid synthesis route and ceramic sintering process. The process for original mixture powder was shown in Figure 1. Nano- BaTiO_3 powders were mixed directly with ethanol and ball-milled for 4 hours. Appropriate amounts of metal nitrates $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (5.7260 g); $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (15.8314 g), and citric acid were first dissolved into a beaker in a minimum amount of deionized water (150 mL). The pH of the solution was approximately 2. Appropriate amounts of ball-milled BaTiO_3 (pH-9) were added into the beaker. A small amount of ammonia and deionized water was added to the solution to adjust the pH value to about 7.5. The mixed solution was then put into an oven to dry for 72 hours at 130°C . In this process, the solution was heated and stirred to transform into a xerogel. The dried gel was burnt in a self-propagating combustion manner until all the gel was burnt out completely to form loose powder.

A simultaneous thermal analyzer (NETZSCH STA 449C) was used for thermogravimetric analysis and differential scanning calorimetry (TG and DSC) of the combustion process. The decomposition behavior of the resulting dried powder was studied at a heating rate of $10^\circ\text{C}/\text{min}$ from the room temperature to 1300°C . On the basis of the TG and DSC results, the synthesized $0.6\text{BaTiO}_3\text{-}0.4\text{NiFe}_2\text{O}_4$ powder was pelletized at a pressure of 220 MPa using polyvinyl alcohol as a binder. The pellets were sintered at 1150°C for 4 hours.

The density of sintered pellet was determined by Archimedes' method. The phase structure was analyzed using a $\text{Cu K}\alpha$ (0.15406 nm) X-ray Diffractometer (XRD) (PW-1830, Philips, Netherlands). A scanning electron microscopy (SEM, 1530 YP, Leo Co., Germany) was used for analyzing the microstructure of the ceramic sample. The complex dielectric permittivity and loss over a broad frequency range (1 kHz~1 MHz) were measured in vacuum with a HP 4192A impedance analyzer. The low temperature data were obtained starting from liquid nitrogen temperature. The magnetization hysteresis was performed by superconducting quantum interference device (SQUID). Ferroelectric performance was measured using a TF analyzer 2000 FE-Module (at 1 Hz).

3. Results and Discussion

The sintered $0.6\text{BaTiO}_3\text{-}0.4\text{NiFe}_2\text{O}_4$ ceramic is dense with a density of $5.409\text{ g}/\text{cm}^3$, which is equivalent to 93.92% of the

FIGURE 1: Processing route for preparing uniformly distributed slurry.

FIGURE 2: TG and DSC curves of the composite.

theoretical density (the half of the sum of BaTiO_3 density of $6.02\text{ g}/\text{cm}^3$ and NiFe_2O_4 density of $5.368\text{ g}/\text{cm}^3$).

Figure 2 shows the decomposition behavior of the synthesized powder obtained by DSC and TG measurements. The decomposition reaction proceeds mainly via three stages. The initial TG mass loss up to 130.5°C corresponds to the dehydration of the precursor. Next mass loss in the temperature range $200\sim 400^\circ\text{C}$ corresponds to the decarboxylation of oxalates, which results in an exothermic peak in the DSC curve at 268.9°C . Further weight loss in the temperature range of $400\sim 600^\circ\text{C}$ is due to the decomposition of residual $\text{Fe}(\text{NO}_3)_3$ and $\text{Ni}(\text{NO}_3)_2$ with an exothermic peak at 487.7°C . The total mass change is approximately 49.89%.

Figure 3 shows the XRD patterns. The particulate composite contains both the BaTiO_3 phase with a ferroelectric tetragonal perovskite structure and the NiFe_2O_4 phase with a ferromagnetic cubic spinel structure and no other impure phase is observed from the XRD results, which suggests that there is no significant chemical reaction during the sintering.

Figure 4 shows the surface SEM of the dense diphasic microstructure of $0.6\text{BaTiO}_3\text{-}0.4\text{NiFe}_2\text{O}_4$ multiferroic ceramic. The average grain size of the composite ceramic is about 1 micrometer.

FIGURE 3: The results of XRD analysis for the composite.

FIGURE 4: Microstructure of surface area of the sintered composite by SEM.

The result of dielectric constant and dielectric loss tangent as a function of frequency was shown in Figure 5. With the increase of frequency, both the dielectric constant and the dielectric loss tangent decrease continuously. The high dielectric loss tangent (0.05~0.70) at low frequencies are mainly attributed to the dipoles which resulted from the change in valance of cations, such as $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Ni}^{2+}/\text{Ni}^{3+}$ [9, 10].

Nickel ferrite possesses a low magnetic anisotropy and a high initial permeability. Figure 6 shows magnetic hysteresis ($M\sim H$) of the composite at 5 K and 290 K, respectively. The sample exhibits typical magnetic hysteresis behavior at 290 K, which indicates the ferromagnetic characterization of the $0.6\text{BaTiO}_3\text{-}0.4\text{NiFe}_2\text{O}_4$ ceramic. The saturation magnetizations are $\sim 5\text{ emu/g}$ and $\sim 2.8\text{ emu/g}$ at the temperatures of 5 K and 290 K, respectively. With the increase of temperature, the saturation ferromagnetic magnetization of the composite

FIGURE 5: Dielectric constant (a) and dielectric loss tangent (b) as a function of frequency.

ceramic decreased and was much lower than that of pure NiFe_2O_4 , which corresponded with the high nonmagnetic phase (ferroelectric) in this composite [11].

The small hysteresis in Figure 6 indicates the week ferromagnetism of the composite. The magnetic properties are mainly determined by the content of NiFe_2O_4 phase. In this composite, the nonmagnetic BaTiO_3 phase prevents the interaction of the magnetic poles in the magnetic particles.

Quasistatic ferroelectric measurements indicate ferroelectric hysteresis as shown in Figure 7. NiFe_2O_4 ferrite phase has a low resistivity compared to the BaTiO_3 ferroelectric phase, which leads to a large conductivity of the multiferroic composite ceramic [12]. With the increase of temperature, the ferroelectric loop becomes lossy due to the influence of the relatively high conductivity in NiFe_2O_4 phase, which may originate from the mixed valence of the magnetic ions (e.g., Fe^{2+} and Fe^{3+}) or from oxygen vacancies during the sintering process of the biphasic ceramic [13, 14]. High conductivity usually leads to a pseudohysteresis loop and even low electric

FIGURE 6: Ferromagnetic hysteresis M - H curve at different temperatures (5 K, 290 K).

FIGURE 7: Ferroelectric hysteresis loops of the 0.6BaTiO₃-0.4NiFe₂O₄ composite.

field endurance. At room temperature, the curve looks like a Lissajous plot, which is not a reliable ferroelectric loop. The ferroelectric remnant polarization strength of the 0.6BaTiO₃-0.4NiFe₂O₄ ceramic is approximately 105 $\mu\text{C}/\text{cm}^2$ at 300 K. The addition of the nonferroelectric NiFe₂O₄ phase hinders and pins the domain wall motion of ferroelectric regions and leads to the increase of the remanent polarization in the biphasic ceramic (the remanent polarization of the pure BaTiO₃ ceramic is $\sim 2 \mu\text{C}/\text{cm}^2$) [15–17].

4. Conclusions

Multiferroic ceramic of 0.6BaTiO₃-0.4NiFe₂O₄ was synthesized via a chemical sol-gel precursor technique and ceramic sintering process. On basis of the XRD results, the nanopowder-synthesized ceramic contains both the ferroelectric tetragonal BaTiO₃ phase and the ferromagnetic cubic NiFe₂O₄ phase. The ferromagnetic M - H hysteresis and ferroelectric P - E hysteresis properties demonstrate its multiferroicity.

Conflict of Interests

The authors do not have any conflict of interests in their submitted paper.

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