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The static and hyper-frequency magnetic properties of a ferromagnetic–ferroelectric composite

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ABSTRACT

This paper reports the static and hyper-frequency magnetic properties, as well as their relationship with microstructure, of the ferromagnetic–ferroelectric co-fired composite ceramic, $(1-x)Ba_2Zn_{1.2}Cu_{0.8}Fe_{12}O_{22}-xPb(Ni_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}O_3$. The X-ray diffraction results did not detect any other phase in the co-fired ceramics, but found a crystal structural distortion of ferrite phase. Scanning electron microscopy photos showed that two phases' grains matched well and stacked compactly and the hexagonal ferrite changed its grain morphology. The saturation magnetization increased with the reduction of magnetic phase in the range of $0<x<0.65$ because of the stress-induced structural distortion. The permeability decreases monotonically with the reduction of magnetic phase in the whole composition range.

1. Introduction

In recent years, ferromagnetic–ferroelectric composite is one of the most attractive subjects in terms of materials science. Many new properties induced by the coupling between ferromagnetic and ferroelectric phases, such as magnetoelectric and magnetooptical effects [1–4], have been arousing much attention. Their multifunctionality is also greatly needed in the novel integrated components, with the rapid development of portable electronic products and wireless technology [5–7]. Hence, many material systems, such as $BaTiO_3$+NiCuZn ferrite, $Pb(ZrTi)O_3$+NiCuZn ferrite and $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$+NiCuZn ferrite, have been prepared, and exhibit fine dielectric and magnetic properties [7–14].

It is better to achieve both large magnetization and polarization for multiferroic materials. But it is hard to reach due to the dilution effect in ferromagnetic–ferroelectric composites. The properties of composites are not only dominated by that of each phase, but also affected by the co-firing behavior and microstructure. Then, it is possible to enhance magnetization or polarization inverse to the dilution effect by controlling the microstructure. In this paper, we focus on the relationship of co-firing behavior and microstructure with the magnetic properties of the co-fired composite ceramics, $(1-x)Ba_2Zn_{1.2}Cu_{0.8}Fe_{12}O_{22}-x Pb(Ni_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}O_3$, where $Ba_2Zn_{1.2}Cu_{0.8}Fe_{12}O_{22}$ (BZCF) is a Y-type hexagonal ferrite and $Pb(Ni_{1/3}Nb_{2/3})_{0.8}Ti_{0.2}O_3$ (PNNT) is a typical relaxor ferroelectric. The saturation magnetization is found enhanced with the reduction of magnetic phase, which is controlled by the microstructure. This work suggests that it is feasible to enhance magnetization and polarization simultaneously in a multiferroic composite by modulating the microstructure.

2. Experimental procedure

In this experiment, $(1-x)$BZCF–xPNNT composite ceramics were prepared by the standard ceramics method, where PNNT's molecular fraction of x varied from 0 to 0.97. PNNT was fabricated via a columbite-type route, using analytical reagent (AR) grade PbO, NiO, Nb_2O_5 and TiO_2 (Beijing Chemical Works, China) as raw materials. The precursor of $NiNb_2O_6$ was formed at 1000 °C for 3 h, and then mixed with PbO and TiO_2 according to molar ratio. After ball-milling for 24 h, the resulting mixture was calcined at 880 °C for 3 h to form PNNT. For BZCF, AR grade $BaCO_3$, Co_3O_4, ZnO, CuO and Fe_2O_3 (Beijing Chemical Works, China) were weighed and mill-mixed for 24 h. After drying, the mixtures were calcined at 1000 °C to form BZCF. The PNNT and BZCF powders were mixed in a ball mill. After drying and prilling, the granules were pressed in

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a stainless-steel die under a pressure of 7 MPa. The pressed toroidal samples (20 mm outside diameter, 10 mm inside diameter, about 3 mm thickness) were sintered in the temperature range of 950–1100 °C for 4 h in air and then cooled in the furnace. During the sintering process, the samples were covered with the same powder to minimize evaporation loss of lead oxide.

The phase composition were characterized by X-ray diffraction (XRD), using a Rigaku X-ray diffractometer equipped with CuK$_\alpha$ radiation ($\lambda = 1.5405$ Å). Field emission scanning electron microscope (SEM, JEOL, JSM-6301F) was used to observe the microstructure of fracture surface of the sintered specimens. The magnetization measurement was measured on a vibrating sample magnetometer (VSM, LakeShore VSM 7307) at room temperature. For each composition, three samples were used in the VSM measurement, and the measurement was done twice. The frequency dependence of the composites' complex permeability was recorded by Agilent E4991A RF impedance/material analyzer from 1 MHz to 1 GHz.

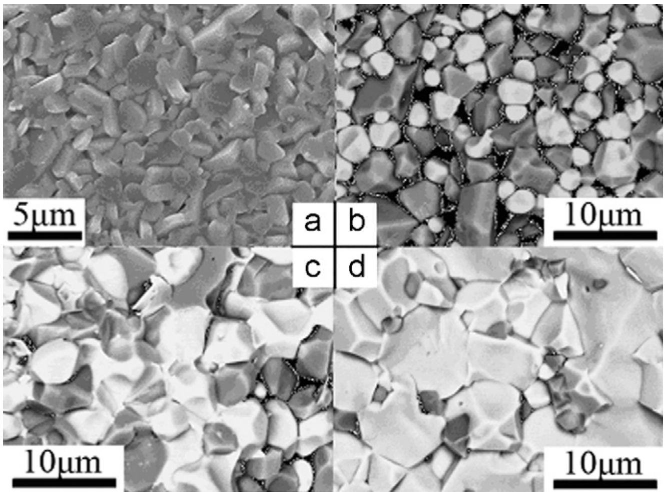

Fig. 1. SEM photos of the samples sintered at 1050 °C: (a) $x = 0$; (b) $x = 0.65$; (c) $x = 0.87$ and (d) $x = 0.97$ (a: secondary electron image; b, c and d: backscattered electron image).

3. Results and discussion

Fig. 1(a–d) shows the microstructure of the co-fired composite ceramics sintered at 1050 °C for 4 h ($x = 0$, 0.65, 0.87 and 0.97). The grain morphology in the composites can be observed using SEM, as BZCF and PNNT grains are distinctively black and white in the backscattering electron images. Each sample exhibits a dense microstructure, while the grains of two phases distribute homogeneously and match very well. In addition, the grain morphology changes obviously with the composition. In the pure ferrite sample ($x = 0$), the grains are plate-like and many of them have hexagonal shape (Fig. 1(a)). But in the co-fired ceramics (Fig. 1(b–d)), the planar grains of hexagonal ferrite become equiaxed crystals just as those ferroelectric grains. The ferrite's grain size declines with the rise of PNNT's amount. Because the equiaxed crystal is more favorable for a compact-stack microstructure than planar crystal, the surrounding equiaxed grains of PNNT will modulate the grain growth of BZCF and assimilate their grain shape into equiaxed crystal during the co-firing process. It is well known that the internal stress cannot be avoided in the co-fired ceramics due to different densification rate of two phases. In the $(1-x)$BZCF–xPNNT co-fired ceramics, the compact-stacked grains and the grain morphology change of BZCF imply a notable internal stress in the co-fired ceramics.

To characterize the crystal structure and phase composition, XRD spectra of green (before sintering) samples and sintered samples are compared in Fig. 2. After the XRD spectra are well indexed, no other phase was found after co-firing process, i.e. no obvious chemical reaction takes place between BCZF and PNNT. While x is higher than or equal to 0.95, there is no difference between the XRD patterns of green samples and those of sintered samples. Only perovskite phase can be detected, because its electron density is much lower than that of complex Y-type

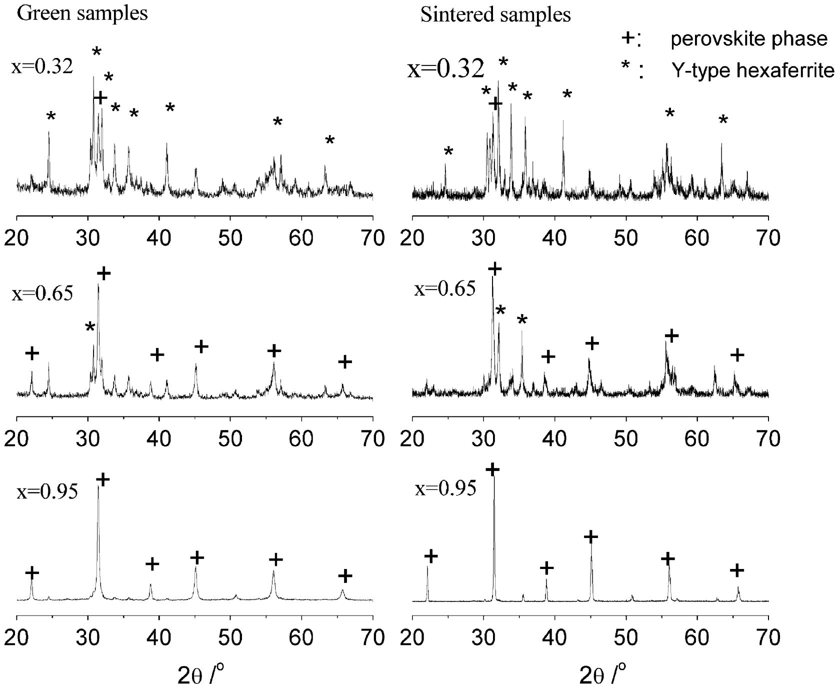

Fig. 2. XRD spectra of the samples before sintering and after sintered at 1050 °C for 4 h.