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Structure and properties of PMN–PT/NZFO laminates and composites

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Abstract

Magnetoelectric (ME) materials of laminated and bulk composites of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ (PMN–PT) and Zn-doped ferrite $Ni_{0.8}Zn_{0.2}Fe_3O_4$ (NZFO) were prepared. The weight ratio of PMN–PT to NZFO in the composites was 5:1. ME coefficients of the laminated and bulk samples at 1.1 kOe magnetic bias were 91 mV/cm Oe and 64 mV/cm Oe, respectively. The ME coefficient of the bulk sample reached 406 mV/cm Oe under a magnetic bias of 0.26 kOe, which was much higher than the reported value in the composite of PZT and nickel ferrite. One of the findings in this study is that a non-uniform distribution of magnetic material in the bulk may lead to enhanced ME effect.

Keywords: C. Magnetostrictive; D. Composite; PMN–PT; Nickel ferrite

1. Introduction

In the past few decades, extensive research has been conducted on the magnetoelectric (ME) effect in single phase and composite materials. In materials that are magnetoelectric, the induced polarization is related to the magnetic field. The effect was first observed in antiferromagnetic Cr_2O_3, with a ME coefficient of 20 mV/cm Oe at room temperature [1]. Composites are of interest for the enhancement of ME effects [2,3]. The ME composites of primary interest in the past were nickel or cobalt ferrite with $BaTiO_3$. However, the measured coefficient values were 2–3 orders of magnitude smaller than predicted values [4]. The main reasons include low resistivity for ferrites and chemical reactions between the two phases. These problems could be eliminated in a laminated structure [2,5]. However, poor bonding between the layers could lead to deteriorated ME properties [6].

Straightforward way of increasing the magnitude of the ME response is to choose constituents with large magnetostrictive and piezoelectric coefficients. PMN–PT is a relaxor-type ferroelectric material which exhibits much higher piezoelectric constant than the most widely used $Pb(Zn,Ti)O_3$ (PZT). For magnetostrictive materials, we choose nickel ferrite, which, according to the previous report, has slight interdiffusion effect compared with other materials such as $CoFe_2O_4$ [7].

In this report, $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$ (PMN–PT) and Zn-doped ferrite $Ni_{0.8}Zn_{0.2}Fe_3O_4$ (NZFO) were prepared. Laminated structure of PMN–PT/NZFO/PMN–PT and bulk composite were fabricated. The ME effect of the two samples are studied.

2. Experimental procedure

2.1. Preparation of ME laminates and composites

The powder of PMN–PT was prepared with a polyethlylene glycol (PEG)-modified solid-state reaction method using PbO, MgO, Nb_2O_5 and TiO_2 oxides in molar proportions [8]. The oxides were presintered at 850 °C for 4 h to obtain perovskite phase. The presintered powder was then pressed into pellets with polyvinyl alcohol (PVA) as a binder and sintered at 1100 °C for 2 h. Similarly, the piezomagnetic ferrite phase was prepared using ZnO, NiO and Fe_2O_3 as raw materials. The mixed oxides were presintered at 1200 °C for 10 h to obtain spinel phase. The presintered powder was pressed into pellets and sintered at 1250 °C for 2 h.

The PMN–PT pellet was coated with silver electrode for dielectric testing and poling process. For laminated ME structure, the PMN–PT and NZFO pellets were stacked together

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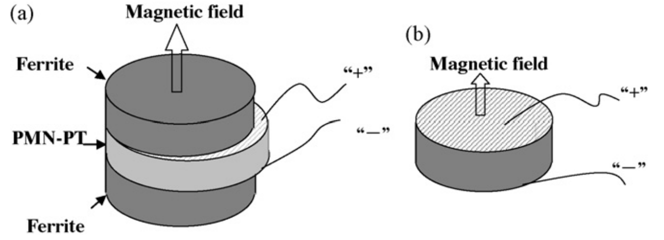

Fig. 1. Schematic structures of ME laminated structure (a) and bulk composite (b).

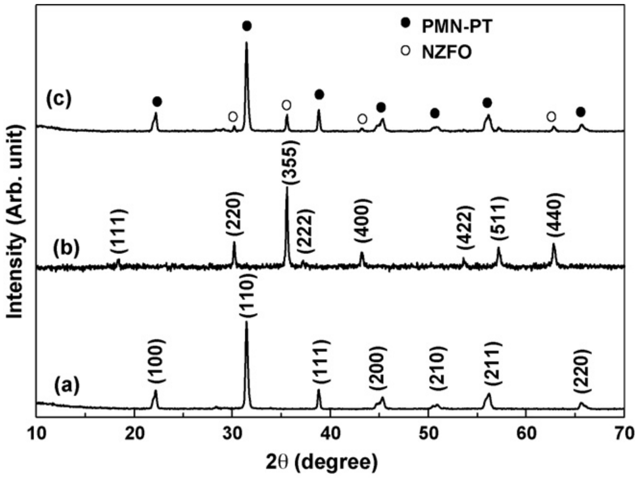

Fig. 2. X-ray diffraction spectra of the (a) PMN–PT powders calcined at 850 °C for 2 h, (b) NZFO powder calcined at 1200 °C for 10 h and (c) PMN–PT/NZFO ceramics sintered at 1100 °C for 2 h.

by silver epoxy and heated at 80 °C. The structure was illustrated in Fig. 1 (a). The diameter of PMN–PT is larger than that of the NZFO to allow the connection of electrode to the voltage detector.

For bulk composite preparation, the two kinds of presintered powders were mixed and ground in an agate mortar. The weight ratio of PMN–PT to NZFO was 5:1. In order to reduce the chemical diffusion between PMN–PT and NZFO grains, the compressed pellets were sintered at a relatively low temperature of 1100 °C for 2 h. The bulk sample is shown in Fig. 1 (b). The thickness of all the pellets was 0.6 mm.

2.2. Characterization

The crystal structure of the calcined powders was analyzed using X-ray diffraction (XRD) with CuKα radiation (Bruker D8 Advance, Bruker AXS Inc., Madison, WI with λ = 1.5418 Å). The microstructure of the ceramics was examined using field emission scanning electron microscopy (FE-SEM, Model JSM 6335F, JEOL, Tokyo, Japan).

The dielectric measurements were carried out as a function of frequency in the range of 100 Hz–100 MHz at room temperature using LCR meter bridge (HP 4284A).

The samples with electrodes were poled in silicone oil at 180 °C under an electric field of 30 kV/cm for 20 min and slowly cooled down to room temperature. The piezoelectric coefficient of the PMN–PT composite was measured by a piezo d_{33} meter (Model ZJ-3B). The ME coefficient α_E is determined by the induced electric field generated in the PECP under a small ac magnetic field of 10 Oe (generated by a solenoid) superposed onto a dc magnetic bias H_{Bias} of up to 2.5 kOe (generated by a pair of permanent NdFeB magnets). The induced electric field was measured with a high input impedance circuit and oscilloscope.

3. Results and discussion

Fig. 2 shows the XRD results of the PMN–PT powder, NZFO powder and PMN–PT/NZFO ceramics. PMN–PT exhibits perovskite structure and NZFO exhibits desired spinel structure. The calculated lattice parameters of the pseudo-cubic structure of PMN–PT and cubic NZFO are 4.00 and 8.25 Å, respectively. The ceramics exhibit both perovskite and spinel phases, and no other phases are detected.

Fig. 3 presents the SEM morphology of the PMN–PT and NZFO ceramics. Size of the PMN–PT ceramic sintered at 1100 °C ranges 1–3 μm as shown in Fig. 3(a). The surface of NZFO is very smooth with the grain size ranging 1–3 μm.

Fig. 4 presents the SEM surface morphology of the PMN–PT/NZFO composite. As shown in Fig. 4, the densified grain clusters are surrounded by small particles. The inhomogeneous morphology is caused by the nonuniform mixing of PMN–PT and NZFO powders. Besides, the sintering of NZFO ceramics usually needs a temperature higher than 1200 °C, hence the

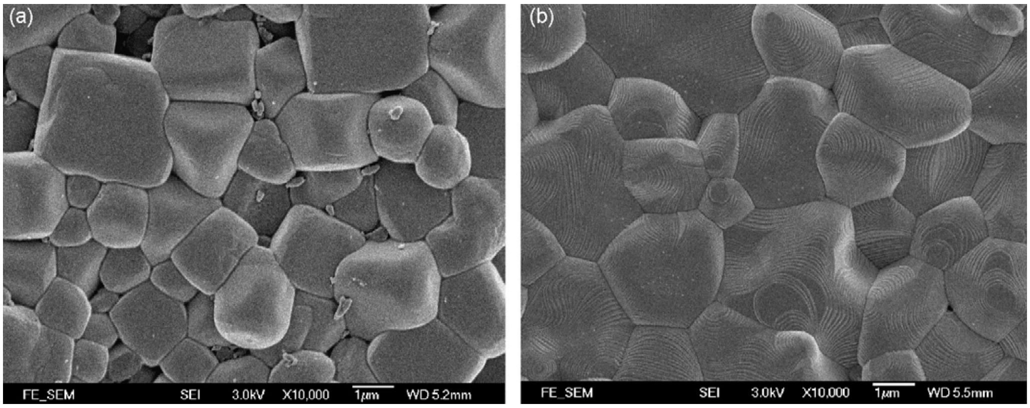

Fig. 3. SEM images of (a) PMN–PT ceramics sintered at 1100 °C for 2 h and (b) NZFO ceramics sintered at 1250 °C for 2 h.

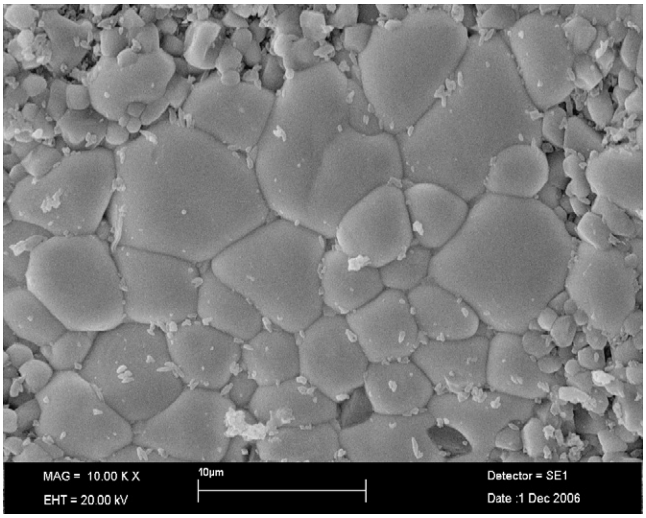

Fig. 4. SEM image of the PMN–PT/NZFO bulk composite sintered at 1100 °C for 2 h.

NZFO powders in the composites have not grown into large grains which results in the nonuniform and less densified composite ceramic.

The variation of dielectric constant (ε_r) with frequency for the PMN–PT and composite is shown in Fig. 5. The ε_r of pure PMN–PT sample was around 3200 at 1 kHz while that of the composite decreased to 2000. The ε_r of the composite decreases at lower frequencies and remains constant at higher frequencies. The higher values of ε_r at low frequencies is likely caused by the electrode polarization, which will not contribute to the dielectric properties at higher frequencies. The measured piezoelectric coefficient d_{33} of the PMN–PT ceramic after poling was 288 pC/N. The d_{33} of the composite was reduced to 156 pC/N.

The ME coefficients α_E of the laminated and bulk samples were 91 mV/cm Oe and 64 mV/cm Oe, respectively, under a bias magnetic field of 1.1 kOe. Fig. 6 shows the representative data on H_{bias} dependence of α_E at room temperature and 1 kHz for the bulk PMN–PT/NZFO. The H_{bias} dependence of α_E essentially tracks the strength of piezomagnetic coupling coefficient $q = \delta\lambda/\delta H$. With the increase of H_{bias}, piezomagnetic coupling coefficient q increases, and reaches a maximum value at $H_{bias} = 0.26$ kOe, which is the same as the magnetic bias that maximum α_E yields. After that, q decreases rapidly and tends toward zero when the magnetostriction reaches saturation, so the ME coupling gradually decreases. The maximum α_E value is 406 mV/cm Oe, which is much higher than that for PZT–ferrite composite. The reported highest α_E of PZT–ferrite composite is only 115 mV/cm Oe [9]. In this study, the PMN–PT and NZFO were not homogenously mixed causing an individually growth in each cluster. Therefore, the chemical diffusion between PMN–PT and NZFO may be reduced compared with the composite in which piezoelectric and magnetic grains distributed uniformly. As a result, an increased ME coefficient α_E can be achieved. The ME coefficient of the composite will be increased by optimizing the sintering process.

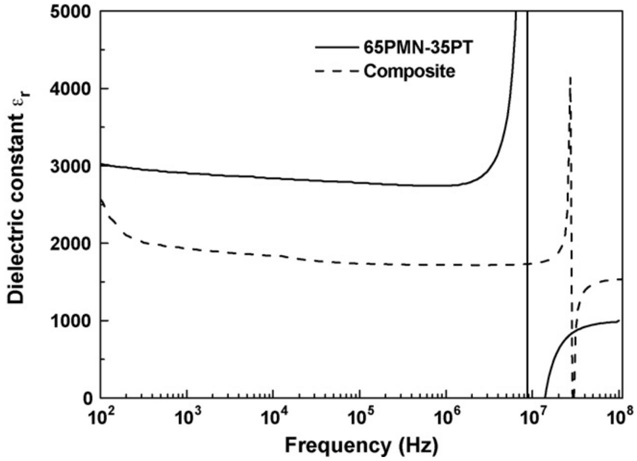

Fig. 5. Dielectric constant of the PMN–PT ceramic and PMN–PT/NZFO composite.

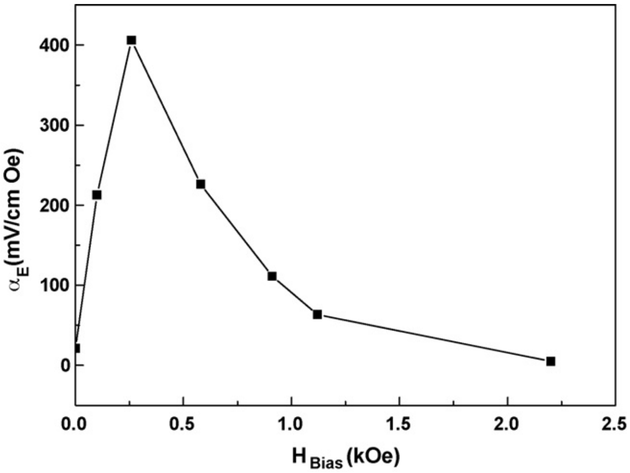

Fig. 6. ME voltage coefficient of the PMN–PT/NZFO composite as a function of applied magnetic bias measured at 1 kHz.

4. Conclusions

ME coefficients of laminated structure and bulk composite of PMN–PT/NZFO were compared. Although the α_E was lower in the composite compared with that in the laminated structure, a high value of 406 mV/cm Oe has been obtained for the PMN–PT/NZFO composite which is much higher than the reported value of PZT/ferrite. PMN–PT with the excellent piezoelectric performance contributes to an improved ME response. Observations in this study also show that uniform mixing of the piezoelectric and magnetostrictive materials in the composite is not a necessity to generate a high voltage output.

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