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Multiferroic and enhanced microwave absorption induced by complex oxide interfaces*

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$NiFe_2O_4$ (NFO)/ZnO composite nanoparticles with different ZnO components were investigated, which were prepared by a simple wet chemical route method. The magnetoelectric coupling between magnetostriction from NFO and piezoelectricity from ZnO was induced by the surface coating NFO nanoparticles of ZnO layer, NFO/ZnO composite showed ferroelectric properties and the remanent electric polarization reached 0.08 μC/cm. Moreover, the changes of resistance at different room temperatures reached about 2% under 3 T magnetic fields comparing with that of zero magnetic fields. Furthermore, multiferroic NFO/ZnO resulted in enhancement of microwave absorption due to magnetoelectric coupling.

Keywords: magnetostrictive, piezoelectricity, microwave absorption, magnetoelectric coupling

PACS: 75.80.+q, 77.84.–s, 84.90.+a, 75.85.+t **DOI:** 10.1088/1674-1056/27/1/017503

1. Introduction

Multifunctional materials exhibit a coexistence of two or more properties, such as magnetic, electric, optical, etc. There is a tremendous flurry of research interest in multiferroic materials that exhibit multiple primary ferroic order parameters simultaneously and that have potential applications in the field of spintronics with fundamental science and novel significant technology. The abundance of intrinsic multiferroic materials is sharply limited by the competing symmetry requirements for each type of ferroic order. Currently, the investigation of multiferroic materials is mainly in composite ferroelectric (FE)/ferromagnetic (FM) structures[1–3] and intrinsically multiferroic materials.[4–7] In most single-phase multiferroics, the intrinsic coupling between polarization and magnetization at the atomic scale is generally weak and also at low temperature, which limits their practical applications. Therefore, a substantial effort committed to obtain large ME coupling has been undertaken by some research teams recently and a lot of promising perspectives have been obtained.

Zinc oxide (ZnO) has attracted more and more attention, owing to its versatile properties including electric, optical, microwave absorption, etc. ZnO is a semiconductor with a wide energy gap, which results in potential applications such as short-wave light-emitting devices and high-frequency filters.[8–11] Moreover, the substitution of transition-metal ions into the Zn sites leads to ferromagnetic ordering. Recently, Ding's group[12] observed the coexistence of ferromagnetism and ferroelectricity in doped ZnO and further realized the mutual manipulation of ferromagnetic–ferroelectric properties. Physically, the composition of magnetostrictive material and piezoelectric material should improve magnetoelectric response. Therefore, in this work, we report multiferroic and magnetoresistance in composite nanoparticles, which contained magnetostrictive ($NiFe_2O_4$) and piezoelectric phases (ZnO). There was interface stress transfer between $NiFe_2O_4$ and ZnO layer due to $NiFe_2O_4$ particles coated ZnO layer, which induced the mutual manipulation of ferromagnetic–ferroelectric properties in $NiFe_2O_4$/ZnO composite. Moreover, enhanced optimum reflection loss (RL) value and absorption frequency range were found in the 70% content rate sample. Such materials may have potential applications in microwave devices.

2. Experimental procedure

The $NiFe_2O_4$ particles were prepared by a co-precipitation method described in our previous work.[13] In order to composite NFO particles with ZnO, a wet chemical route was performed.[14] The prepared $NiFe_2O_4$ particles were ultrasonically dispersed in a 0.1 mol/L $Zn(CH_3COO)_2$ dimethyl sulfoxide (DMSO) solution. A 0.5 mol/L $N(CH_3)_4OH$ (TMAH) absolute ethanol (EtOH) solution was added dropwise to the $Zn(CH_3COO)_2$ solution under vigorous stirring. After a full reaction, the resulting compound was precipitated from DMSO by addition of ethyl acetate. The compound was washed by ethyl acetate four times and then dried in a dry oven. By changing the mass of dispersed NFO particles, the mass ratio of ZnO and NFO was controlled. Finally, samples with different $NiFe_2O_4$ content rates of 0%, 10%, 30%, 50%, 70%, 90%, and 100% were prepared. The samples were pressed into round flakes and

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annealed at 800 °C for 2 h in air atmosphere for further investigation. The crystallographic and microstructure measurements of the samples were performed by using x-ray diffraction (XRD, X'Pert PRO PHILIPS with Cu $K\alpha$ radiation) and transmission electron microscopy (TEM, Tecnai TMG2F30), respectively. A vibrating sample magnetometer (VSM, EV9 MicroSense) and an MPMS magnetometer based on a superconducting quantum interference device (SQUID, Quantum Design) were employed to determine the static magnetic properties of the samples. The microwave magnetic properties were determined by using a vector network analyzer (PNA, Agilent E8363B). A Radiant Precision Premier II (Radiant Technologies Inc., Albuquerque, NM, USA) tester system was used to obtain polarization–electric field (P–E) curves.

3. Results and discussion

The XRD patterns of samples with different NFO content rates were obtained to analyze the composition of the samples. The results were summarized in Fig. 1(a). All the samples are well crystallized with well-defined diffraction peaks, which referred to NFO (311) with a cubic crystalline structure (JCPDS card No. 54-0964) and ZnO (101) with a hexagonal wurtzite structure (JCPDS card No. 36-1451), no other phase was detected. We can clearly see from the XRD results that NFO and ZnO phases were divided obviously, that is to say, the two materials exist independently. Peaks show deviations from NFO (311) and ZnO (101) of pure samples (100% and 0% samples), all peaks of the composite samples show shifts towards smaller angle, which ascribes to the expansion of lattice. The expansion could be caused by the replacement of Ni^{2+} (ionic radii is 0.78 Å) by Zn^{2+} (ionic radii is 0.82 Å).[15] To confirm the XRD results and figure out the microstructure of the two materials TEM images were taken, and the images of 70% NFO sample were displayed in Fig. 1(b). From the images, we can clearly see that the ZnO crystal grows on the surface of the NFO particles and is well crystallized. Clear lattice fringes were observed in all samples indicating the defect-free nature of the sample with high degree of crystallinity, which elucidated that all samples obtained were monocrystalline complexes.

Figure 2 shows the magnetization hysteresis loops for different NFO content rate samples. The magnetic moment was divided by the content rate of NFO to maintain comparability. The M_s obtained from the figure is summarized in the inset. The results are quite similar to the results in our previous work.[13] Samples show ferrimagnetism except the pure ZnO sample which is normally a nonmagnetic material. The M_s of the samples first increases with the increase of ZnO content rate, after reaching its highest level of 79 emu/g (that is much larger than the theoretical value of 47.5 emu/g[16]) at content rate of 50%, the M_s begins to decrease with increase of ZnO content. We know that the heat treatment may introduce Zn^{2+} into the $NiFe_2O_4$ lattice and form $Ni_{1-x}Zn_xFe_2O_4$ ($0 < x < 1$). With the increase of ZnO, more interface between $NiFe_2O_4$ and ZnO appears, which leads to the increase of M_s. When NFO is composed with more ZnO, the superabundance of Zn^{2+} can cause the increase of antiferromagnetic in ferrite. As a result, M_s decreases when ZnO content rate is over 50%.

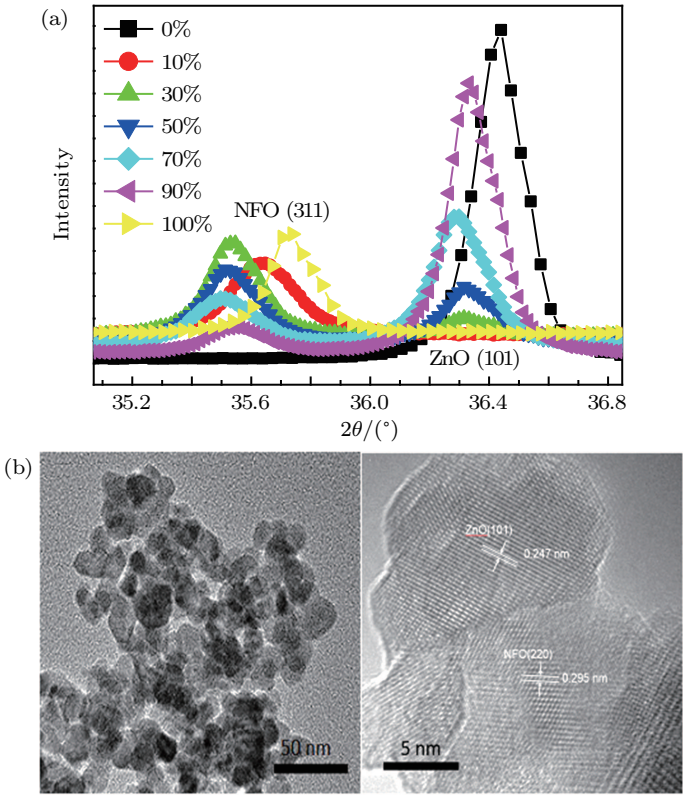


Fig. 1. (color online) (a) The XRD patterns of composite nanoparticles with different NFO content rates. (b) TEM images of composite nanoparticles.

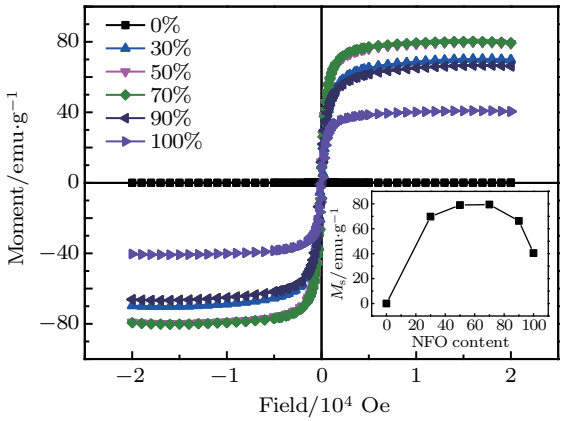


Fig. 2. (color online) The VSM curves of samples with different NFO content rates and the inset is M_s as the function of NFO content rate.

In order to investigate the electric polarization characteristics, we measured P–E curves of the composite samples. The

results expressed in Fig. 3 indicate that the samples show obvious ferroelectricity. With the increase of NFO content rate, ferroelectric of the sample becomes stronger and stronger; however, when NFO is 90%, the sample behaves with more Ohm characteristic. It is well known that ZnO is a piezoelectric material, and apparently ZnO content in the sample contributes the polarization under an electric field. As a result, the sample shows ferromagnetic (provided by NFO) and ferroelectric (provided by ZnO) at the same time. Materials that are magnetically and electrically polarizable can exhibit ME coupling, that is, a change of magnetization induced by an applied electric field or change of polarization induced by an applied magnetic field.[14]

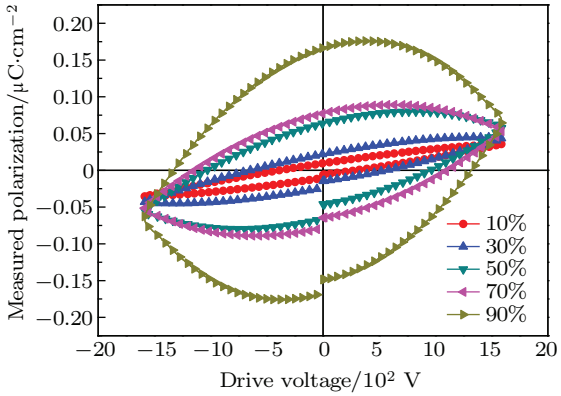


Fig. 3. (color online) The *P*–*E* curves of composite samples.

As for a sample with both ferromagnetic and ferroelectric properties, it is highly possible that the sample can express ME effects. For the purpose of investigating ME effects, we then investigated the resistance change of 70% sample versus magnetic fields at 310 K, 270 K, and 250 K to study how the magnetic field can affect the electrical conductivity of the sample. In order to perform the measurement, Pt electrodes were deposited on both faces of the sample by magnetron sputtering beforehand. The sample was firstly magnetized by a magnetic field of 30000 Oe, then the field was decreased to zero and reversely increased to −30000 Oe. In the meantime, the resistance of the sample was measured. Figure 4 shows the measurement results: $\Delta R/R$ versus magnetic fields at different temperatures. We can observe that the curves are expressed differently with previous reports on spinel ferrites.[17–20] The sample shows its largest resistance when the magnetic field is 30000 Oe at all temperatures we used. As the field decreases from its highest value, the resistance begins to decrease. For the curves measured at 270 K and 250 K the resistance arrives at a valley and then starts to increase, showing a peak at 0 Oe. However, for the curve measured at 310 K, the resistance continues to drop and shows a valley at 0 Oe. Since the conductivity of NFO is much larger than that of ZnO, the nature of the sample's resistivity reflects the property of NFO content mostly. Because NFO is piezomagnetic,[21,22] it could cause stress when the magnetic field was applied across the sample. The stress transfers through the sample and then into piezoelectric ZnO generating the electric polarization of ZnO. Because of the coupling at the interface between NFO and ZnO, charge status of NFO and ZnO would be changed, which results in the change of conductivity of NFO and ZnO.[23] Since NFO is also a magnetoresistance material, the total effect should be a superimposed effect of ZnO inducted charge status change and intrinsic magnetoelectric effect of NFO. That is to say, the whole sample would experience a resistivity change affected by both ferromagnetic (provided by NFO) and ferroelectric (provided by ZnO) under a changing magnetic field.

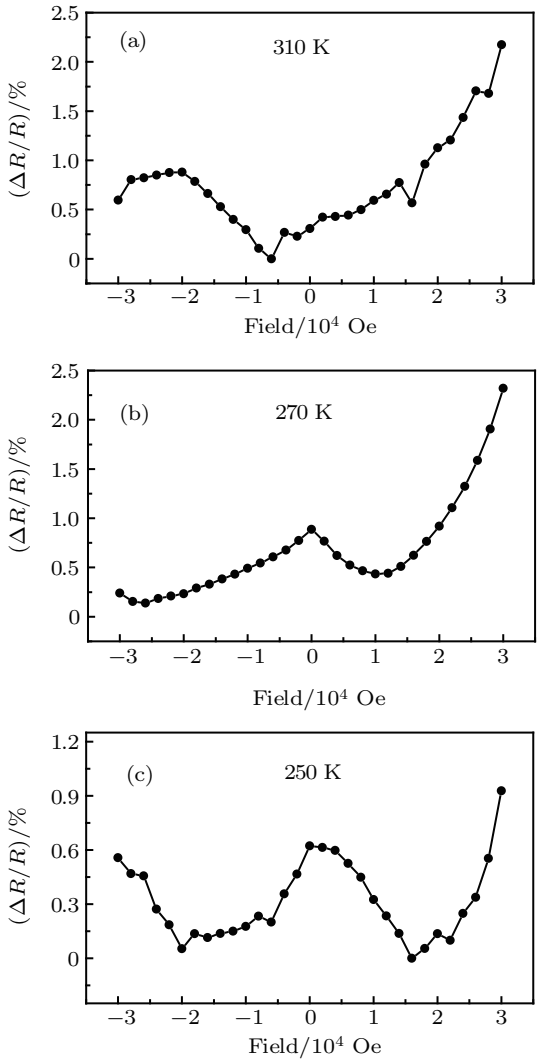


Fig. 4. The $\Delta R/R$–H curves of 70% NFO sample under (a) 310 K, (b) 270 K, and (c) 250 K.

In order to investigate the application of magnetoelectric coupling in NFO/ZnO composite, the microwave absorption properties of the samples were studied systematically. We measured the complex relative permeability and permittivity

spectra of the composite samples by a coaxial method on the PNA using the transmission/reflection mode within the range of 0.1–18 GHz. (In the measurement, the NFO/ZnO composite particles were mixed with paraffin by 80% in wt%, so the electromagnetic properties can also be regarded as the properties belonging to NFO/ZnO–paraffin composite). The reflection loss (RL) and reflection loss factor were calculated by using the complex permittivity and permeability.[24,25] Figure 5 shows the calculated RL spectra of 30%, 70%, 90%, and 100% samples with different thicknesses.

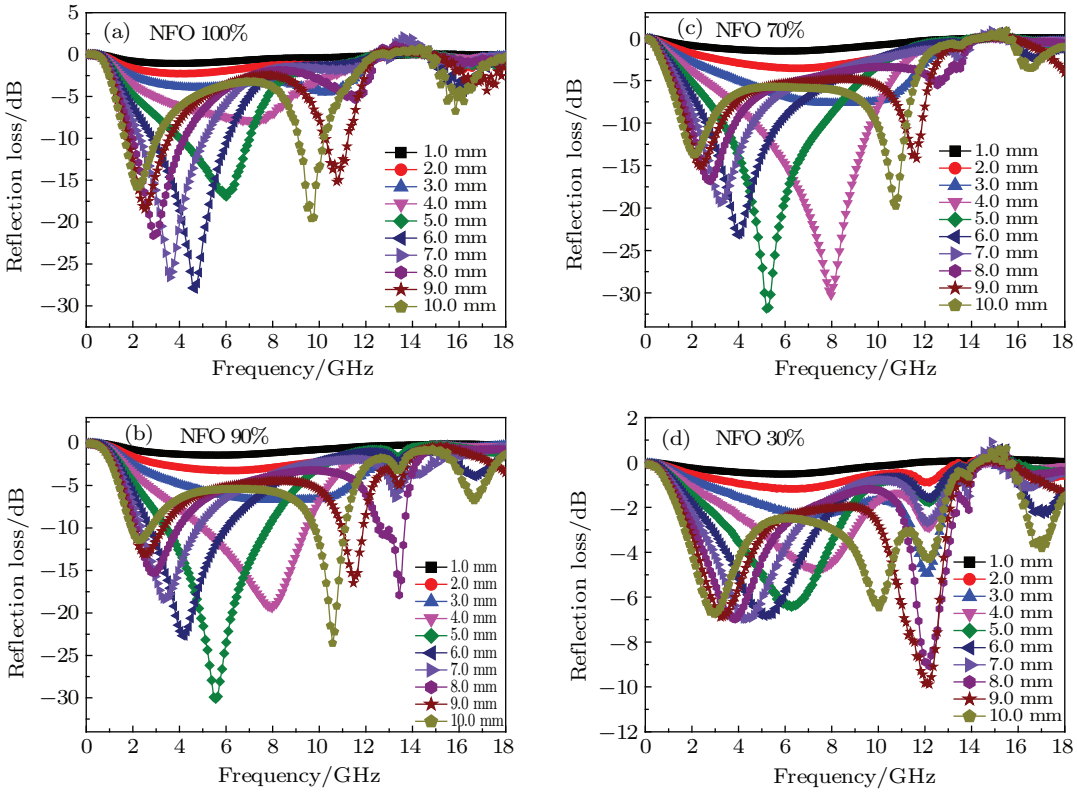


Fig. 5. (color online) Calculated RL spectra of 100% (a), 90% (b), 70% (c), and 30% (d) samples with different thicknesses.

It can be seen that the optimum RL value of 70% sample is 32.5 dB at 5.2 GHz, lower than the optimum RL values of 30%, 90%, and 100% samples which are 7.2, 30, and 29 dB, at 4.2, 5.5, and 4.6 GHz, respectively. Meanwhile, the absorption frequency range of 70% sample with RL less than 10 dB (represent to the 90% RL of the incident microwaves) is from about 1.8 to 10 GHz for most of the corresponding absorber thickness, the frequency range is wider than 30%, 90%, and 100% samples which are none, 3.9 to 7.7, and 1.9 to 9.9 GHz, respectively. As a result, microwave absorption property of NFO is improved by compounding with ZnO, this may be caused by the ME coupling between the two materials. Through ME coupling, the microwave energy may be dispersed and converted between magnetic energy and electric polarization energy, as a result, more microwave energy can be consumed when the microwave transfers to and reflects from the sample.

4. Conclusion

In summary, we have shown a simple way to combine ZnO and NFO nanoparticles together to produce a compound and the composite sample showed both ferroelectric and ferromagnetic properties. The 70% composite sample showed a magnetoresistance effect which is different from the normal spinel ferrites and an enhanced microwave absorption property was observed. The two effects can be concluded into the coupling of ferroelectric and ferromagnetic components at the interface of NFO and ZnO.

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