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Electromagnetic properties of ferroelectric-ferrite ceramic composites

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Abstract

The $NiFe_2O_4$ and $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramic composites are prepared by conventional solid state reaction method. The microstructural and morphological properties of the composites are studied by X-ray diffraction analysis and scanning electron microscopy. Results indicate that the ferrite and piezoelectric phases can co-exist in the composites. The relationship between the dielectric constant and frequency (40 Hz–40 MHz) as well as temperature is also investigated. It is noted that the transition temperature of the composites is about 380 °C. A double electric hysteresis loop is observed in our composites. The magnetic properties are relatively weak according to the magnetic hysteresis loop. With increase in the content of the ferrite phase, the permeability increases. The electromagnetic properties of the as-prepared composites are tunable according to the content of the $NiFe_2O_4$ phase.

Keywords: Ferroelectric–ferrite composites; Dielectric constant; Hysteresis loop; Permeability

1. Introduction

As one knows, when a ferromagnetic phase and a ferroelectric phase coexist in ferroelectric-ferrite composite materials, novel effects, which include magneto-electric, magneto-optic, as well as other coupling effect, are expected due to an interaction between the magnetization and electric polarization. The magnetoelectric (ME) effects and electromagnetic properties of the composites have been widely studied [1–6]. The ME effect is a coupled effect, in which the application of electric field induces magnetization and magnetic field induces electric polarization [7–10]. It is a product property exhibiting a complex behaviour. A suitable combination ferromagnetic phase and a ferroelectric phase gives rise to this property. The ME composites are promisingly exploited as sensors, waveguides, switches, phase invertors, transducers, modulator, etc.

To obtain a better ME composite, the magnitude of the magnetostriction coefficient of ferrite phase and piezoelectric coefficient of the piezoelectric phase must be high. Also the resistivity of both phases should be high so as to avoid a leakage of the accumulated charges. Considering that the magnetostriction coefficient of Ni ferrite is higher, hence, Ni ferrite is chosen as a ferrite phase in the present study. Similarly, $Pb(Zr_{0.52}Ti_{0.48})$(PZT) is used as a piezoelectric phase due to high piezoelectric constant and high dielectric permittivity. In this paper, the ceramic composites of the $NiFe_2O_4$ and $Pb(Zr_{0.52}Ti_{0.48})O_3$ were prepared using the conventional solid state reaction method. The dielectric, ferroelectric, ferromagnetic properties of the composites were also characterized and investigated.

2. Experimental procedure

In the preparation of the ME composites, the reactant for $NiFe_2O_4$ was Ni_2O_3 and Fe_2O_3 powders, while that for $Pb(Zr_{0.52}Ti_{0.48})O_3$ was PbO, ZrO_2 and TiO_2 powders. The ferrite powder was pre-sintered at 750 °C for 2 h, and the ferroelectric powder was also pre-sintered at 850 °C for 2 h. Then, the pre-sintered ferrite and ferroelectric powders with different molar ratios were well mixed. After the powders were mixed with 5 wt% polyvinyl alcohol (PVA, 8% concentration) as a binder and granulated with a 60-mesh to 100-mesh sieve. The granulated powders were pressed in a stainless steel die under a pressure of 10 MPa for pellet and 20 MPa for toroidal specimens. All the specimens were sintered for 2 h at different

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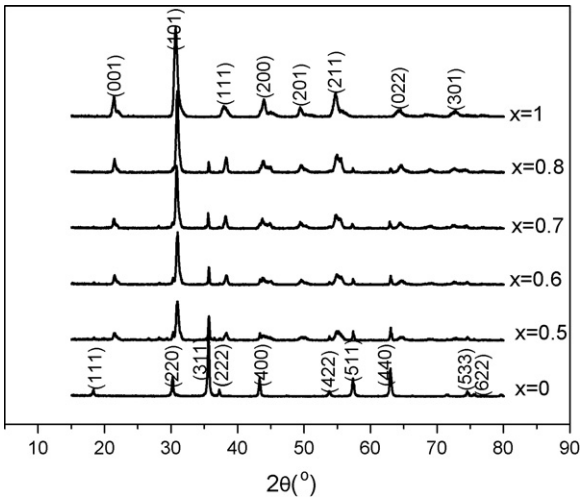

Fig. 1. XRD patterns of the $x\mathrm{Pb}(\mathrm{Zr}_{0.52}\mathrm{Ti}_{0.48})\mathrm{O}_3 + (1-x)\mathrm{NiFe}_2\mathrm{O}_4$ composites sintered at 1210 °C.

temperatures of 1150, 1200, 1210, 1220, and 1250 °C in air. Thus, four $x\mathrm{Pb}(\mathrm{Zr}_{0.52}\mathrm{Ti}_{0.48})\mathrm{O}_3 + (1-x)\mathrm{NiFe}_2\mathrm{O}_4$ composite samples with different x values including 0.5, 0.6, 0.7, and 0.8 were prepared.

The phase characterization of the composites was performed by using Rigaku D/max-2400 X-ray diffraction (XRD) with Cu Kα radiation. Scanning electron microscopy (SEM, JSM-6360) was used to reveal the morphological and microstructural properties of the composites. The dielectric measurements were carried out as a function of frequency in the range of 40 Hz–40 MHz at room temperature from a HP4294 impedance analyser. The variation of dielectric constant with temperature was studied at the frequencies of 1 kHz, 10 kHz, 100 kHz and 1 MHz; date was collected using a HP4284 Impedance Analyzer interfaced to a computer. Ferroelectric performance was measured using a TF ANALYZER 2000 FE-Module (frequency of test at 1 Hz, at room temperature). Magnetic hysteresis loop were carried out using a vibrating sample magnetometer (VSM, Lakeshore 7307, USA). The permeability values (μ_i) of the composites were measured using a HP4294 impedance analyser.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the XRD patterns of the $x\mathrm{Pb}(\mathrm{Zr}_{0.52}\mathrm{Ti}_{0.48})\mathrm{O}_3 + (1-x)\mathrm{NiFe}_2\mathrm{O}_4$ sintered at 1210 °C for 2 h. It can be seen from Fig. 1 that the tetragonal perovskite and the cubic spinel phases are both present in the composites for $x = 0.5$, 0.6, 0.7, 0.8. With increase in the content of x, the peak intensity of $\mathrm{Pb}(\mathrm{Zr}_{0.52}\mathrm{Ti}_{0.48})\mathrm{O}_3$ increases, while the peak intensity of $\mathrm{NiFe}_2\mathrm{O}_4$ decreases. All the peaks can be identified and no intermediate phase or interfacial phase is observed from XRD results. These results indicate that no significant chemical interaction occurs between the $\mathrm{Pb}(\mathrm{Zr}_{0.52}\mathrm{Ti}_{0.48})\mathrm{O}_3$ and $\mathrm{NiFe}_2\mathrm{O}_4$.

The SEM micrographs of the composites with various ferrite phase contents and sintered at 1210 °C for 2 h are shown in Fig. 2. Here, white regions are $\mathrm{Pb}(\mathrm{Zr}_{0.52}\mathrm{Ti}_{0.48})\mathrm{O}_3$ and dark particles are $\mathrm{NiFe}_2\mathrm{O}_4$ ferrite. Results indicate that no third phase is observed i.e. there is no chemical reaction or interdiffusion between two phases. Thus, the SEM results further confirm the conclusions obtained by XRD.

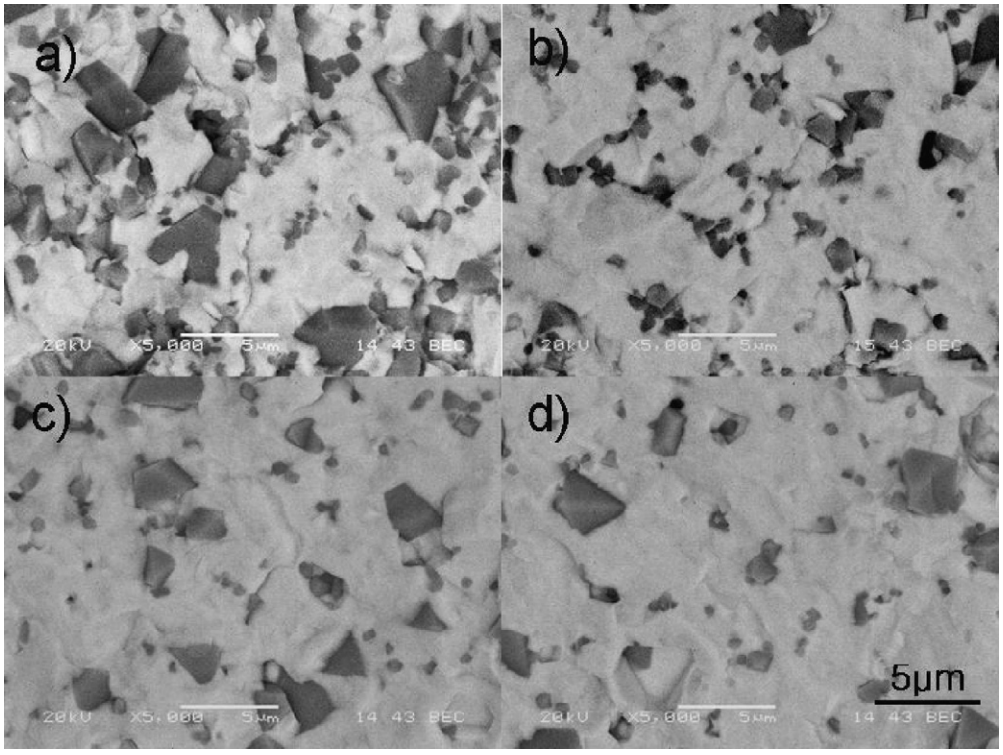

Fig. 2. SEM micrographs of the composites with (a) $x = 0.5$, (b) $x = 0.6$, (c) $x = 0.7$, (d) $x = 0.8$, sintered at 1210 °C for 2 h.

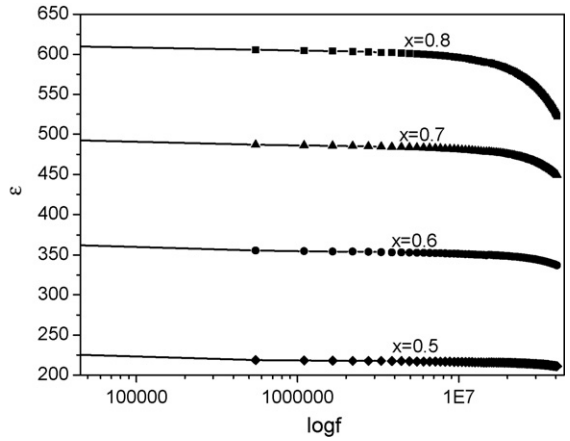

Fig. 3. Variation of dielectric constant with frequency for the $x\mathrm{Pb}(\mathrm{Zr}_{0.52}\mathrm{Ti}_{0.48})\mathrm{O}_3 + (1-x)\mathrm{NiFe}_2\mathrm{O}_4$ composites.

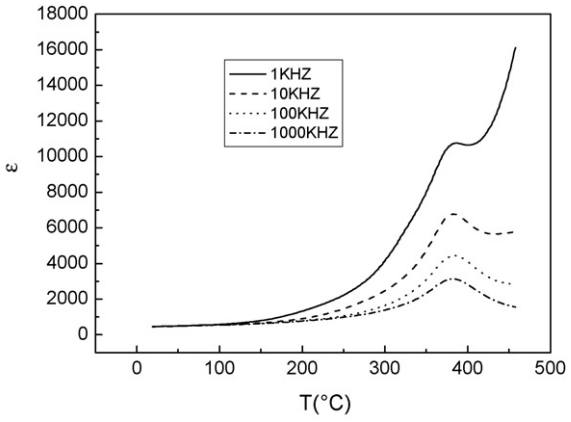

Fig. 4. Variation of dielectric constant with temperature for composite ($x = 0.7$).

3.2. Dielectric properties

The variation of dielectric constant with frequency for the composites is shown in Fig. 3. The figure reveals that the dielectric dispersion can be clearly observed in all composites. The value of ε basically remains constant at lower frequency, but starts to decrease at higher frequency, and this phenomenon becomes more obvious for the those samples at $x = 0.7$ and 0.8. It is also noted that the value of ε increases with the increase of the $\mathrm{Pb}(\mathrm{Zr}_{0.52}\mathrm{Ti}_{0.48})$ content. It is probably related to the fact that dielectric constant of $\mathrm{Pb}(\mathrm{Zr}_{0.52}\mathrm{Ti}_{0.48})$ is higher, but that of Ni ferrite is lower, leading to a increase in the dielectric constant of the composites.

Dielectric constant vs. temperature for composite ($x = 0.7$) are shown in Fig. 4. It can be seen that ε increases slowly with increase temperature up to Curie temperature (Tc) and starts to decrease. The results reveal the appearance of the diffused phase transition as reported in Ref. [11]. The transition temperature is about 380 °C at all studied frequencies. This indicates that the phase structures of the $\mathrm{Pb}(\mathrm{Zr}_{0.52}\mathrm{Ti}_{0.48})$ and Ni ferrite are not destroyed.

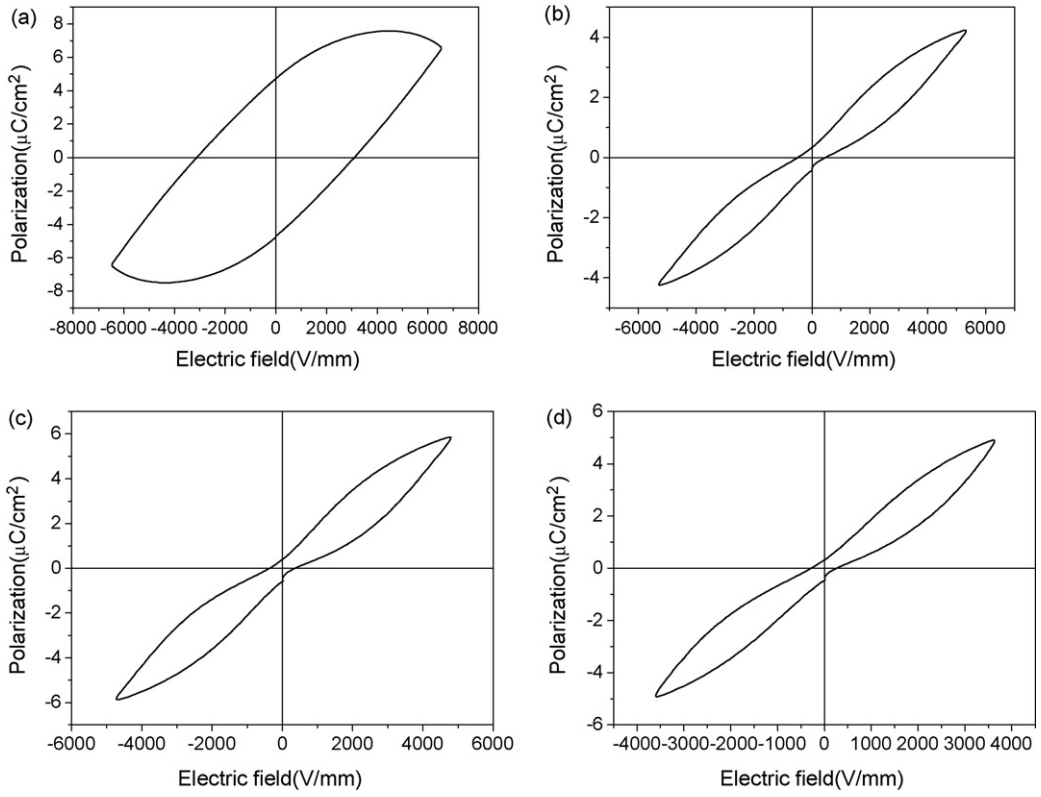

Fig. 5. Electric hysteresis loops of the composites (a) $x = 0.5$, (b) $x = 0.6$, (c) $x = 0.7$, (d) $x = 0.8$.

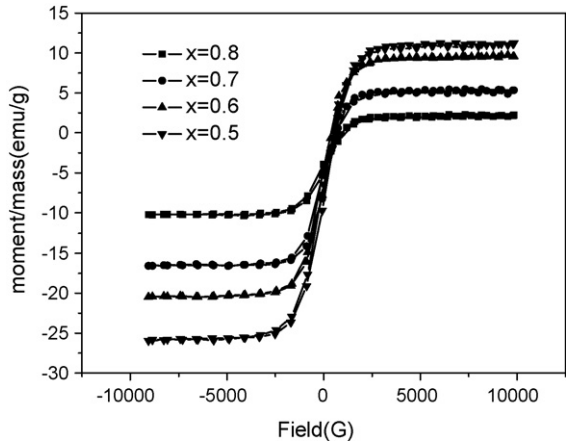

Fig. 6. Magnetic hysteresis loops of the composites for $x = 0.5$, 0.6, 0.7, 0.8.

3.3. Ferroelectric properties

Fig. 5 shows electric hysteresis loops of the composites for $x = 0.5$, 0.6, 0.7, 0.8, respectively. The results indicate that the electric hysteresis loops of the composite for $x = 0.5$ can not attain the saturation. The presence of $NiFe_2O_4$ leads to lower resistance ratio of the composites and lower undertaking electric voltage, so that the sample is not fully polarized. However, with increase $Pb(Zr_{0.52}Ti_{0.48})O_3$ content, the electric hysteresis loops of the composites tend to saturate, and show the phenomena of double hysteresis loop for $x = 0.6$, 0.7, 0.8, respectively. The remanent polarization of the composites is lower and their value is 0.31, 0.40, 0.42 μc/cm^2, respectively. An explanation is possibly that Fe^{2+} ion becomes Fe^{3+}, leading to appear oxygen vacancy and increase space charge. It is considered that space charges have a pinning effect for the ferroelectric domain, so that the domain wall reversal is difficult. Thus, the composites were polarized difficultly.

3.4. Magnetic properties

Fig. 6 shows magnetic hysteresis loops of composites. The composites exhibit typical magnetic hysteresis of the magnetic materials, indicating that the composites are magnetically ordered materials. The variation of the saturation magnetization of the composites with the x is plotted in Fig. 7. It is clearly observed that the saturation magnetization of the composites decreases linearly with increase the $Pb(Zr_{0.52}Ti_{0.48})O_3$ content, the phenomenon is consistent with that reported in Ref. [12]. Because the $Pb(Zr_{0.52}Ti_{0.48})O_3$ is inherent nonmagnetic nature and stops continuity of $NiFe_2O_4$ ferrite, the magnetic of composites decreases with increase the $Pb(Zr_{0.52}Ti_{0.48})O_3$ content.

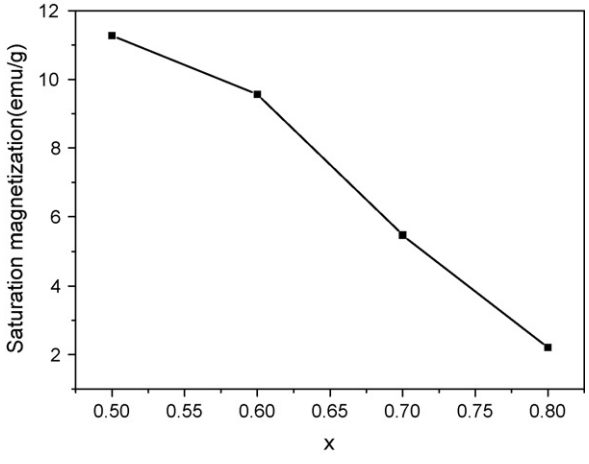

Fig. 7. The saturation magnetization of the composites.

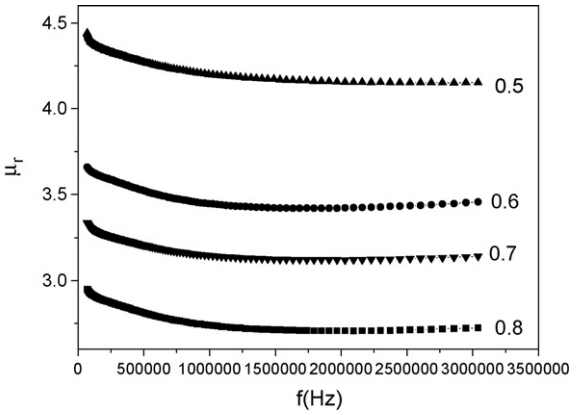

Fig. 8. The relation of permeability with frequency for composites.

The magnetic spectra (frequency at 70 KHz–3 MHz) are shown in Fig. 8. It can be seen that the permeability decreases slowly with a lower frequency, however, it remains constant at a higher frequency. With increase in the value of x under the same frequency, the permeability tends to decrease. In the composites, the permeability is closely related to the defects due to the co-firing and the existent of the nonmagnetic $Pb(Zr_{0.52}Ti_{0.48})O_3$. Therefore, with increase the $Pb(Zr_{0.52}Ti_{0.48})O_3$ content, the permeability decreases.

4. Conclusions

The $xPb(Zr_{0.52}Ti_{0.48})O_3 + (1 - x)NiFe_2O_4$ composites have been prepared by the conventional ceramic technique. The ferrite and piezoelectric phases were cubic spinel and tetragonal perovskite, respectively. The normal dielectric dispersion has been observed from the relation of dielectric constant with frequency. The dielectric constant increases with the increase of x. The phase transition temperature is about 380 °C. The double hysteresis loops are caused due to the effect of ferroelectric domain pinning. The magnetic properties of the composites are weak. With the content of ferrite phase increasing, the magnetic properties of the composites increase. The electromagnetic properties of the composites can be tunable according to the addition of the $NiFe_2O_4$ content.

Acknowledgements

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