Journal of Magnetism and Magnetic Materials 325 (2013) 47–51

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Study of $0.1Ni_{0.8}Zn_{0.2}Fe_2O_4-0.9Pb_{1-3x/2}La_xZr_{0.65}Ti_{0.35}O_3$ magnetoelectric composites

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ARTICLE INFO

Article history:
Received 5 July 2012
Received in revised form
21 July 2012
Available online 15 August 2012

Keywords:
Dielectric properties
Electric polarization
Magnetization
Poling
Magnetoelectric composite

ABSTRACT

Magnetoelectric composites of nickel zinc ferrite (NZF) and La substituted lead zirconate titanate (PLZT) having representative formula $0.1Ni_{0.8}Zn_{0.2}Fe_2O_4-0.9Pb_{1-3x/2}La_xZr_{0.65}Ti_{0.35}O_3$ ($x=0$, 0.01, 0.02 and 0.03) were synthesized by a conventional solid state route. X-ray diffraction analysis was carried out to confirm the coexistence of individual phases. Scanning electron microscope micrographs were taken for microstructural study of the samples. Dielectric properties were studied as a function of temperature and frequency. To study ferroelectric and magnetic ordering in composite samples, *P–E* and *M–H* hysteresis loops were recorded respectively. *M–H* hysteresis loops were taken for electrically poled and unpoled samples to confirm magnetoelectric coupling between the two phases (NZF and PLZT). La substitution results in significant improvement in dielectric, ferroelectric and piezoelectric properties of composite samples.

1. Introduction

The area of magnetoelectric (ME) materials has attracted many researchers from both groups (ferroelectricity and magnetism) because these materials exhibit ferroelectric and ferromagnetic/ferrimagnetic properties of matter. These materials have potential applications in many multifunctional devices such as magnetic field sensors, multiple state memory elements, transducers, electro-optic devices, filters, oscillators and phase shifters [1–6]. The ME effect in these materials is defined as an induced electric polarization in external magnetic field or an induced magnetization in external electric field. These materials are classified into two groups: single phase and two phase (composites). Single phase ME materials have coexistence of ferroelectric and magnetic orders in single phase and exhibit direct ME coupling. Though the experimental evidences of ME effect in single phase systems were observed during the first half of 20th century the materials showing ME coupling were found to be rare due to some limiting factors which restrict the coexistence of ferroelectricity and magnetism in a single phase [7,8]. Two phase systems exhibit indirect coupling between ferroelectricity and magnetism. This indirect coupling takes place via stress and results in magnetostriction induced deformation and the generation of piezoelectric charge [9–12] i.e. one phase should be magnetostrictive or piezomagnetic and other should be piezoelectric or electrostrictive. The most widely studied systems that have been reported correspond to substituted $NiFe_2O_4$, $CoFe_2O_4$, $MnFe_2O_4$, $ZnFe_2O_4$, Terfenol, etc. with substituted PZT, PMN-PT, PVDF and $BaTiO_3$ [13].

For the present work, bulk composites of Ni–Zn ferrite and La substituted PZT with general formula $0.1Ni_{0.8}Zn_{0.2}Fe_2O_4-0.9Pb_{1-3x/2}La_xZr_{0.65}Ti_{0.35}O_3$ ($x=0$, 0.01, 0.02 and 0.03) were synthesized by a conventional solid state reaction route. The presented composites are ferroelectric rich ferrite–ferroelectric composites with small content (10%) of the ferrite phase. The reason is that composites with higher ferrite content show lossy *P–E* loops due to high conductivity of ferrite phase as compared to that for ferroelectric phase and are also difficult to pole. Higher value of ferrite content also results in lower ME output due to the leakage charges developed in the ferroelectric grains which reduces the charges generated during the ME effect [14,15]. Further, La content (x) in ferroelectric phase was selected from 0 to 0.03 which can be attributed to the fact that for higher La content in PZT, the disordering effect of La becomes important, resulting in considerable decrease in values of remanant polarization (P_r) and saturation polarization (P_s) [16,17].

2. Experimental work

2.1. Material synthesis

The ferrite phase was prepared using AR grade NiO, ZnO and Fe_2O_3. The powder mixture was ball milled, dried and then

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http://dx.doi.org/10.1016/j.jmmm.2012.08.011

calcined at 1000 °C for 4 h. A small amount of MnO_2 (0.5% by weight) was added to the calcined powder to increase the resistivity of the ferrite. After ball milling and drying, the powder mixture was re-calcined at 1100 °C for 4 h. AR grade PbO, ZrO_2, TiO_2 and La_2O_3 for ferroelectric phase (PLZT) were weighed in required molar proportions and mixed. An excess of 2% PbO was added to compensate lead loss during sintering. The mixture of raw materials was milled in distilled water using zirconia balls. The dried powder was calcined at 800 °C for 4 h. The reacted powder mixture was again ball milled, dried and then re-calcined at 1000 °C for 4 h. NZF–PLZT composites with general formula $0.1Ni_{0.8}Zn_{0.2}Fe_2O_4-0.9Pb_{1-3x/2}La_xZr_{0.65}Ti_{0.35}O_3$ were prepared by mixing the two phases. The mixing process was carried out by ball milling in distilled water. After drying the mixture, small amount of diluted polyvinyl alcohol (2–3 drops) was added to the powder mixture as a binder and then the powder mixture was pressed into circular disks of ~1 mm thickness and 15 mm diameter using a hydraulic press. The pellets were finally sintered at 1200 °C for 4 h in a programmable furnace.

2.2. Characterization

Experimental density of sintered pellets was determined using Archimedes principle. Theoretical density of the samples was calculated using the lattice parameters. The X-ray diffraction (XRD) data was recorded using a Philips XPERT-PRO diffractogram with Cu-K_α ($\lambda=1.5406$ Å) in the range of $2\theta=20-70°$ with step size of 0.01°. Scanning electron microscope (SEM) micrographs of the freshly broken pieces of sintered samples were obtained using a JEOL JSM 6510LV, Japan. For measuring electrical properties, the sintered pellets were ground and then electroded properly using silver epoxy on flat surfaces and subsequent heating at 400 °C for 30 min. The dielectric properties were measured as a function of frequency (100 Hz–1 MHz) at room temperature and as a function of temperature (35–500 °C) using an Agilent 4263B LCR meter. *P–E* hysteresis loops were recorded at 20 Hz using an automated *P–E* loop tracer based on the Sawyer–Tower circuit. For electric poling, samples were heated to 150 °C and a dc electric field (~15 kV/cm) was applied for 1 h. Then the samples were cooled to room temperature in the presence of field. *M–H* loops were recorded using a Lake Shore 735 VSM Controller, Model 662, interfaced with a computer.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the XRD patterns for composite samples with $x=0.01$ and 0.03 and confirms the coexistence of both phases (NZF and PLZT). These XRD patterns show well defined peaks with specific indices characteristics of cubic spinel structure of ferrite phase and rhombohedral perovskite structure of ferroelectric phase [16,18]. No additional peaks were observed. Intensity and number of peaks corresponding to NZF are very small due to lower concentration of ferrite phase. The values of lattice constant '*a*' corresponding to both phases were calculated for all the samples and are given in Table 1 for comparison. There is a slight decrease in the values of lattice constant of ferroelectric phase which may be due to substitution of less ionic size La at Pb site ($r(Pb^{2+})=163$ pm and $r(La^{3+})=150$ pm). The values of lattice constant of ferrite phase are random which may be due to stresses induced by ferroelectric phase surrounding the ferrite phase [19]. Experimental, theoretical and relative density for all the samples were determined and are given in Table 1. Such variation in density values is already observed in many ferroelectric ceramics [20–22]. Fig. 2 shows the SEM micrographs for all composite samples. It can be easily observed that the average grain size decreases with increase in La substitution. Individual phases cannot be distinguished in SEM micrographs because of the small concentration of ferrite phase.

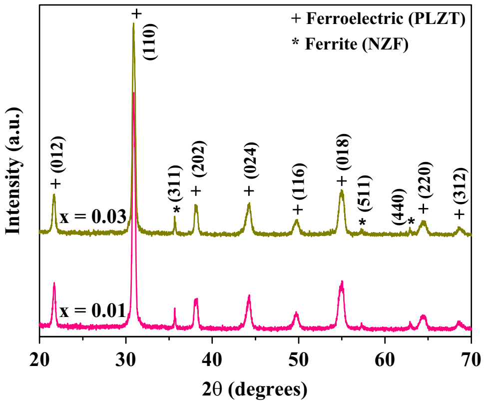

Fig. 1. XRD patterns for composite samples with $x=0.01$ and 0.03.

Table 1
Structural parameters for all composite samples

Parameters	*X*			
	0	0.01	0.02	0.03
Lattice constant '*a*' (ferroelectric phase) (Å)	4.104	4.097	4.095	4.092
Lattice constant '*a*' (ferrite phase) (Å)	8.353	8.342	8.346	8.348
Experimental density (g/cm^3)	6.88	6.79	6.87	6.81
X-ray density (g/cm^3)	7.75	7.72	7.73	7.71
Relative density (%)	88.8	88.0	88.9	88.3

3.2. Dielectric properties

Fig. 3 shows the variation of dielectric constant (ε) and dielectric loss ($\tan\delta$) with temperature for all samples at 100 kHz. It can be observed easily that initially dielectric constant increases with increase in temperature and reaches a maximum value at a particular temperature followed by decrease with further increase in temperature for all composite samples. This temperature corresponds to ferroelectric Curie temperature (T_c). A decrease in T_c was observed with increase in *x* (La substitution) which may be due to substitution of less ionic size substituent and shrinkage in PZT lattice [23]. Higher values of dielectric loss at higher temperatures were observed. This may be due to the thermal conductivity losses which occur as a result of thermally activated electron hopping between Fe^{2+}/Fe^{3+} and Ni^{2+}/Ni^{3+} ions present in NZF phase [24].

Frequency dependence of dielectric properties at room temperature was also studied for all samples and is shown in Fig. 4. Higher values of dielectric constants were observed at lower frequencies which may be because of space charge polarization due to the presence of inhomogeneities in the structure [25]. The dielectric constant decreases with increase in frequency because ionic and orientation polarizations decrease with increase in frequency for all the samples. For samples with $x=0$ and 0.01, dielectric constant (ε) and loss ($\tan\delta$) rise steadily toward lower frequencies. This low-frequency behavior can be explained on the basis of electronic charge carriers generated due to Pb^{2+} vacancies [26]. With further increase in La substitution, this low-frequency dispersion decreases which may be due to decrease in concentration of Pb^{2+} vacancies (La^{3+} ions substitute Pb^{2+} ions) and the donor effect of La substitution that counteracts the