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Letter

Resistivity dependent magnetoelectric characterization of $Ni_{0.2}Co_{0.8}Fe_2O_4 + Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ composites

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ABSTRACT

The magnetoelectric (ME) composites with compositions (x) $Ni_{0.2}Co_{0.8}Fe_2O_4 + (1 - x)Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ (BPZT – barium lead zirconate titanate) in which $0 \le x \le 1$ mol% was prepared by standard ceramic double sintering method. The presence of two phases in the composites such as ferrite and ferroelectric was confirmed by X-ray diffraction studies (XRD). The study of variation of DC resistivity with temperature of all the samples shows n-type conductivity. Magnetic property such as AC susceptibility reveals the existence of single domain (SD) and mixed (SD + MD) particles in the composites. Static ME voltage coefficient as a function of applied DC magnetic field was studied. The ME response is found to be dependent on the content of ferrite phase and the maximum value of ME coefficient 536 μV/(cm Oe) was observed for 15% of ferrite phase in composites.

1. Introduction

The composite materials consisting of ferrite (piezomagnetic) and ferroelectric (piezoelectric) phases are known as magnetoelectric (ME) composites. These composites shows ME property however, this property is absent in their constituent phases [1]. ME property of a ferroelectro-magnet is the electric polarization on the application of AC or DC magnetic field $(ME)_H$ or the magnetic polarization on the application of AC or DC electric field $(ME)_E$ [2,3]. ME composites are used as sensors, isolators, phase shifters, modulators, wave-guides, transducers, etc. [4,5]. The materials showing ME conversion can also be used as thin film wave-guides in integral optics and fiber communication technology [6]. The ME effect was first observed in antiferromagnetic Cr_2O_3 compound, i.e. the single-phase materials [7,8] and later some single-phase crystal families were found to show the ME effect [9]. Alternatively, ferrite/ferroelectric composite ceramics were reported to exhibit a large ME effect than those of the single-phase materials [10,11], which results from the magnetic–mechanical–electrical interaction between the ferrite/ferroelectric phases. The ME coefficient of composites largely depends on the equilibrium of two phases and perfect mechanical coupling between the grains and the resistivity of composites [12]. Such ME composites can be prepared by sintering ferrite and ferroelectric phases together by using the standard ceramic method.

Nan and co-workers [13] proposed the first simplified approximation and the first rigorous theoretical method to calculate the effective ME properties of ferrite/ferroelectric ceramic composites. Since then, many researchers have investigated the ME coupling behaviour in the ferrite/ferroelectric composites both experimentally and theoretically [14–17]. Kanamadi et al. [18] reported ME conversion of the order of 248 μV/(cm Oe) in Ni–Cu $Fe_2O_4 + Ba_{0.5}Pb_{0.5}Ti_{0.5}Zr_{0.5}O_3$ composites prepared by ceramic method. Though the ferrites chosen were less magnetostrictive, due to larger Jahn–Teller distortion the samples show higher ME effect. Suryanarayana and co-workers [19] studied $NiFe_2O_4 + BaTiO_3$ and $CoFe_2O_4 + BaTiO_3$ composites and reported ME voltage coefficient of the order of 160 μV/(cm Oe). However, the research work on ME composites are restricted only to the measurement of ME effect but not much work has been done on the resistivity dependent ME effect. The selection of suitable combination of ferrite and ferroelectric materials to achieve better ME effect is, however a challenging task. In order to achieve better ME output, the piezomagnetic coefficient of ferrite phase and piezoelectric coefficient of ferroelectric phase must be high. In the present work nickel–cobalt mixed ferrite has been chosen to introduce large Jahn–Teller distortion in the ferrite lattice with lead and zirconium doped barium titanate which may yield maximum ME signal.

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In this paper we report the dependence of $(dE/dH)_H$ on composition and magnetic field of $Ni_{0.2}Co_{0.8}Fe_2O_4$ + BPZT composites with the existence of single domain (SD) and mixed (SD + MD) particles. In the composites the high resistivity ferrite phase has been selected because it is one of the important requirements for getting high ME voltage and maximum value of ME voltage coefficient of 536 μV/(cm Oe) for 15% of ferrite phase + 85% of ferroelectric phase in composites has been observed.

2. Experimental

2.1. Synthesis of ME composites

The composites of (Ni–Co) ferrites and BPZT ferroelectrics were synthesized by double sintering ceramic method. The ferrite phase was prepared by normal solid-state reaction using analytical reagent grade NiO (99.8% purity), CoO (99.5% purity) and Fe_2O_3 (99.3% purity) powders in stoichiometric ratios. Similarly the ferroelectric phase was prepared with BaO (99.6% purity), PbO (99.8% purity), ZrO_2 (99.3% purity) and TiO_2 (99.5% purity). The $Ni_{0.2}Co_{0.8}Fe_2O_4$ was presintered at 800 °C and BPZT was presintered at 1050 °C for 10 h. The presintered phases were milled for 3–4 h, after mixing in required molar proportions (i.e. 15%, 30% and 45% ferrite phases with 85%, 70%, and 55% ferroelectric phases, respectively) and uniaxially pressed in a die to form pellets (2–3 mm thick and 10 mm diameter) using hydraulic press. Final sintering of the constituent phases and their composites was carried out at 1150 °C for 12 h at the heating rate of 100 °C/h and then cooled to room temperature at the same rate in a programmable furnace.

2.2. Characterization

The crystalline phases of the samples were identified with the help of X-ray diffractometer (Philips Model PW-1710) with Cu Kα radiation (λ = 1.514 Å). The DC resistivity was measured in the temperature range 200–600 °C by two probe method. The two field AC susceptibility measurements was carried out in the temperature range of 100–800 °C at 263 Hz in an rms field of 7 Oe.

In order to observe ME effect, the composites are poled electrically and magnetically, both are useful for observing better ME effect in the composites [20]. Electric poling was carried out in an AC field of 2 kV/cm during cooling of the samples and the samples were magnetically poled by applying DC magnetic field of 6 kOe at room temperature. Using the same setup static ME voltage coefficient $(dE/dH)_H$ of the samples was measured with Keithley electrometer (Model 2000) in a DC magnetic field.

3. Results and discussion

3.1. XRD analysis

The X-ray diffraction (XRD) patterns of the composites show two well defined sets of diffraction peaks (Fig. 1). Formation of cubic spinel structure of ferrite phase and tetragonal perovskite structure of ferroelectric phase was confirmed by characterizing the constituent phases. However, the intensity of the ferroelectric phase peaks decreases with its content in the composites. The calculated lattice parameters are almost equal to their constituent phases and no structural change was observed with the variation of molar percentage of constituent phases (Table 1). But slight variation in lattice parameters with change in mol% of either of the phases is due to the differences in the ionic size of the component ions. The Co^{2+} ions have longer ionic radius (0.82 Å) then Ni^{2+} (0.78 Å) and Fe^{3+} (0.67 Å).

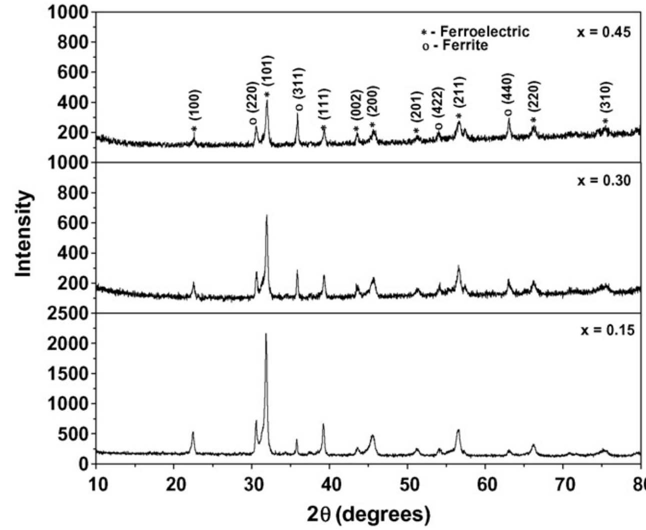

Fig. 1. XRD patterns of $xNi_{0.2}Co_{0.8}Fe_2O_4 + (1-x)Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ ME composites.

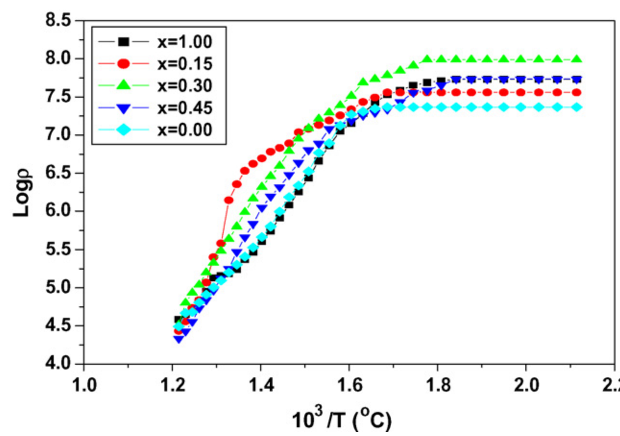

Fig. 2. Variation of DC resistivity with temperature for $xNi_{0.2}Co_{0.8}Fe_2O_4 + (1-x)Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ ME composites.

3.2. Electrical resistivity

The temperature dependent electrical resistivity is as shown in Fig. 2. It shows two trends of conductivity, the first trend observed at lower temperature is due to the impurities may be attributed to the ordered states of the ferroelectric phase. The resistivity of ferroelectric phase is high as compared to ferrite phase therefore at low temperature region the resistivity due to impurities along with ferroelectric phase leads to ordered ferroelectric phase. The second trend that occurs at higher temperature is due to polaron hopping and may be attributed to the disordered para-electric

Table 1
Data on lattice parameter, resistivity, Curie temperature and ME voltage coefficient of $xNi_{0.2}Co_{0.8}Fe_2O_4 + (1-x)Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ ME composites.

Composition (x)	Lattice parameters of phase (Å)				ρRT × 10^7 (Ω cm)	T_C (°C)	$(dE/dH)_H$ (μV/(cm Oe))
	Ferrite	Ferroelectric					
	'a'	'a'	'c'	'c/a'			
0.00	–	4.031	4.032	1.0002	6.0	–	–
0.15	8.339	3.977	3.978	1.0002	9.7	700	536
0.30	8.320	4.087	4.008	1.0002	7.5	710	530
0.45	8.307	3.958	3.959	1.0002	5.0	740	520
1.00	8.372	–	–	–	4.2	760	–