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Magnetoelectric properties of particulate and bi-layer PMN-PT/$CoFe_2O_4$ composites

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ABSTRACT

Our studies comprise electrical dielectric and magnetoelectric properties of $CoFe_2O_4$ (CFO) and $Pb(Mg_{1/3}Nb_{2/3})_{0.67}Ti_{0.33}O_3$ [PMN-PT] magnetoelectric composites. The individual phases were prepared by conventional ceramic method. The particulate composites of ferrite and ferroelectric phases were prepared in ferroelectric rich region. Presence of both the phases in the composites was confirmed using X-ray diffraction techniques. The scanning electron microscopic images recorded in backscattered mode were used to study the microstructure of composites. Lattice constant, dielectric constant, electrical resistivity, ferroelectric, and magnetic properties of individual as well as particulate composites were studied. Further the bi-layer composites were made using the discs obtained from the powders of individual phases where hot press technique was employed to obtain disc of individual phases. CFO phase used in bi-layer composites was obtained using chemical co-precipitation technique. Magnetoelectric (ME) measurements were carried out on both, particulate and layered magnetoelectric composites. Comparison of ME signal obtained from particulate and layered composites revealed that the layered composites gives superior magnetoelectric signal. ME data obtained for layered composites show good agreement with the theoretical model.

1. Introduction

The magnetoelectric (ME) effect is an electric polarization in response to an applied magnetic field; observed in two phase composites made up of ferrite and ferroelectrics. An applied magnetic field produces deformation in ferrite due to magnetostriction and results in an induced electric polarization due to piezoelectric effect in ferroelectric phase. Two types of composites, bulk and layered, have been studied extensively. Bulk composites have the advantage of superior mechanical strength over layered samples. One could easily control physical, magnetic, electrical, and ME parameters with proper choice for the two phases and their content [1–5]. But in case of bulk composites α_E values were smaller in two to three orders of magnitude than that of theoretically predicted values. Such low values are due to low resistivity of ferrites, which (i) limits electric fields used for electric polling of the composites and consequently a poor piezoelectric properties and (ii) produces a leakage current that results in the loss of induced voltage. These difficulties could be easily surmounted in layered composites [4,5].

A key point for obtaining large magnitude of ME response is to select magnetostrictive (ferrite) and piezoelectric phases having high values of magnetostrictive and piezoelectric coefficients, respectively. Interestingly, $CoFe_2O_4$ is known for higher value of magnetostriction amongst spinel ferrites [6,7]. Cobalt ferrite in single crystal form exhibit high anisotropic magnetostriction values in the range of 600–900 ppm, depending on the composition, whereas, for sintered polycrystalline form these values are close to 230 ppm [8]. Hence in the present studies $CoFe_2O_4$ was selected as a magnetostrictive phase. Piezoelectric single crystals of PMN-PT and PZN-PT near the morphotropic phase boundary (MPB) were found to exhibit giant piezoelectric effects, about ten time larger than that of conventional ceramics [9]. The enhancement in dielectric constant ($\varepsilon' > 6000$) and piezoelectric constant ($d_{33} = 600$ pC/N) in the MPB region has been observed in polycrystalline PMN-PT, which is higher than that of polycrystalline PZT [10]. As reported in the literature the selection of PMN-PT a piezoelectric phase in ME composites show enhancement in ME voltage coefficient as compared to other ME composites [11]. Hence, PMN-PT in the MPB region was selected as a ferroelectric phase due to its strong piezoelectric properties amongst various piezoelectrics.

This report is concern with the synthesis of particulate and layered composites containing $Pb(Mg_{1/3}Nb_{2/3})_{0.67}Ti_{0.33}O_3$ (PMN-PT) a piezoelectric phase and $CoFe_2O_4$ (CFO) as magnetostrictive phase. Comparative studies of nature of magnetoelectric interactions in bulk and layered composites have been carried out.

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2. Experimental

2.1. Bulk composites

PMN-PT ceramic in morphotropic phase boundary (MPB) region was prepared by the Columbite technique using the procedure reported elsewhere [12]. The CFO phase was prepared using conventional ceramic technique. Individual phases viz. PMN-PT and CFO were sintered at 1250 °C for 12 h. Three composites were prepared by mixing 85% PMN-PT+15% CFO [85/15 (A_1)], 70% PMN-PT +30% CFO [70/30 (A_2)], and 55% PMN-PT+45% CFO [55/45 (A_3)]. The composites were shaped into pellets of diameter 10 mm and thickness of 1–1.5 mm and sintered at 1100 °C for 12 h. The final sintering temperature of composites was optimized so as to get PMN-PT and CFO phases only without any intermediate or new phase. Phase formation of the sample was confirmed using X-ray diffraction (XRD) technique, which was performed on Bruker D8 Advance X-ray diffractometer. Surface morphology of the composites was recorded using scanning electron microscope (SEM) (JEOL, Model JSM-6360A). Dielectric properties were recorded using HIOKI 3532–50 LCR HiTESTER at room temperature. Room temperature ferroelectric hysteresis loop i.e. polarization with applied electric field was recorded using automatic *P–E* hysteresis loop tracer system at 50 Hz using *P–E* loop tracer (Marine India Elect. Pvt. Ltd, India). Magnetostriction measurements were carried out on CFO sample using wide range strain indicator (Vishay measurements model 3800). The resistance strain gage was fixed in the plane surface of magnetostrictive layer using super glue. The measurements were carried out for '*H*' parallel or perpendicular to the plane of the sample plane. Magnetic field '*H*' was applied (i) parallel to the sample plane and strain gage to note λ_{11} and (ii) perpendicular to strain gage and parallel to sample plane to note λ_{12}.

2.2. Layered composites

PMN-PT powder obtained using Columbite technique and CFO powder obtained by chemical co-participation method [13] were separately pressed into rods of 10 mm diameter and thickness of about 6 mm treated at 7 MPa at 750 °C for 45 min with hot press facility. Then the rod was cut into discs of 0.5 mm thickness. Silver electrodes were deposited on 0.5 mm thick PMN-PT disc and then poled in an electric field of 20 kV/cm as the sample was cooled from 170 °C to room temperature. Bilayers were then made with the PMN-PT layer bonded to CFO using 0.01–0.03-mm-thick layer of a quick-dry epoxy. The thickness of the epoxy layer was found to affect the ME coupling, and the optimum thickness for maximum ME coupling was in the range 0.01–0.02 mm. The data provided here are for bilayers with a 0.02-mm-thick layer of epoxy.

2.3. Magnetoelectric measurements

Variation of ME voltage as a function of DC magnetic field for orientations (i) parallel to the plane of the sample (i.e. transverse) and (ii) perpendicular to the plane of the sample (i.e. longitudinal) were noted for bulk ME composites. The bilayer samples were placed in a shielded holder and subjected to bias field *H* and ac magnetic field of dH=3 Oe at 100 Hz parallel to '*H*'. The ME voltage coefficient was estimated from $\alpha_E=\delta E/\delta H=\delta V/t\ \delta H$ where δV is the measured voltage across the sample and '*t*' is the thickness of PMN-PT layer. The measurements were made for two different field orientations. With the sample represented by (1 and 2), the transverse coefficient $\alpha_{E,\,31}$ was measured for *H* and d*H* parallel to the sample plane. The longitudinal coefficient $\alpha_{E,\,33}$ was measured for all the magnetic fields perpendicular to the sample plane. In case of particulate composites, ME voltage developed across the sample was recorded as a function of DC magnetic field, which was further used to find out ME voltage coefficient [14]. The schematic representations of (a) layered and (b) bulk composites are shown in Fig. 1.

3. Results and discussion

3.1. Particulate composites

3.1.1. Structural and microstructural analysis

The XRD pattern of the individual phases and composites are shown in Fig. 2. X ray diffraction pattern of the powders of individual phases CFO and PMN-PT, does not show any un-reacted or intermediate phase. Lattice parameters of CFO and PMN-PT were calculated and given in Table 1. In case of bulk composites two sets of well defined diffraction line were observed; one of the set corresponds to the CFO whereas other set corresponds to PMN-PT. Even in case of bulk composites sintered at 1100 °C did not show presence of any un-reacted or intermediate phase. The lattice parameters of the individual phases are in well agreement with the literature. The percentage porosity of all the samples is given in Table 1. As observed from Table 1, the PMN-PT possesses high density as compared with the

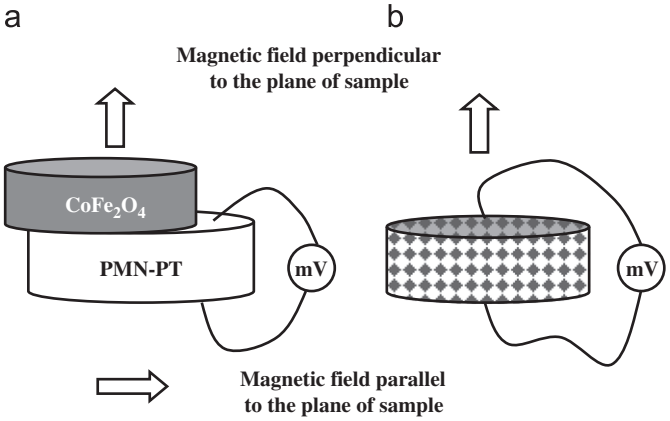

Fig. 1. Schematic representation of (a) ME bi-layer composites and (b) ME bulk composites.

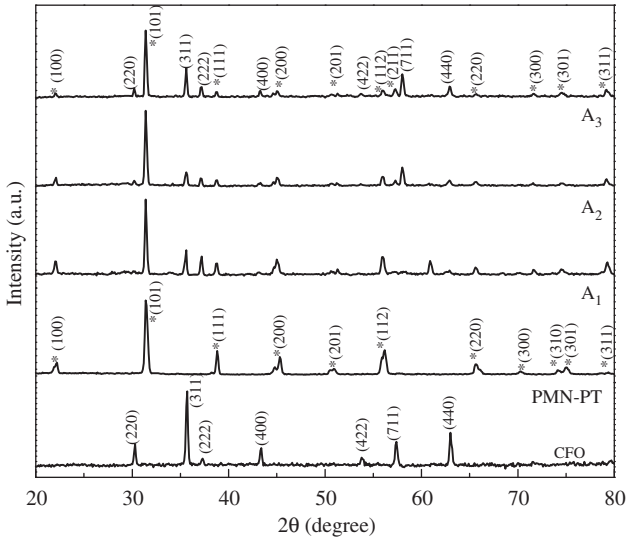

Fig. 2. X-ray diffraction patterns of pure CFO and PMN-PT, [85/15 (A_1)], [70/30 (A_2)], and [55/45 (A_3)] magnetoelectric composites.