

Magnetolectric Effect in Substituted Zinc Ferrite Lead Titanate Particulate Composites

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ABSTRACT

Magnetolectric composites containing PbTiO_3 ZnFeCoO_4 phases have been prepared by standard ceramic technique. The structure and morphology of the composites were examined by means of X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD result showed that the composites consist of spinel ZnFeCoO_4 phase and perovskite PbTiO_3 phase annealing at temperature 750°C . The variation in dielectric constant with the temperature and low frequency it shows dispersion in certain frequency. The dielectric properties are strongly influenced by interface phenomenon (Maxwell Wagner) due to the local electrical inhomogeneity. The peak value of dielectric decreases with increase in temperature. Conductivity, Susceptibility and permeability have been found to vary with temperature and concentration of ferrite phase due to increase in crystalline size. The static value of magnetolectric conversion factor (dE/dx) was measured as function of applied magnetic field. The coexistence of inductive and capacitive natures in the composites favours size reduction and designation simplification in many passive electronic devices such as integrated filters and microwave absorbers.

Keywords: composites, Dielectric properties, magnetic properties, magnetolectric effect, magnetostrictive etc.

1. INTRODUCTION

The magnetolectric composites with piezoelectric and magnetostrictive materials are of interest as transducers, which transform changes in a magnetic field into electric voltage and vice versa [1-3]. It can be used as a magnetic field sensor for an alternative tool of the Hall sensor for magnetic field measurement, or as an electric current measurement.

The unidirectional solidification helps in the decomposition of the eutectic liquid composition into alternate layer of the constituent phase: a piezoelectric perovskite phase and a piezomagnetic spinel phase. Although the measurement voltage coefficient ($dE/dH = 130 \text{ mV/cm. Oe}$) [4] was superior to single phase materials such as Cr_2O_3 solidification process required high temperature and a critical control over the composition especially when one of the components (oxygen) was gas, and the unexpected third phase appeared in the composites [5]. In 1978, they reported on sintered magnetolectric composites of BaTiO_3 and $\text{Ni}(\text{Co,Mn})\text{Fe}_2\text{O}_4$ with excess TiO_2 in terms of the particle size effect, the cooling rate, and the mole ratios of both the phases [5]. They reported a maximum value of the magnetolectric voltage coefficient of 80 mV/cm. Oe in sintered magnetolectric composites. However, this value was still lower than in situ composites, and it required special poling process for high magnetolectric effect.

Sintered magnetolectric composites have many advantages compared to in situ composites [5]. The sintered composites are much easier and cheaper in fabrication than in situ composites. Moreover, molar ratio of phases, grain size of each phase, and sintering temperature are easily controllable. These are some important issues in fabricating the sintered magnetolectric particulate composites. First, no chemical reaction should occur between the piezoelectric and magnetostrictive materials during the sintering process. The chemical reaction may reduce the piezoelectric or magnetostrictive properties of each phase. Second, the resistivity of magnetostrictive phase should be as high as possible. If the resistivity of magnetostrictive is low, the electric poling becomes very difficult due to leakage current. Also, the leakage current reduces the magnetolectric properties of the composites. When the ferrite particles make connected chains, the electric resistivity of the composites is reduced significantly, because of low resistivity of ferrite. Therefore, good dispersion of the ferrite particles in the matrix is highly required in order to sustain sufficient electric resistivity of the composite. Third, mechanical defects such as pores in the interface between two phases should not exist in the composite for good mechanical coupling.

2. EXPERIMENTAL

Preparation of Ferrite phase ZnFeCoO_4 (ZFC)

The ferrite phase was prepared by using analytical grade ZnO , Fe_2O_3 and Co_2O_3 in stoichiometric proportions of these oxides were weighed and mixed thoroughly. These constituents were finely powdered in agate bowls with acetone medium for 10 hrs. The sherry was dried, and dried powders were loosely packed in the form of pellets. These pellets were calcinated in a closed furnace of 1000°C for 10 hrs with $5^\circ\text{C}/\text{min}$ heating/cooling rate with intermediate grinding. After calcinations, these pellets were crushed powdered to obtain fine particle size.

Preparation of Ferroelectric Phase (PTO)

The ferroelectric phase PbTiO_3 was prepared from the starting materials as the analytical grade PbO and TiO_2 as starting materials. These constituents weighed in stoichiometric proportion and mixed thoroughly. These powdered were mixed in agate mortar for 10 hrs in an acetone medium. Later pellets were formed and then calcinated at 600°C for 3 hrs. after calcination these pellets were crushed and finely powdered with agate mortar. These fine powders thus obtained were employed for the preparation of the ME composites.

Preparation of Particulate Composites

The ferromagnetic and ferroelectric phase PbTiO_3 (PTO) and ZnFeCoO_4 (ZFC) powders were mixed in stoichiometric

proportions with generic formula $\text{PbTiO}_3 - (1 - x) \text{ZnFeCoO}_4$ where, $x = 0, 0.25, 0.50, 0.75$ in different batches. The individual batches of powders were mixed thoroughly in acetone media and calcinated further at 950°C for 4hrs and once again these composites were mixed thoroughly and pressed into pellets of diameter 13 mm and thickness 4 mm. The pelletized samples were finally sintered at 1200°C for 6 hrs and slowly cooled. An enough care was taken for volatilization of zinc and lead from the ceramics at sintering temperature.

Characterization

The XRD pattern analysis for formation of spinel, cubic, tetragonal, perovskite mixed structure was done on X-ray diffractometer (model PW – 1830, Philips, Netherland) with copper Cu – $K\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) operated at 45 KV voltage and 40 mA current.

The electrodes required for the electrical measurements were applied on both faces of the samples by applying conducting silver paints. Dielectric measurements as a function of temperature and frequency on different sample we are performed computer controlled impedance analyzer [Model 6500 B Wayne Kerr, UK.]. Dielectric loss and capacitance were measured as a function of frequency in the range of 100 Hz - 1MHz. the ME output was measured applying dc magnetic field at room temperature. To get ME signals the samples were polled both electrically and magnetically. The magnetic field of 6 KOe was applied across the sample in the direction of electric field. The susceptibility measurements were carried out to explore the existence of single and multidomain process of the particle. Similarly permeability measurements were carried out in the frequency range 100Hz – 1 MHz

3. RESULT AND DISCUSSION

Novel ferromagnetic - dielectric particulate composites of PbTiO_3 , ZnFeCoO_4 was prepared by conventional ceramic method. The details of synthesis and characterization were given in previous section. These ferromagnetic-dielectric particulate composites were prepared with a view to using them as ME sensors and transducers. The samples were characterized using Cu – $K\alpha$ radiations using X-ray diffractometer (XRD, Philips model 1710) and Ni as filter. The lattice parameters and the c/a ratio of the constituent phases match well to that reported in the literature [6, 7]. The occurrence of peaks with specific indices characteristics of spinel and perovskite structure confirms cubic spinel structure in ferrite phase and tetragonal perovskite structure in ferroelectric phase of the composites. There are no structural changes observed for both the phases in the composites. The lattice parameters for both the phases in these composites slightly vary with the composition as given table as given in table-1

Table 1. X-ray diffraction data of PbTiO_3 - 75% of ZnFeCoO_4 , $a = 3.9169 \text{ (\AA)}$, $c = 3.946 \text{ (\AA)}$

Angle 2θ deg	d_{obs} (Å)	d_{cal} (Å)	Plane (hkl)
21.783	3.956	3.908	Fo (100)
31.207	2.779	2.784	Fo (101)
31.323	2.769	2.772	Fo (110)

35.012	2.485	2.487	Fe (311)
38.505	2.267	2.267	Fo (111)
44.527	1.973	1.954	Fo (002)
50.449	1.754	1.753	Fo (201)
55.291	1.611	1.611	Fo (112)
56.316	1.584	1.594	Fo (211)
61.875	1.454	1.466	Fo (440)
63.927	1.412	1.392	Fo (202)
73.522	1.249	1.236	Fo (301)

It is clear that there is no intermediate or inter phase formed in all the composites. However the lattice parameter ratio (c/a) varies slightly. Higher peaks (110/101) intensities of the ferroelectric phase in dominant and remains constant intensity of (311) plane suppressed to certain extent. The variation of dielectric constant with frequency at room temperature are shown in figs. (1).

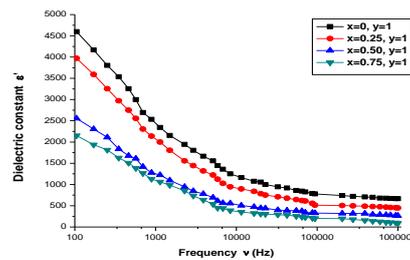


Fig 1:- variation of dielectric constant with frequency for the system (y) $\text{PbTiO}_3 - (1-x) \text{ZnFeCoO}_4$

The dielectric constant initially decreases with frequency and then after reaches a constant value at higher frequencies. At lower frequencies, the dispersion is large, while it is independent of the frequency.

As the frequency increases, ionic and orientation polarization decreases and finally disappears due to the inertia of molecules and ions. The dielectric constants is very large at lower frequencies and while it is independent beyond 10 KHz. It is but natural that ferrite and ferroelectric grains are randomly mixed together in parallel and series modes.

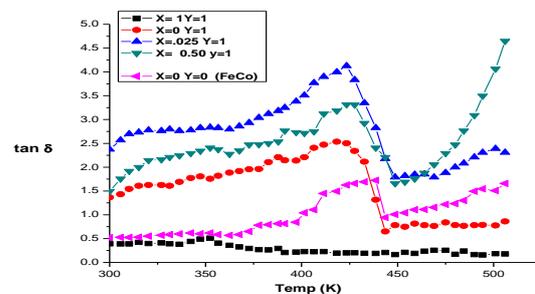


Fig 2 Variation of loss tangent with temperature for the composite system; (y) $\text{PbTiO}_3 - (1-x) \text{ZnFeCoO}_4$

The value of $\tan\delta$ decreases with increase in frequency showing dispersion in certain frequency range similar to dielectric constant (ϵ') versus frequency. The abnormal behavior of two type of charge carriers that is p- type and n- type to the polarization, it is reported that the local displacement of p - type charge carriers take place in opposite direction to that of n - type charge carriers, which decreases the polarization at lower frequencies. The variation of loss tangent with temperature at 1 KHz frequency is shown in figs. (2), from the graphs it is revealed that the loss tangent increases with increase in temperature and reaches at maximum value in the neighborhood of Curie temperature and then descends. The polarons hopping mechanism hold in fair agreement for this type of variation.

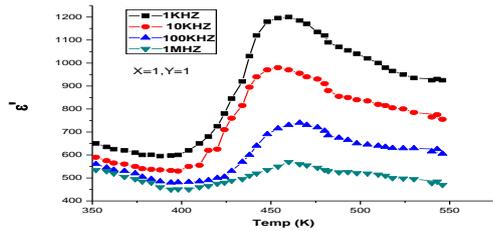


Fig. 3 Variation of dielectric const with temp for ferroelectric system: PbTiO_3

The variation of dielectric constant ' ϵ' ' with temperature at different frequencies 1 KHz, 10 KHz, 100 KHz and 1 MHz in the temperature range 300^0K to 500^0K are diagrammatically represented in figs.(3). In case of composite, the dielectric constant slowly increases with temperature reaches a maximum value (ϵ_{max}) and then decreases.

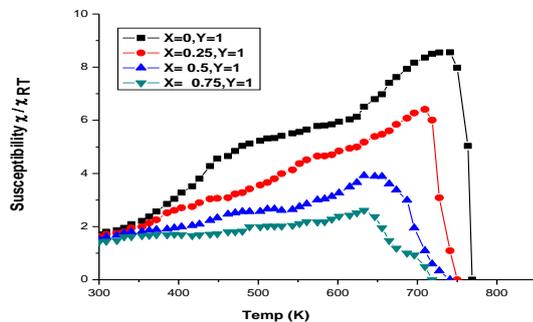


Fig 4 Variation of susceptibility with temp for the system; (y) PbTiO_3 - (1-x) ZnFeCoO_4

The variations of relative or normalized mass susceptibility (χ_T / χ_{RT}) for both the series i.e. Co and Cr substituted ferrites-composites were shown in figs. (4). The variation of ac susceptibility was first carried out on iron metal samples by Hopkinson, it was observed that it touches maxima before transition temperature (T_c) and then fall rapidly to zero. From the graph it has been observed that the relative susceptibility gradually increases up to certain temperature " T_b " called as blocking temperature, which keep on decreasing with increase in ferroelectric content. It is observed that Curie temperature keeps decreasing as decrease in Co content.

The substitution of Zn^{2+} for Fe^{3+} reduces the Curie temperature of ferrite [8]. The decrease in magnetization is due to augmented B-B interactions followed by reduced A-B interactions. Also the presence of Co^{2+} ions in the Cobalt - Zinc ferrite hastens the $\text{Co}^{+2} + \text{Fe}^{+3} \leftrightarrow \text{Co}^{+3} + \text{Fe}^{+2}$ exchange

reaction in octahedral sites, while tetrahedral sites are preferentially occupied by Zinc cation.

The variation in initial permeability with frequency at room temperature was depicted in the figs. (5) for ZCOF-PTO and system. It is clear from the figures that initial permeability is independent of frequency in both the systems. There is a decreasing trend was observed with increases of ferroelectric content. This may be due to presence of anisotropy [9] observed low frequency dispersion in ferrites and they concluded this may be due to the domain wall displacement

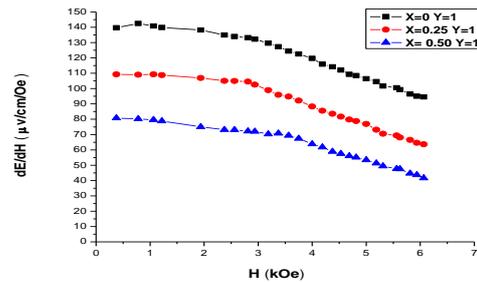


Fig.6. Variation of ME output with magnetic field for the system (y) PbTiO_3 - (1-x) ZnFeCoO_4

The variation in ME voltage coefficient of the samples with different ZCOF content as a function of dc magnetic field are shown in figs. (6). From figures, we can see that the ME coefficient values increases with increase in ferrite content. Stress transfer through the interface between these phases achieves the magnetoelastic coupling. Hence, magneto mechanical and electromechanical resonance in ferrite and ferroelectric phases assume importance. The ME voltage coefficient depends on the mechanical coupling, resistivity and mole fraction of the constituent phases. The resistivity of the composite is temperature dependent property, which decreases in high temperature regions, making the polarization of samples more difficult. Hence ME voltage coefficient was measured at room temperature.

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