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Studies on structural, dielectric and magnetoelectric properties in $CuFe_{1.8}Cr_{0.2}O_4$– $Pb(Mg_{1/3}V_{2/3})O_3$ composites

V.L. Mathe, K.K. Patankar, U.V. Jadhav, A.N. Patil, S.D. Lotake, S.A. Patil *

Physics Department, Shivaji University, Kolhapur-416004 (M. S.), India

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Abstract

$CuFe_{1.8}Cr_{0.2}O_4$–$Pb(Mg_{1/3}V_{2/3})O_3$ composites were prepared using a conventional ceramic double sintering process. The presence of both phases in the composites was confirmed by X-ray diffraction studies. Variation of dielectric constant (ϵ') with frequency in the range 100 Hz–1 MHz and also with temperature for four different frequencies (1 kHz, 10 kHz, 100 kHz, 1 MHz) was studied. The nature of the peaks indicate DPT type behaviour. The static value of magnetoelectric conversion factor, i.e., $DC(ME)_H$ has been studied as a function of intensity of the magnetic field. The maximum value of $DC(ME)_H$ was found to be 164.33 μV/cm/Oe for 70% ferrite phase. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Magnetoelectric effect; DPT type behaviour; Dielectrics and ME composites

1. Introduction

Composite materials consisting of piezoelectric and piezomagnetic phases show a magnetoelectric(ME) effect, which is absent in their constituents phases [1]. The magnetoelectric effect is a coupled (or cross) two field effect, in which an application of electric field induces magnetisation whereas an application of magnetic field induces electric polarisation. This effect in composites entails the combined deformation of the matrix of the piezoelectric and magnetostrictive components. A primary deformation of the ferrite phase causes polarisation of the piezoelectric particles of the composite; on the other hand, electric polarisation of piezoelectric materials causes change in magnetisation of the ferrite phase due to mechanical coupling of piezomagnetic (ferrite) and piezoelectric (ferroelectric) phases [2]. Such magnetoelectric composites are exploited as sensors, waveguides, modulators, switches, phase inverter, rectifier, etc., and find substantial application in the radioelectronics and microwave electronics [3]. A perusal of literature related to this field suggests that the work carried out on such composites is confined to the measurement only of ME effect and is limited to composites containing especially $BaTiO_3$ as a ferroelectric component [4,5] and Co [6] or Ni–Co–Mn [7] as a magnetostrictive component.

In the present communication, we have chosen Cu–Cr ferrite as the magnetostrictive phase and $Pb(Mg_{1/3}V_{2/3})O_3$ as the piezoelectric phase. The Cu–Cr ferrite was very logically chosen, as it is well known that Cu^{+2} and Cr^{+3} ions being Jahn Teller ions can induce lattice distortion. This distortion in the ferrite lattice is coupled to the surrounding piezoelectric phase. In fact, the presence of mechanical distortion in the ferrite lattice is one of the prerequisite for such composites to exhibit ME effect [3]. Moreover, the coupling of distortion in the ferrite lattice to the ferroelectric one can result in piezoelectric effect only if the ferroelectric phase has high piezoelectric coefficient. Hence a ferroelectric phase of relaxor type was aptly chosen. Relaxor ferroelectrics are well known for their high electrostictive coefficient.

2. Experimental

The composites prepared contain two individual phases, one is the ferroelectric [$Pb(Mg_{1/3}V_{2/3})O_3$] and the other the ferrite [$CuFe_{1.8}Cr_{0.2}O_4$]. The ferrimagnetic phase $CuFe_{1.8}Cr_{0.2}O_4$ was prepared through normal

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* Corresponding author. Tel.: +91-231-690-571; fax: +91-231-691-533.

E-mail address: sapatil_2000@yahoo.com (S.A. Patil).

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solid state reaction taking CuO, Cr_2O_3, and Fe_2O_3 in appropriate molar proportions. These basic oxides were mixed and finely ground in agate mortar for couple of hours and presintered at 800°C for 10 h. Similarly the $Pb(Mg_{1/3}V_{2/3})O_3$ was prepared following the same route, by mixing PbO, $MgCO_3$, V_2O_5 in molar proportions and presintering the mixture at 700°C for 12 h. The magnetoelectric composites were prepared by dispersing 15, 30 and 45 mol% of $CuFe_{1.8}Cr_{0.2}O_4$ phase in the matrix of $Pb(Mg_{1/3}V_{2/3})O_3$ phase and were labeled C_2, C_3 and C4, respectively and the pure $Pb(Mg_{1/3}V_{2/3})O_3$ phase was labeled C_1. Next, these mixtures of ferrite and ferroelectric phases were pressed in the form of cylindrical pellets having dimensions of 3–4 mm in thickness and 10 mm in diameter. Finally all these pellets were sintered at 1050°C for 24 h to yield the final products.

The samples were characterized by X-ray diffraction using X-ray diffractometer (PW 3710 model). The variation of dielectric constant (ϵ') and loss tangent (tan δ) at room temperature in the frequency range from 100 Hz to 1 MHz were measured using LCR meter (HP 4284A model). The temperature dependencies of ϵ' and tan δ at four different frequencies viz. 1 kHz, 10 kHz, 100 kHz and 1 MHz, were also measured. The magnetoelectric conversion factor, $DC(ME)_H$, was measured as a function of DC Magnetic field by following the procedure due to Suryanarayana [3]. Prior to this measurement, the samples were poled both electrically and magnetically. These two types of poling are required to realize the ME signal in composites. The poling procedures adopted are described elsewhere [8].

3. Results and discussion

The XRD pattern of the composite C_1 confirms the single ferroelectric phase formation, whereas the XRD patterns of the C_2, C_3 and C_4 reveal the presence of both the ferroelectric $[Pb(Mg_{1/3}V_{2/3})O_3]$ phase and the ferrite ($CuFe_{1.8}Cr_{0.2}O_4$) phases (Fig. 1). The addition of the ferrite ($CuFe_{1.8}Cr_{0.2}O_4$) to ferroelectric $[Pb(Mg_{1/3}V_{2/3})O_3]$ phase reduces the diffraction peak intensity of the latter. The pure $[Pb(Mg_{1/3}V_{2/3})O_3]$, i.e. C_1 has tetragonal crystal structure. The crystal structure of the ferroelectric phase in C_2, C_3, and C_4 composites is cubic while the crystal structure of ferrite phase in these composites is tetragonal for C_2 and C_3 and cubic for C_4. The lattice parameters of both the phases in these composites vary with the composition (Table 1).

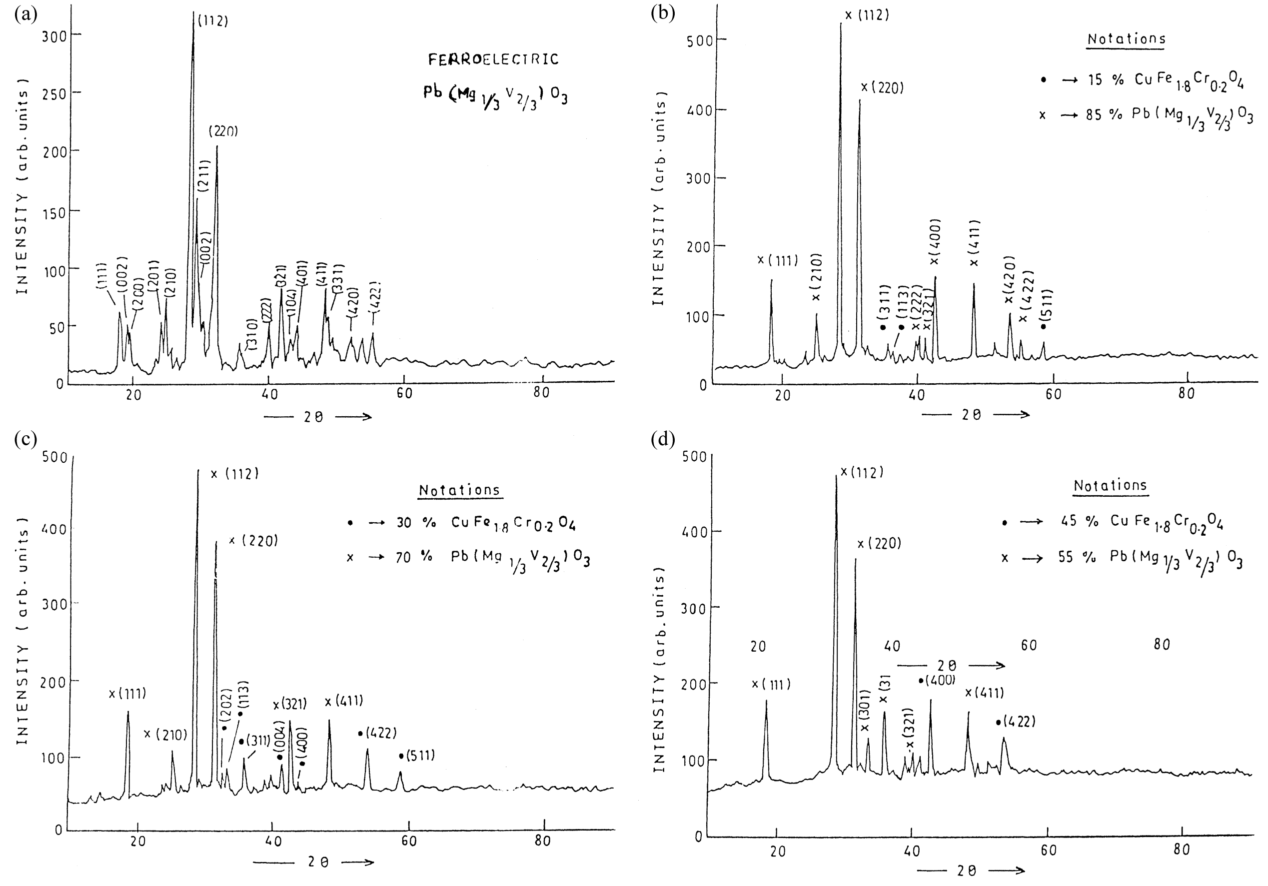

Fig. 1. X-ray diffraction pattern for composites for (a) C_1, (b) C_2, (c) C_3 (d) C_4.

The variation of dielectric constant (ϵ') with frequency in the range 100 Hz to 1 MHz for the composites is shown in Fig. 2. The figure depicts that all the samples exhibit dielectric dispersion. Initially the dielectric constant ϵ' decreases rapidly with frequency but beyond 50 kHz, ϵ' remains fairly constant. The high value of ϵ' in these composites is ascribed to ferroelectric regions being surrounded by non-ferroelectric ones, a situation similar to that existing in relaxor ferroelectrics [9]. The microscopic inhomogeneity gives rise to interfacial type of polarisation. The polaron hopping mechanism resulting in electric polarisation also has its contribution, especially in the low frequency dispersion. These spurious effects are inefficient beyond a certain frequency. The static value of the dielectric constant (ϵ') for all the composites lie in the range 50–70 beyond 50 kHz. Fig. 3 shows the variation of tan δ with frequency. The loss tangent decreases with increasing frequency.

The variation of ϵ' with temperature is shown in Fig. 4. An increase in ϵ' is observed with increasing temperature upto the transition temperature and a decrease thereafter. This is obvious behaviour of ferroelectrics at the transition point. However the nature of the peaks at this temperature vary in C_2, C_3 and C_4. The peaks are broad; reflecting the diffused phase transition (DPT) type behaviour. C_1 being a relaxor ferroelectric, DPT type behaviour is one of its characteristics. For C_2, C_3 and C_4 composites, the ferroelectric regions in these composites are surrounded by a non-ferroelectric region (ferrite), hence DPT type behaviour also observed in these composites is not surprising. The phase transition in relaxor ferroelectric, having microscopic inhomogenities is always a diffuse phase transition. Moreover in relaxors, the peak temperature varies with the frequency [10]. Similar is the case observed in the present composites. The peak temperature shifts toward lower temperature side with increase in frequency for all the composites. Thus the diffused peak is only due to the statistical fluctuations in the micro regions of these composition [11]. The degree of broadness also varies with composition and is measured in terms of diffusivity parameter γ. This diffusivity parameter or degree of broadness (disorder) is calculated using the expression [12]

$$\ln(1/\varepsilon' - 1/\varepsilon'_{\max}) = \gamma \ln(T - T_c) + a$$

where $\epsilon'_{\max}$ is the maximum value of ϵ' as observed at the transition temperature, (T_c) and γ the diffusivity parameter. The values of the γ are reported in Table 1.

It is seen from Fig. 4a to d as well as from the table, that T_c decreases with increase in ferrite content. The variation of dielectric loss with temperature at four different frequencies for the composite C_3 is shown in Fig. 5. Similar variation in dielectric loss is observed for the other composites. The curve shows a peak at a temperature,

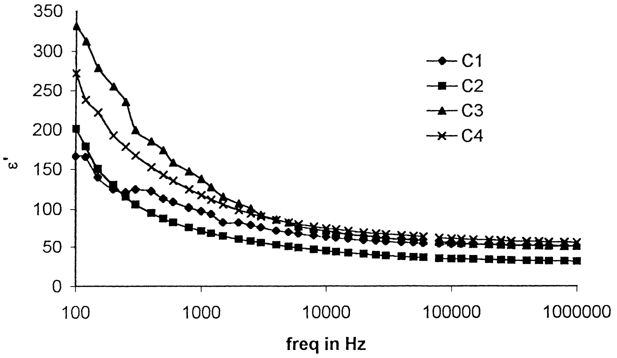

Fig. 2. Variation of dielectric constant (ϵ') with frequency for C_1 and composites.

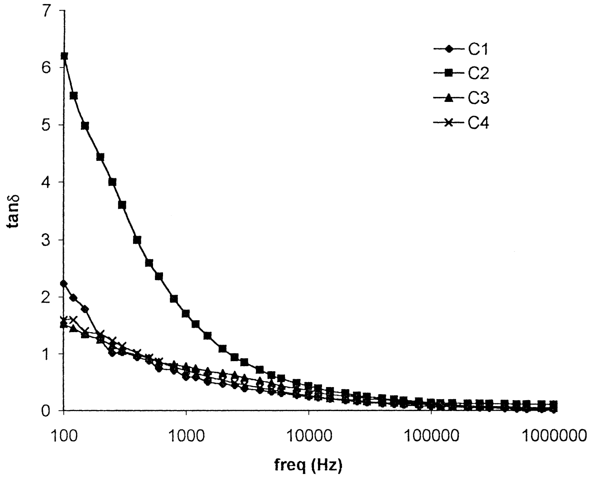

Fig. 3. Variation of loss tangent (tan δ) with frequency for C_1 and composites.

Table 1
Structural and electrical data on composites

Composition of ferrite phase %	Lattice parameter									[dE/dH]$_{\max}$ (μV/cm/Oe) at 1.6 KOe
	Ferroelectric phase			Ferrite phase			At 1 kHz			
	a (Å)	c (Å)	c/a	a (Å)	c (Å)	c/a	$\epsilon'_{\max}$	T_c C°	γ	
C_1 0	8.037	8.78	1.09	–	–	–	322.6	270	1.87	–
C_2 15	8.270	8.270	1.00	8.168	8.391	1.02	214.2	230	1.38	–
C_3 30	8.264	8.264	1.00	8.488	8.928	1.05	315.73	200	2.04	164.33
C_4 45	8.245	8.245	1.00	8.491	8.491	1.00	254.97	170	1.06	159.92

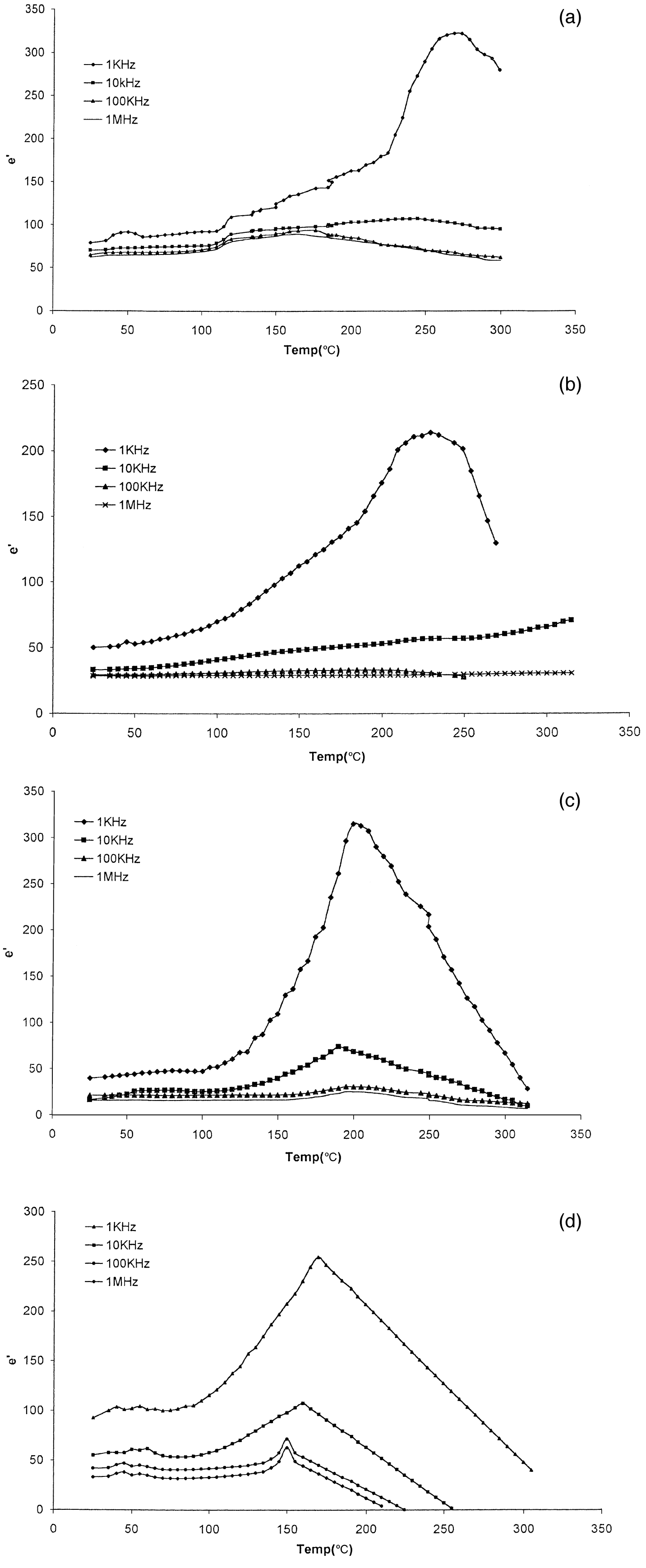

Fig. 4. Variation of dielectric constant (*e*) with temperature for (a) C_1, (b) C_2, (c) C_3, (d) C_4.

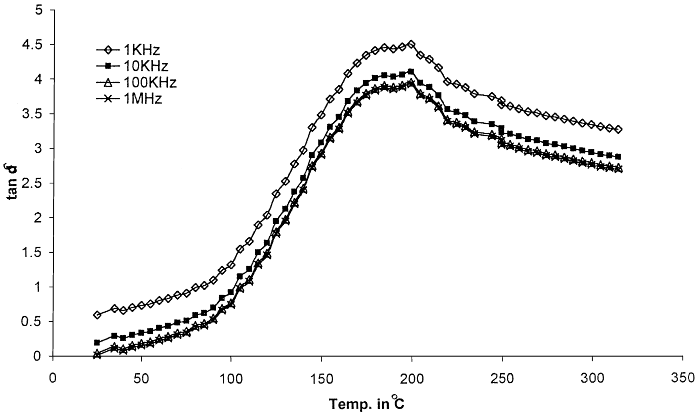

Fig. 5. Variation of loss tangent (tan δ) with temperature for C_3.

close to the Curie temperature of the ferroelectric phase in the composites. Here again the nature of the peaks is broad supporting DPT type behaviour.

The static ME conversion factor, $DC(ME)_H$, developed due to the application of magnetic field was measured for C_3 and C_4 composites. The ME signals in C_3 and C_4 composites show an initial rise, reaches maximum and thereafter decrease with respect to magnetic field. This initial rise is attributed to enhancement in elastic interaction with increasing magnetic field and the decrease in ME signal beyond a certain field is ascribed to the fact that beyond a certain value of critical field magnetisation reaches its saturation, thereby saturating the magnetisation and hence the resulting electric polarisation. Thus the constant electric field will lead to decrease in dE/dH or $DC(ME)_H$ with a further rise in the magnetic field as quoted earlier [3]. In fact, this critical field at which magnetisation reaches its saturation was confirmed from hysteresis measurement. Surprisingly no ME output was observed for C_2 composite. Moreover, the maximum value of ME output observed in C_3 is greater than observed in C_4 (Table 1). It is noted that theϵ', distortion (c/a) and diffusivity parameter(γ) are maximum in C_3 when compared to the other composites. This may be the reason for maximum ME coefficient in C_3.

4. Conclusions

$CuFe_{1.8}Cr_{0.2}O_4$–$Pb(Mg_{1/3}V_{2/3})O_3$ composite ceramics have been prepared by solid state reaction. Formation of the ferrite and the ferroelectric phases in composites has been confirmed. Variations of ϵ' and tan δ with temperature show DPT type behaviour. The observed shift in ϵ' towards the lower temperature side with increasing frequency confirms a relaxor type behavior. The maximum value of ME output is 164.33 μV/cm/Oe and 159.72 μV/cm/Oe for C_3 and C_4 composites, respectively.

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