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Role of sintering on magneto-electric effect in $CuFe_{1.8}Cr_{0.2}O_4$–$Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composite ceramics

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Abstract

Magnetoelectric composites containing $CuFe_{1.8}Cr_{0.2}O_4$–$Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ phases have been prepared by sintering them at different firing temperatures. The particle size for either phase of the composite was found to increase, whereas porosity decreases with increase in sintering temperature. This is due to the increase in the grain size with increase in sintering temperature. Resistivity of the composite decreases with increase in either sintering temperature or with increase in $CuFe_{1.8}Cr_{0.2}O_4$ content. The variation of dielectric constant (ε') with temperature reflects DPT type behaviour. The peak value of dielectric constant ($\varepsilon'_{\max}$) for a composite decreased with increase in its sintering temperature. The maximum value of the magnetoelectric conversion factor $(dE/dH)_{\max}$ equal to 182.7 μV/(cm*Oe) is obtained for 70% $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$–30% $CuFe_{1.8}Cr_{0.2}O_4$ composite when sintered at 1000°C.

Keywords: A. Sintering; Magnetoelectric output; $CuFe_{1.8}Cr_{0.2}O_4$–$Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ ceramics

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1. Introduction

Combining two dissimilar materials produces a composite material, better suited for a particular application than either of the original materials alone. Following the concept of product property suggested by Van Suchtelen [1], a magnetoelectric composite prepared by sintering a mixture of piezomagnetic and piezoelectric material exhibits a phenomenon called a magnetoelectric effect (ME effect), which is not exhibited by the composing phases on their own. The ME effect is a product of the piezomagnetic effect (magnetic–mechanical effect) in the piezomagnetic phase and the piezoelectric effect (mechanical–electrical effect) in the ferroelectric phase and is a coupled electric and magnetic phenomenon by elastic interaction [2]. Wood and Austin [3] indicated possible applications of the magnetoelectric crystals as well as the characteristics of over 15 devices whose operation range varies from audio to optical frequency, including modulators, switches, phase inverters, switches, rectifiers, coupled wave generators, and sensors. For many of these applications, the ME output must be enhanced. Boomgaard et al. [4], have reported that the resulting signal in the magnetoelectric composites depends on various factors such as particle size, dc resistivity and mole ratio. These parameters in turn depend upon the sintering temperature and time. Small fluctuations in the above mentioned parameters gives rise to a fairly large scatter in the ME signal of composites prepared under similar conditions. Thus, the ME effect is a structural dependent property. Moreover, if any intermediate or impurity phases are present in a sintered composite, it may also adversely affect the ME signal [5]. So, there is a need to optimize the sintering conditions to yield better results. The present paper communicates the role of sintering on various physical properties such as the dc resistivity, dielectric constant and the magnetoelectric output (dE/dH) for $CuFe_{1.8}Cr_{0.2}O_4$–$Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composites prepared at different sintering temperatures. PBZT has superior dielectric and piezoelectric properties [6] and Cu^{2+} being a Jahn–Teller ion induces mechanical distortion in the ferrite lattice [7]. The large piezoelectric coefficient and good mechanical coupling are two of the prerequisites for a composite to exhibit a large ME effect. Hence, we focussed our attention on a

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combination of $CuFe_{1.8}Cr_{0.2}O_4$–$Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composites and investigated it intensively.

2. Experimental details

2.1. Preparation of composites

These composites contain two phases, one ferroelectric and the other ferrimagnetic. The ferrimagnetic phase chosen was $CuFe_{1.8}Cr_{0.2}O_4$. It was prepared through normal solid state reaction using CuO, Cr_2O_3 and Fe_2O_3 in molar proportion. The ferrite was presintered at 800°C for 10 h. Similarly, the same route, starting with BaO, PbO, ZrO_2 and TiO_2 taken in molar proportion and presintered at 850°C for 4 h, gave the $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ phase. After presintering, the constituent phases were thoroughly mixed and the mixtures were presintered at 900°C to prepare magnetoelectric composites of varying compositions of $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ and $CuFe_{1.8}Cr_{0.2}O_4$. The $CuFe_{1.8}Cr_{0.2}O_4$ phase taken in 15, 30 and 45 mol% was dispersed in the matrix of $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ (abbreviated as PBZT for brevity) to prepare the composites. These composites were then pressed into cylindrical pellets measuring nearly 1 cm in diameter and 0.3 cm in thickness. They were then fired at different sintering temperatures, namely, 1000, 1050 and 1100°C to yield the final products. X-ray diffractograms and SEM micrographs of these samples sintered at different temperatures were studied. Dielectric constant versus temperature measurements were carried out at 1 kHz frequency using an LCR meter, HP 4284A model. dc resistivity was measured using digital nanoammeter and dc microvoltmeter using a two-probe technique. Magnetoelectric output (dE/dH) was measured as a function of static magnetic field for the present ceramics prepared at different sintering temperatures [5]. Prior to the measurements of dE/dH, electric poling and magnetic poling was carried out. The procedure adapted for poling was similar to that stated as procedure 1 in [8]. Magnetic poling was carried out at room temperature by placing the sample in a strong dc magnetic field of 5 KOe.

3. Results and discussions

The X-ray diffraction pattern of the 70% PBZT composite sintered at three different sintering temperatures is shown in Fig. 1. Fig. 1 reveals that no other phases apart from $CuFe_{1.8}Cr_{0.2}O_4$ and $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ was present. This is also true for both the 85% PBZT and 55% PBZT composites. For the 85% PBZT composite, only the ferroelectric phase appeared for all the three sintering temperatures, whereas XRD for 70% PBZT and 55% PBZT reveals the presence of both the $CuFe_{1.8}Cr_{0.2}O_4$ and $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ phases clearly at all the three sintering temperatures. It is attributed to the fact that the ferrite phase for 85% PBZT composite is diluted and thereby suppressed by the dominant $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ phase, indicating much lower scattering factor when compared to $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ phase. This is also supported by the fact that $CuFe_{1.8}Cr_{0.2}O_4$ starts to appear only by increasing $CuFe_{1.8}Cr_{0.2}O_4$ content at a particular sintering temperature. There are no structural changes but slight variations in the lattice parameters of both the phases are observed. Both the phases have a tetragonal crystal structure for samples sintered at 1050 and 1100°C temperatures. The lattice parameters for all the three composites when sintered at 1000°C are as follows. For 85% PBZT composite, PBZT phase has $a=4.02$ Å and $c=4.066$ Å. Next, for 70% PBZT composite, PBZT phase has $a=4.023$ Å and $c=4.151$ Å and $CuFe_{1.8}Cr_{0.2}O_4$ phase has $a=8.6736$ Å and $c=8.6836$ Å. Similarly for 55% PBZT composite, lattice parameters are $a=4.023$ Å and $c=4.351$ Å for PBZT phase and $a=8.6748$ Å and $c=8.6884$ Å for $CuFe_{1.8}Cr_{0.2}O_4$ phase. The average particle size of both the phases in the composites for a few reflections widely spaced in 2θ range were calculated using Scherrer's formula, $P_{hkl}=(k\ \lambda)/(\beta_{1/2}\ \cos\theta_{hkl})$–(1), where $k=0.89$ and $\beta_{1/2}=$ half peak width and are given in Table 1. It is clear from the table that the particle size for both the phases of the composites increases with increasing sintering temperature. Moreover, the X-ray diffractograms of composites sintered at various temperatures (Fig. 1) depict that the broadness of peak decreases and the peak becomes sharper as the sintering temperature is raised. This is also true for other samples. This is attributed to the fact that grain growth usually occurs at high sintering temperatures [9,10]. The SEM micrographs shown in Figs. 2 and 3 for 70% PBZT composite indicate average grain size of 1.95 μm when sintered at 1000°C and 2.2 μm when sintered at 1050°C. Careful observations of the particle size for both the phases of different compositions (Table 1) indicate that the grain growth is larger for $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ and is obvious since the content of $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ phase is large compared to that of the $CuFe_{1.8}Cr_{0.2}O_4$ phase in composites.

Fig. 4 shows the variation of dc resistivity with temperature for different composites sintered at different sintering temperatures. The resistivity of the composite is a result of resistivities of $CuFe_{1.8}Cr_{0.2}O_4$ crystallites and $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ crystallites being connected in series and parallel [4]. It can be deduced from Table 1 that the resistivity of $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ in composites is higher than that of $CuFe_{1.8}Cr_{0.2}O_4$, indicating a parallel mode. Moreover, from the figure, it is clear that the resistivity of all the composites decreases with increase in sintering temperature but there is no difference in the ferroelectric phase transition temperature.

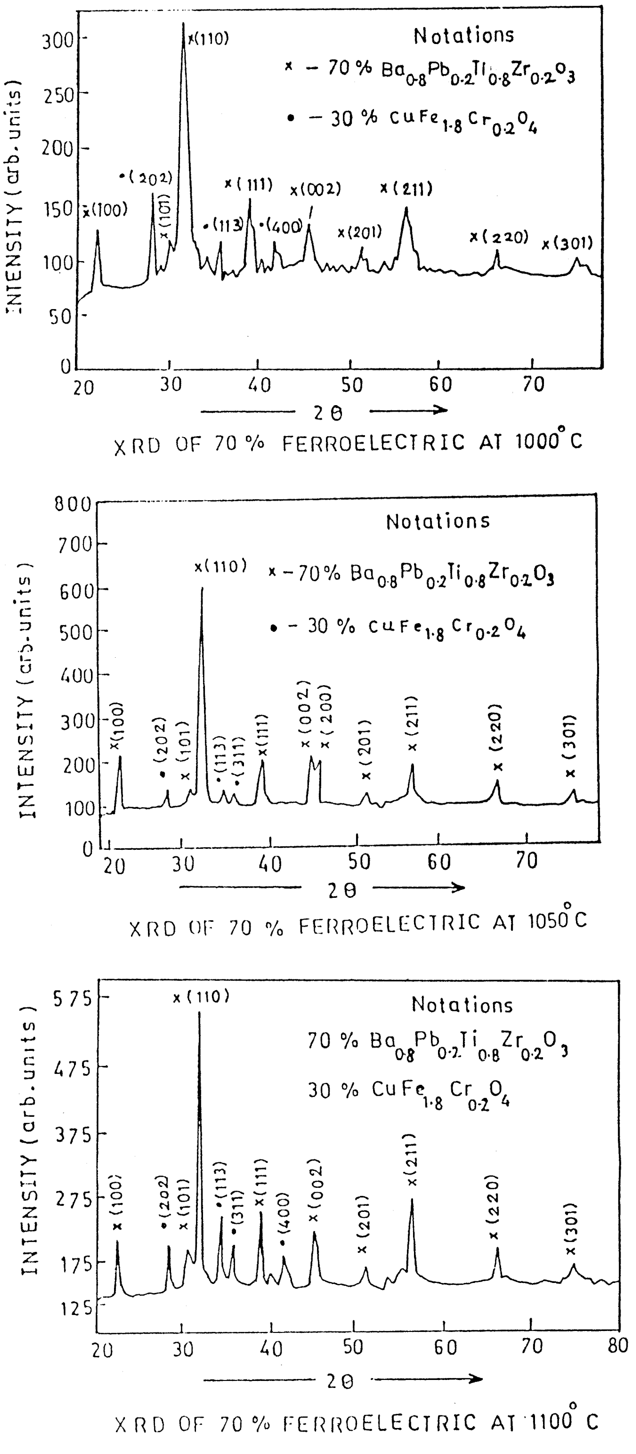

Fig. 1. XRD of 70% $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$–30% $CuFe_{1.8}Cr_{0.2}O_4$ composite sintered at different sintering temperature.

This observation is similar to that obtained in Fig. 5 for dielectric versus temperature plots. As the sintering temperature increases, the individual grains of the composites become larger and come closer, thus increasing the grain to grain contact and thereby reducing the porosity. This is clear from the micrographs depicted in Figs. 2 and 3. It is well known that pores invariably introduce the insulating paths to electrons. Hence, decrease in porosity (Table 1) for higher sintering temperatures leads to decrease in resistivity of composites.

Fig. 5 shows the variation of ε' with temperature at 1 kHz frequency for various composites sintered at different sintering temperatures. It can be seen that the sintering temperature has no influence on the ferroelectric phase

Table 1
Structural and electrical data of various composites sintered at different sintering temperatures

Sintering temperature	Mole % of PBZT	Particle size		γ	ε'_{max} at 1 kHz	Porosity (%)	ρ_{dc} at RT (MΩ-cm)	Average grain size	ME output dE/dH in μV/cm/Oe
		Ferro (μm)	Ferri (μm)						
1000°C	85% (B1)	0.0937	–	–	320.16	15	1.2	1.2	Not detected
	70% (B2)	0.0913	0.1158	1.188	180.4	15.8	1.95	1.95	182.7
	55% (B3)	0.0711	0.064	1.64	133.27	18.7	0.345	0.345	173.17
1050°C	85% (C1)	0.234	–	–	130.16	12.9	1.4	1.4	Not detected
	70% (C2)	0.267	0.246	1.037	150.04	12.55	2.2	2.2	163.42
	55% (C3)	0.091	0.081	1.468	128.27	12	0.76	0.76	150.17
1100°C	85% (D1)	0.312	–	–	105.16	9.9	2.5	2.5	Not detected
	70% (D2)	0.272	0.312	1.506	125.04	9.88	2.8	2.8	Not detected
	55% (D3)	0.106	0.092	1.464	103.27	9.87	0.9	0.9	Not detected

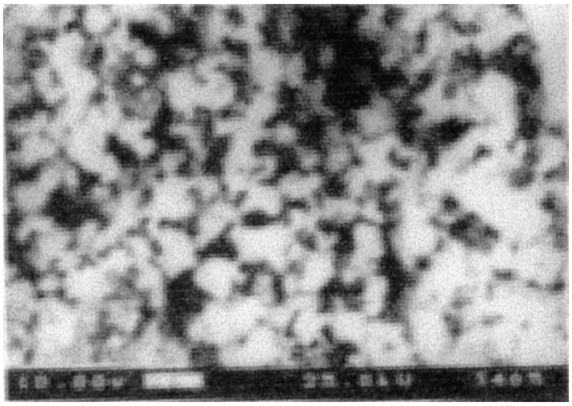

Fig. 2. SEM micrograph of 70% $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$–30% $CuFe_{1.8}Cr_{0.2}O_4$ composite sintered at 1000°C.

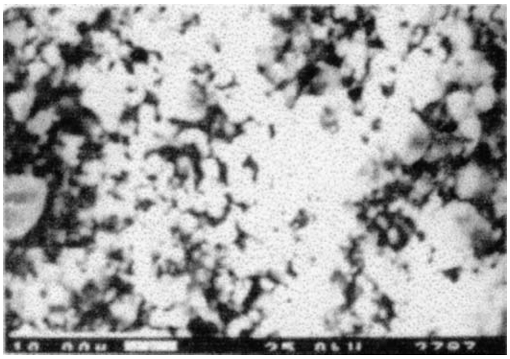

Fig. 3. SEM micrograph of 70% $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$–30% $CuFe_{1.8}Cr_{0.2}O_4$ composite sintered at 1050°C.

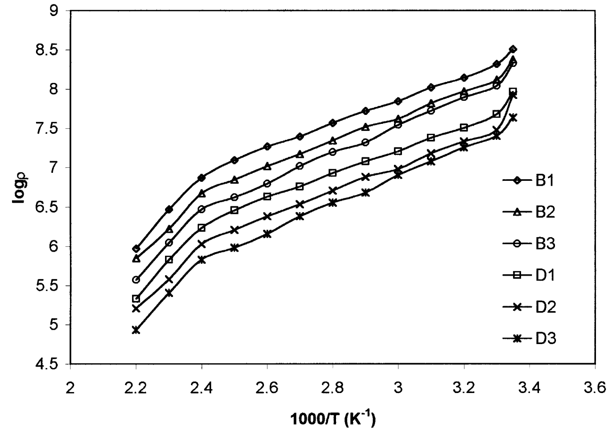

Fig. 4. Variation of dc resistivity (logρ) with temperature [1000/T(K)].

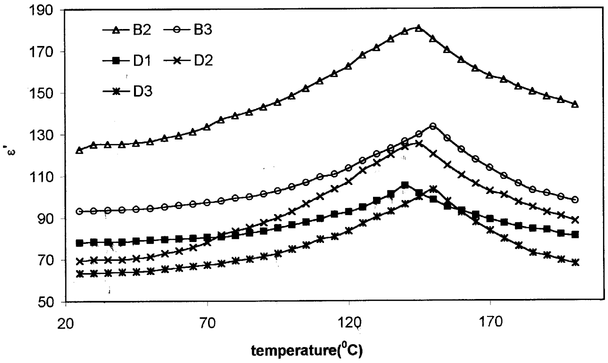

Fig. 5. Variation of dielectric constant (ε') with temperature in °C.

transition in various composites. Within the investigated range of temperature, ε'_{max} decreases with increasing sintering temperature. Similar results were obtained for $Ni(Co,Mn)Fe_2O_4$–$BaTiO_3$ composites by other workers [4]. For every sintering temperature, ε'_{max} was found maximum in 70% PBZT composite. Moreover, the plots of ε' versus temperature depicts diffused phase transition 70% PBZT and 55% PBZT composites. In the case of composites, the DPT type phase transition is ascribed to the fact that ferroelectric regions are surrounded by non-ferroelectric regions (ferrite), similar to that reported earlier for different composites [7]. The diffusivity parameter lies between 1 and 2 (Table 1), supporting DPT type of behaviour in both the composites [7].

4. Dependence of ME output on various parameters

4.1. Particle size and grain size

It is known from the previous work [4] that there is an intimate relation between the particle size of individual phases and the efficiency of magnetoelectric conversion.

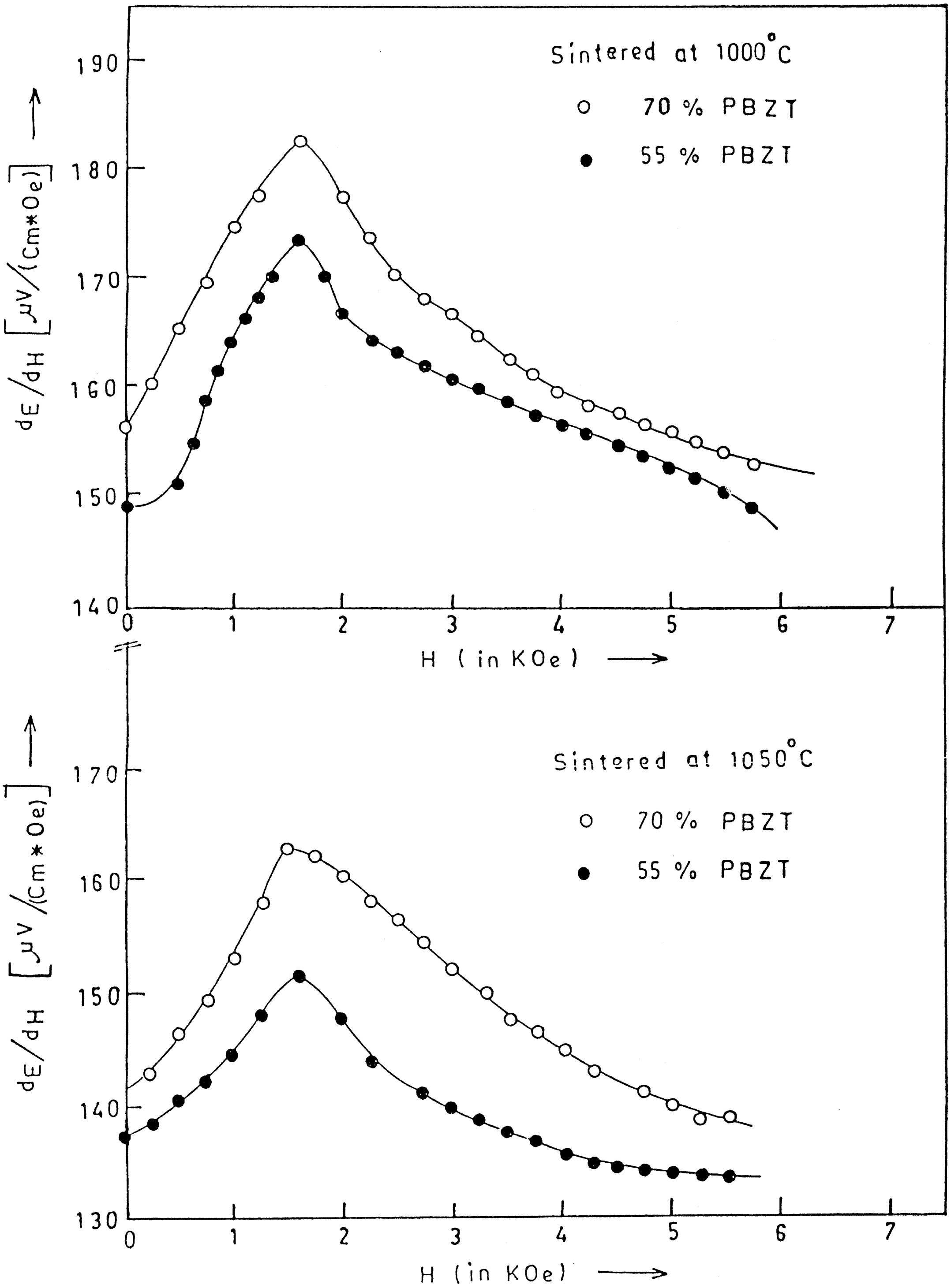

Fig. 6. Variation of static magnetoelectric conversion factor (dE/dH) with magnetic field (in KOe).

In the present work, for a particular composite, the linear static ME output (dE/dH) decreases with increasing particle size of either phases of the composite (Table 1). This is attributed to the fact that large grains can be polydomain and small ones cannot [4], hence, less effective in inducing a high piezomagnetic and piezoelectric coefficient. It has already been noted that the piezoelectric properties of any ferroelectric vary considerably with particle size, especially large grains and, hence, large particles are poorer in elastic coupling [11].

The influence of the mole ratio of both the phases on ME output is a difficult task to explain. If there were no depolarising field, if dilatation coefficients of both the phases were exactly the same and if the mechanical coupling coefficients were independent of mole ratio, the ME output would be maximum for 50% piezomagnetic–50% piezoelectric composite [4]. It is not so in the present case. The maximum value is obtained for 70% $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composite sintered at 1000°C. The shift in the maxima towards a higher content of ferroelectric is attributed to the fact that the low resistivity of $CuFe_{1.8}Cr_{0.2}O_4$ phase offers a conducting path to the developed charges, thereby decreasing dE/dH. It is obvious, as an increase in ferrite content decreases the resistivity of composite (Table 1). Naturally, it may be expected to achieve high ME output in 85% $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composite. To our surprise, no ME signal was detected in this composite for all the three sintering temperatures. The reason is that there may be weak magnetoelectric interactions in this composite [5]. In fact, 85% $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ XRD has resulted in only a $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ phase, though sintered at three different temperatures.

The variation of static ME conversion factor with dc magnetic field for composites sintered at different sintering temperature was measured for the present samples (Fig. 6). In case of 70% and 55% $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ composites, both sintered at 1000 and 1050°C, ME output shows an initial rise, reaches a maximum value and thereafter decreases. This observation is akin to that obtained by other workers [7,12,13]. Initial rise in ME output with magnetic field is mainly due to enhancement in elastic interaction with increasing magnetic field [2]. The maximum value of dE/dH at 1.6 KOe are noted in Table 1. It was confirmed from the hysteresis measurement that intensity of magnetisation reaches its saturation value at 1.6 KOe. Therefore, beyond this field, the magnetisation and strain thus produced would produce a constant electric field in the piezoelectric phase. This leads to decrease in dE/dH with increasing in magnetic field beyond 1.6 KOe [5,7,12,13]. No ME signal was detected in any of the composites, which were sintered at 1100°C. This is again attributed to the decrease in the resistivity. The resistivity for all the composites at this temperature falls below 10^8 Ohm cm. The order 10^8 ohm cm is the minimum required resistivity for composite to exhibit ME output [5]. The magnitude of ME signal in the present composites is comparable with the values obtained for $CoFe_2O_4$–$BaTiO_3$ composites, though $CoFe_2O_4$ is highly magnetostrictive, when compared to $CuFe_{1.8}Cr_{0.2}O_4$ ferrite [12]. Moreover, $LiFe_5O_8$–$BaTiO_3$ composites have resulted in no ME signal, in spite of the high resistivity and giant magnetostriction exhibited by lithium ferrite as reported earlier [5].

5. Conclusions

The sintering process brings about many microstructural changes in the composite ceramics. The ME effect is a structural dependent property. The increase in the particle sizes of both the phases together with the increase in average grain size and decrease in resistivity and dielectric constant with increase in sintering temperature resulted in decrease of ME signal. The mole ratio of the constituent phases has also an influence on the resulting ME signal. In the present study, ME output is found to be maximum in 70% PBZT–30 % $CuFe_{1.8}Cr_{0.2}O_4$ composite sintered at 1000°C.

References

[1] J. Van Suchtelene, Phillips Res. Rep. 27 (1972) 28.
[2] Ce-wen Nan, Phys. Rev. B. 50 (1994) 6082.
[3] D. Wood, A.E. Austin, Int. J. Magnet. 5 (1974) 303.
[4] J. Vanden Boomgaard, R.A.J. Born, J. Mater. Sci. 13 (1978) 1538.
[5] S.V. Suryanaryana, Bull. Mater. Sci. 17 (1994) 1259.
[6] V.M. Laletin, Sov. Technol. Phys. Lett. 17 (1991) 342.
[7] K.K. Patankar, S.A. Patil, K.V. Sivakumar, R.P. Mahajan, Y.D. Kolekar, M.B. Kothale, Mater. Chem. Phys. 65 (2000) 97.
[8] J. Vanden Boomgaard, A.M.J.G. Van Run, J. Van Suchtelen, Ferroelectrics 14 (1976) 727.
[9] A.L. Stuijts, C. Kooy, Sci. Ceram. 2 (1965) 231.
[10] T.B. Medikeri, M. Phil thesis, Shivaji University, Kolhapur, August, 1988.
[11] H. Motegi, S. Hiskins, J. Phys. Soc. Japan 29 (1970) 524.
[12] A. Hanumaiah, T. Bhimasankaram, S.V. Suryanaryana, G.S. Kumar, Bull. Mater. Sci. 17 (1994) 405.
[13] R.P. Mahajan, K.K. Patankar, M.B. Kothale, S.A. Patil, Bull. Mater. Sci. 23 (4) (2000) 273.