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# Dielectric behaviour and magnetoelectric effect in cobalt ferrite–barium titanate composites

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**Abstract.** Composites of $BaTiO_3$ and $CoFe_2O_4$ have been prepared with various compositions by double sintering method. The presence of the two phases has been confirmed by XRD. Variation of dielectric constant with temperature in these samples has been studied. All the samples have shown linear magnetoelectric conversion in the presence of static magnetic field. The magnetoelectric effect ($dE/dH$) has been studied as a function of intensity of magnetic field. The maximum value of the conversion factor $(dH/dH)_{max}$ was found to be 0·16 mV/cm/Oe.

**Keywords.** Dielectric behaviour; magnetoelectric effect; cobalt ferrite–barium titanate composites.

## 1. Introduction

Van Suchtelene (1972) predicted magnetoelectric conversion as a product property in some two-phase materials. The property would be exhibited when a piezoelectric and a piezomagnetic material are combined in proper proportion to form a composite body. Subsequent to the prediction, ME conversion in ferrite–barium titanate composites was experimentally reported by Boomgaard *et al* (1974, 1978). The composites can be prepared either by solid-state reaction or by unidirectional cooling. While there are experimental advantages of choosing any desired composition in the solid-state route, the existence of a eutectic or eutectoidal point between the participating phases is a necessary condition if unidirectional cooling is to be employed. In their exhaustive work Boomgaard *et al* (1974) reported ME conversion in Ni(Co, Mn)$Fe_2O_4$–$BaTiO_3$ prepared by solid-state route and $CoFe_2O_4$–$BaTiO_3$ prepared by unidirectional cooling. They observed the highest value of magnetoelectric conversion ($dE/dH$) of 80 mV/cm/Oe in 60% Ni(Co, Mn) $Fe_2O_3$–40% $BaTiO_3$ composite. They also studied the dependence of ($dE/dH$) on various process parameters, compositions and particle size of the unidirectional phases. Interestingly, in the unidirectionally prepared $CoFe_2O_4$–$BaTiO_3$ composite they reported a high value of ($dE/dH$) of 130 mV/cm/Oe (Boomgaard *et al* 1974). In this paper we report the dependence of ($dE/dH$) on composition and magnetic field of $CoFe_2O_4$–$BaTiO_3$ prepared by solid-state reaction route. In addition, this system offers an opportunity for a detailed investigation of dielectric and ferroelectric behaviour as a function of ferrite composition.

## 2. Preparation of magnetoelectric composites

These composite materials contain two individual phases, one ferroelectric and the other ferrimagnetic. The ferrimagnetic phase chosen was cobalt ferrite. It was prepared through normal solid-state reaction taking CoO and $Fe_2O_3$ in molar ratios. The ferrite was presintered at 1050°C for 2 h. After presintering the raw material, it was ground to a fine powder. The magnetoelectric composites were prepared by taking $CoFe_2O_4$ prepared by us and $BaTiO_3$ available in the market (A R Grade), with varying compositions of $BaTiO_3$ (molar 40%, 50% and 60%). These compositions were mixed with 2% polyvinyl alcohol as a binder and pressed into pellets of thickness of around 1–2 mm and diameter 10 mm, using a unidirectional pressure of $10^9 N/m^2$. The pelletized samples were sintered at 1250°C for 30 min and slow-cooled from 1250 to 1000°C at 50°C/h and later furnace-cooled. The entire sintering process was done in a programmable furnace.

## 3. Experimental

### 3.1 *XRD*

The samples were characterized by X-ray diffraction (XRD) (Phillips model 1730/PW 1390) using FeK$\alpha$ radiation. From XRD (figure 1) it was observed that the composite samples had barium titanate and cobalt ferrite phases predominantly and also some extra unidentified peaks. The intensity of barium titanate peaks increased with increasing percentage of barium titanate in the composite.

### 3.2 *Electrical poling*

The sign of the magnetoelectric conversion in our samples depended on the polarization direction of the ferroelectric phase. Therefore the electrical poling was done for all the compositions at 150°C, which is 30°C above ferroelectric transition temperature $T_c$ of $BaTiO_3$. At room temperature the external field of 7·5 kV/cm was applied. The field started decreasing at about 90°C and was about 3–5 kV/cm at 150°C, depending on the composition. The sample was kept at this temperature for 30 min and was cooled to room temperature in the presence of external field.

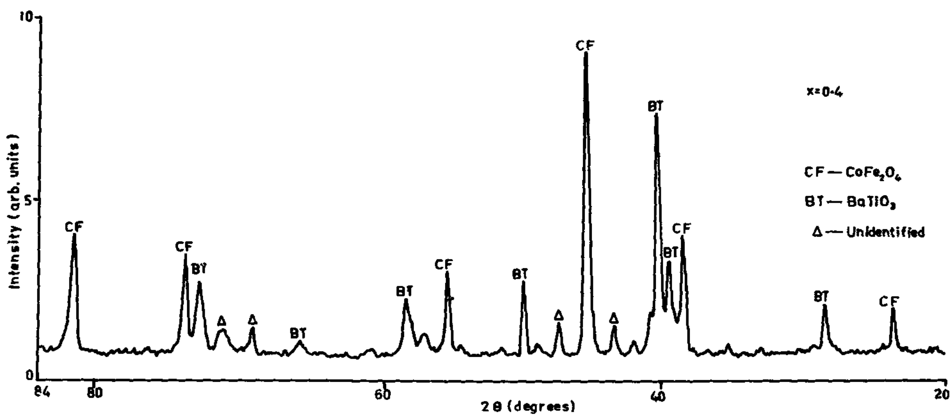


**Figure 1.** XRD diffractogram of 60% $CoFe_2O_4$–40% $BaTiO_3$.

## 4. Results and discussion

The dielectric permittivity $\varepsilon_r$ in all the compositions have been measured in the temperature range RT to 130°C for which silver-coated pellets were used. The dielectric measurements were carried out at 10 kHz frequency using a HP impedance analyser model 4192A. In the composites, as the concentration of barium titanate increased the transition temperature ($T_c$) was found to increase from 115°C to 120°C as shown in figure 2. Above the transition temperature the dielectric constant decreased continuously. The $\varepsilon_{T_c}$ (dielectric constant at $T_c$) and $\varepsilon_{RT}$ (dielectric constant at RT) for the three composites are tabulated in table 1. The decrease in $T_c$ can be due to a small proportion of an unidentified phase as evidenced in XRD or due to Fe impurity from the ferrite phase. The variation of $\varepsilon$ beyond $T_c$ also does not follow Curie–Weiss law and the transition appears to be of diffuse type (Lines and Glass 1977). The dc resistivity measurements at RT were also carried out in these samples and are given in table 1.

The magnetoelectric coefficient ($dE/dH$) of the composite which is the product of the piezomagnetic (ferri) deformation and the piezoelectric (ferro) generation largely depends on the electrical resistivity of the sample and the mechanical coupling between the two phases. We have measured magnetoelectric conversion (MEC) for three

**Table 1.** Dielectric data of $CoFe_2O_4$–$BaTiO_3$ composites.

| Composition | $\rho_{RT}$ | $\varepsilon_{RT}$ | $\varepsilon_{TC}$ | $T_c$ | MEC |
|---|---|---|---|---|---|
| 60% $CoFe_2O_4$–40% $BaTiO_3$ | $1{\cdot}35 \times 10^8$ | 209 | 1145 | 115 | 0·10 |
| 50% $CoFe_2O_4$–50% $BaTiO_3$ | $9{\cdot}10 \times 10^8$ | 098 | 1488 | 117 | 0·11 |
| 40% $CoFe_2O_4$–60% $BaTiO_3$ | $1{\cdot}26 \times 10^9$ | 144 | 625 | 120 | 0·16 |

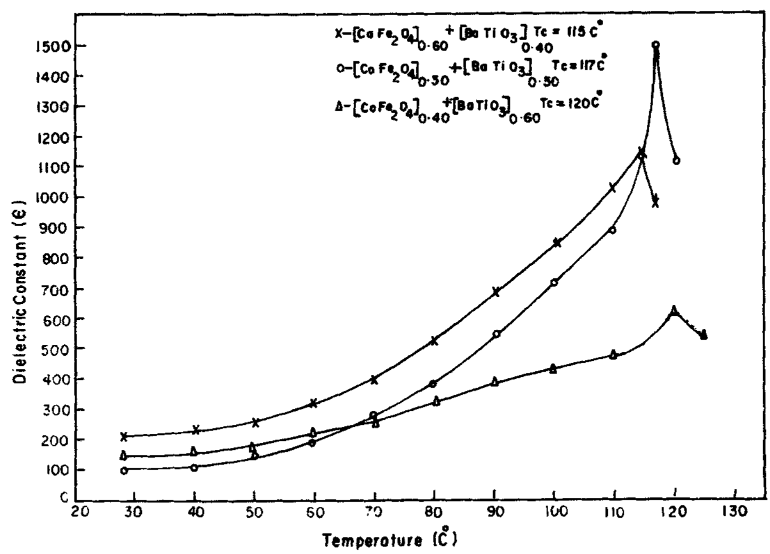


**Figure 2.** The variation of dielectric constant with temperature at 10 kHz frequency. (×, 60% $CoFe_2O_4$–40% $BaTiO_3$; O, 50% $CoFe_2O_4$–50% $BaTiO_3$; Δ, 40% $CoFe_2O_4$–60% $BaTiO_3$).

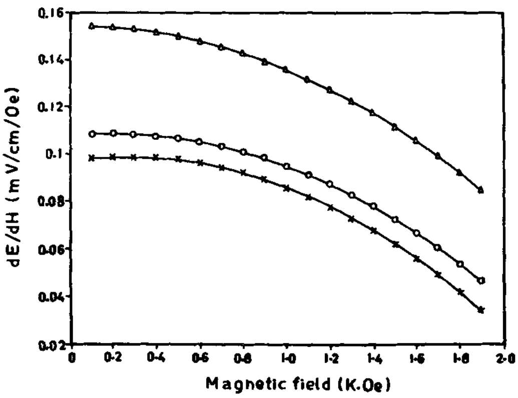


**Figure 3.** The variation of magnetoelectric conversion factor ($dE/dH$) with dc magnetic field. (×, 60% $CoFe_2O_4$–40% $BaTiO_3$; ○, 50% $CoFe_2O_4$–50% $BaTiO_3$; Δ, 40% $CoFe_2O_4$–60% $BaTiO_3$).

compositions of $CoFe_2O_4$ and $BaTiO_3$ as a function of intensity of DC magnetic field. The magnetoelectric conversion factor for different compositions from 0·1 kOe to 2 kOe in the presence of dc magnetic field was determined by measuring the voltage across the sample with 610C Keithley electrometer. Figure 3 shows the typical dependence of the magnitude of MEC with varying magnetic field for the three different composites. The maximum value of $dE/dH$ has been observed in a composition containing 60 mol% barium titanate and is 0·16 mV/cm/Oe.

From figure 3 it is also observed that the composites show a decrease in $dE/dH$ with increase of DC magnetic field beyond $H = 600$ Oe for all the composites. As already mentioned, the MEC is the result of piezomagnetic strain in spinel phase which creates piezoelectric charge in the ferroelectric phase and hence the latter would depend upon the variation of piezomagnetic coefficient with the intensity of magnetic field. In the spinels, the magnetostrictive coefficient reaches saturation at a certain value of magnetic field.

In the case of cobalt ferrite, the magnetostriction as well as the intensity of magnetization reach saturation around 600 Oe (Cullity 1972). Therefore, beyond this field the magnetostriction and the strain thus produced would also produce a constant electric field in piezoelectric phase and hence making $dE/dH$ to decrease with increasing $H$ beyond a critical field. This result has been observed in all the three samples. The present data on $CoFe_2O_4$–$BaTiO_3$ prepared by solid-state route are much lower than those of Boomgaard *et al* (1974) prepared by unidirectional cooling. The lower values obtained in this work may be attributed to the spinel phase ($CoFe_2O_4$) having resistivity value lower by four to five orders of magnitude than the piezoelectric phase. Presumably the ferrite phase offers a leakage path for the charges developed across the piezoelectric phase. Attempts are being made to increase the resistivity of the spinel phase, to reduce leakages and also to prepare the materials by other processing routes.

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## References

Boomgaard J Van Den, Terrel D R, Born R A J and Giller F I 1974 *J. Mater. Sci.* **9** 1705
Boomgaard J Van Den and Born R A J 1978 *J. Mater. Sci.* **13** 1538
Cullity B D 1972 *Introduction to magnetic materials* (Addison-Wesley Publishing Company)
Lines M E and Glass A M 1977 *Principles and applications of ferroelectrics and related materials* (Oxford: Clarendon Press)
Suchtelene J V 1972 *Philips Res. Rep.* **27** 28