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MAGNETOELECTRICITY IN PIEZOELECTRIC–MAGNETOSTRICTIVE COMPOSITES

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In a composite material consisting of a piezoelectric and a piezomagnetic phase which are mechanically coherent, electric and magnetic fields are converted into each other by a two-step process involving mechanical deformation as the intermediate step. We have developed such a material on the basis of a Co ferrite–Ba titanate eutectic which is unidirectionally solidified so as to obtain an aligned two-phase structure. The maximum value of the magnetoelectric effect obtained at present is 0.13 V/cm Oe at room temperature. The dimensionless quantity $4\pi(dP/dH)$ is 0.2 or a factor of 200 higher than the best single-crystal material known at room temperature (Cr_2O_3).

INTRODUCTION

In a composite material with two phases, each phase has its own set of characteristic physical parameters. This enables the materials designer to obtain new or enhanced properties in two steps by distributing subfunctions over the two phases. In this way, the composite as a whole can be designed to show "product properties"[1] with a higher yield than any single-phase material or which can even be completely new. A successful example is the magnetic-to-electric field conversion (and vice versa) in the piezoelectric–piezomagnetic composites described here. In this case, the intermediate step in the two-step process is mechanical deformation. In this paper we will focus on the magnetic-to-electric field conversion.

Until now, the largest magnetoelectric effect at room temperature in single-phase materials is found in Cr_2O_3, described by Astrov in 1960.[2] At room temperature, Cr_2O_3 has a dE/dH coefficient of ~0.02 V/cm Oe. In composites we have obtained values up to 0.13 V/cm Oe. However, a technically more relevant parameter is $4\pi(dP/dH)$. In Gaussian units this factor is dimensionless and equal to the analogous parameter $4\pi(dM/dE)$.[6] For single-crystal Cr_2O_3 it has the value $8 \cdot 10^{-4}$, for the Co ferrite-$BaTiO_3$ composite 0.17; i.e. larger by a factor of 200. The energy content per unit volume is typically larger by a factor of about 10^3.

An *a priori* order-of-magnitude estimate of the effects in the composite material can be made on the basis of the data for the bulk materials, in the following idealized situation:

1) The two phases, in the shape of lamellae or needles, are aligned with the applied magnetic or electric field.

2) Both phases are also poled in this direction.

3) Depolarizing effects are left out of consideration.

4) The dielectric constant of the $BaTiO_3$ phase is much higher than that of the ferrite phase.

5) The Young's moduli of the two phases are equal.

6) Perfect coupling between the phases (i.e., no cracks).

Then we have:

$$\left(\frac{dE}{dH}\right)_{\text{composite}} = \left(\frac{dl}{dH}\right)_{\text{comp}} \times \left(\frac{dE}{dl}\right)_{\text{comp}}$$

$$= \left(\frac{dl}{dH}\right)_{\text{ferrite, bulk}} \times f$$

$$\times \left(\frac{dE}{dl}\right)_{BaTiO_3\text{, bulk}}$$

where f is the volume fraction of the ferrite. Using (optimistic) values of $(1/l)(dl/dH) = 5 \cdot 10^{-7}$ Oe^{-1} for pure Co ferrite and $dE/dl = 2 \cdot 10^7$ Volt/cm for $BaTiO_3$, and putting $f = 0.5$, we find a "theoretical" upper limit of 5 V/cm Oe for the composite.

EXPERIMENTAL

Preparation: Unidirectional Solidification

We have prepared magnetoelectric composites by unidirectional solidification of a eutectic melt. This is a well-known method used to obtain aligned composites with periodicity in the micron range.[3] We used the method of edge-defined film-fed growth developed by LaBelle and Mlavski.[4] Details of the equipment and experimental conditions can be found in a previous paper.[5]

The resulting phases are the pairs in a eutectic reaction, i.e. they are saturated solutions of one another and their composition cannot be chosen freely. The volume fractions of the phases are fixed for the same reason. However, in a system with more than two components, there are several degrees of freedom remaining to allow improvements. We have performed such a search in the Fe-Co-Ti-Ba-O system. By sampling, we found a range of compositions yielding regular eutectic structures. Starting materials were $BaCO_3$, $CoCO_3$, TiO_2 and Fe_2O_3, all of 99.9% purity.

According to x-ray analysis, the two phases are $BaTiO_3$ (perovskite structure) and solid solutions of $CoFe_2O_4$ and $CoTi_2O_4$ (spinel structure). Figure 1 shows a cross-section perpendicular to the growth direction of a typical specimen. The growth rate was varied between 0.3 and 6 cm/h, and the oxygen pressure was fixed at 2.5% O_2 in N_2 (1 atm.) in order to obtain sufficient electrical resistivity. The ⟨100⟩ directions of both phases are parallel to one another and to the growth direction.

Samples with a slight excess of TiO_2 have a cellular structure as shown in Figure 2. Finned dendrites of this type are typical of the case in which one of the phases is faceted but which grow with a "coupled" two-phase solid-liquid interface.

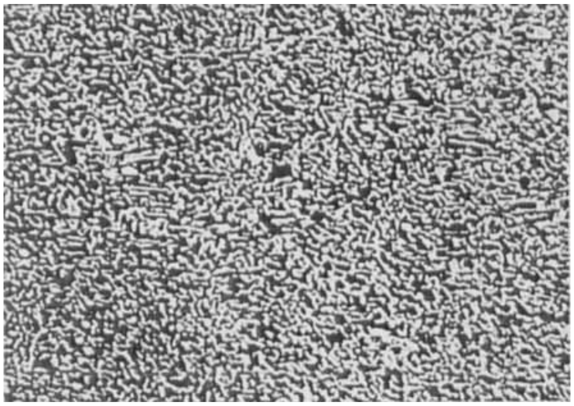

FIGURE 1 Unidirectionally solidified magnetoelectric eutectic composite. Composition: see Table I (column I). Growth rate 1.8 cm/h. Transverse cross-section, 60 x.

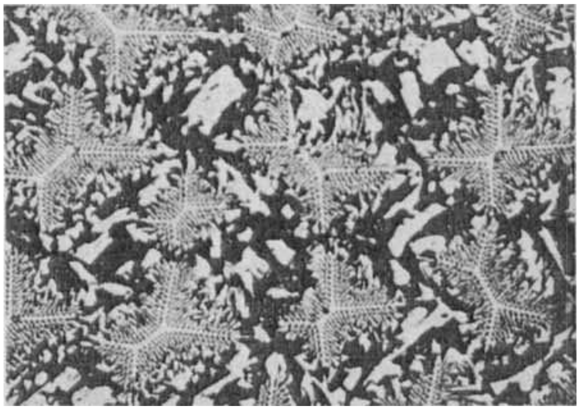

FIGURE 2 Unidirectionally solidified magnetoelectric composite, slightly off-eutectic (rich in TiO_2). Composition: see Table I (column II). Growth rate 0.3 cm/h. Transverse cross-section, 130 x.

Poling Procedures and Measurements

Electric poling was achieved by cooling the samples slowly from a temperature well above the ferroelectric Curie temperature in an electric field of 10 kV/cm. Samples were discs (5 mm diameter, 1 mm thickness) cut from a unidirectionally solidified rod. Silver-paste electrodes were applied to the ends.

Measurements of the dE/dH coefficient were made as a function of a dc magnetic bias field up to 6 kOe. This automatically includes the effect in a magnetically poled sample at zero bias field. Cooling in a magnetic field from above the ferromagnetic Curie temperature gave no improvement of the properties at room temperature.

The dE/dH coefficient was measured directly by applying an ac magnetic input signal of 1 kc/sec, 10 Oe amplitude parallel to the sample axis, and feeding the output signal into a MOSFET transistor as a first stage for amplification. Corrections were made for the shunting capacitance of the leads.

The piezomagnetic effect was measured with semiconductor strain gauges applied to specimens of 1.5 cm length.

For very small signals, measurements were made using a mechanical resonance technique. The output signal is then higher by a factor Q = mechanical quality factor (typically, Q = 500–1000). This type of measurement also enables the "partial" conversion factors (dl/dH and dE/dl) and also Young's modulus to be determined together with the overall effect.

The $BaTiO_3$ phase is electrically shunted by the ferrite phase since its resistivity is higher by a factor of about 100. The relaxation time is $\tau = \epsilon_0 \, \epsilon_{rel.} \, \rho$, where $\epsilon_{rel.}$ and ρ are the dielectric constant and the resistivity of the composite. For frequencies lower than $\nu = (2\pi\tau)^{-1}$ the signal decreases due to internal leakage currents. For the samples tested, the cutoff frequency is typically 3 Hz at room temperature.

RESULTS

Results are summarized in Table I for samples of the two compositions corresponding to the microstructures of Figure 1 and Figure 2, respectively. Comparable quantities for Cr_2O_3 are given in the third column.

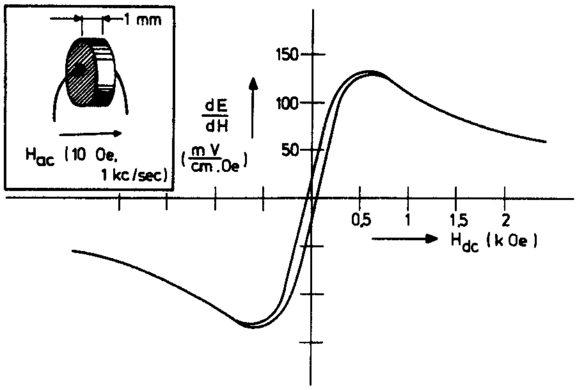

FIGURE 3 Conversion coefficient *dE/dH* as a function of applied magnetic bias field (insert: specimen shape). Composition: as in column II, Table I.

Figure 3 shows the dependence of *dE/dH* on the applied H_{dc} bias field. The hysteretic behaviour reflects that of the ferrite phase; the $BaTiO_3$ behaves linearly for the stresses involved. The zero-bias magnetoelectric effect has a memory and can be positive or negative depending on the magnetic history. Its value (the width of the hysteresis curve) depends on the demagnetizing factor of the sample. For the short disc-shaped samples

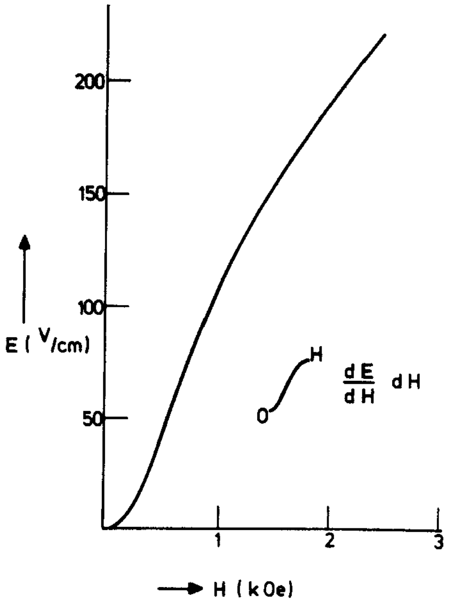

FIGURE 4 Total generated electric field ($\int_0^H (dE/dH)\, dH$) corresponding with Figure 3.

TABLE I

	I	II	Cr_2O_3
Composition (mol %)	BaO 27.83	27.19	
	TiO_2 34.48	36.00	
	CoO 28.62	27.96	
	Fe_2O_3 9.07	8.85	
Growth rate	1.8 cm/h	0.3 cm/h	
Ferroelectric Curie temp	60°C	90°C	
Dielectric constant (20°C, 1 kHz	500	500	
Ferromagnetic Curie temp	130°C	115°C	34°C (Néel)
Magnetic permeability	2	2	~1
Maximum *dE/dH* coefficient	0.01 V/cm Oe	0.13 V/cm Oe	0.02 V/cm Oe
occurring at bias field H_{dc}	~500 Oe	~500 Oe	
$\alpha = (4\pi \cdot dP)/dH$	0.02	0.22	0.0008
Total el. field generated by magnetic field of 2 kOe	10 V/cm	130 V/cm	~40 V/cm
Maximum piezomagnetic strain *dS/dH*	$-5 \cdot 10^{-9}$/Oe	$-5 \cdot 10^{-9}$/Oe	
Young's modulus	1.25×10^{12} dyne/cm^2	1.25×10^{12} dyne/cm^2	
DC electrical resistivity (20°C)	10^9 Ω cm	10^9 Ω cm	
Lowest frequency cutoff	3 c/sec	3 c/sec	

the remanent value is about 10% of the maximum value; for long specimens it can be ~50%. Figure 4 shows the integral of Figure 3, i.e. the response of the composite on a magnetic field pulse starting from zero.

We have also measured the magnetoelectric effect in the direction perpendicular to the growth direction. i.e. the direction of the fibers. As was to be expected, the dE/dH coefficient was considerably smaller; for all samples we found about one half of the effect in the growth direction.

Inverse Effect (electric-to-magnetic field conversion)

Theoretically the reverse effect, when expressed as $4\pi(dM/dE)$, should have the same value as $4\pi(dP/dH)$, i.e. the dimensionless factor α.[6] Our measurements resulted in "reverse" α values slightly lower than $4\pi(dP/dH)$.

CONCLUSIONS

A composite magnetoelectric material can be prepared by unidirectional solidification of a eutectic melt. Its performance exceeds that of the best known single-phase magnetoelectrical material at room temperature by two orders of magnitude. The magnetoelectric effect is the result of the mechanical coupling between a piezomagnetic and a piezoelectric phase. The new material constitutes a medium for which magnetic, electrical and mechanical quantities can act as input and/or output parameters.

The research on magnetoelectric composites is being continued to include ceramic composites. Their performance can reach values up to 20% of the unidirectionally solidified composites.

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