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An *in situ* grown eutectic magnetoelectric composite material

Part 2 *Physical properties*

A. M. J. G. VAN RUN, D. R. TERRELL, J. H. SCHOLING
Philips Research Laboratories, Eindhoven, The Netherlands

A eutectic composite material with the mixed spinel cobalt ferrite-cobalt titanate and the perovskite barium titanate as co-existing phases has been prepared, which shows a magnetoelectric effect due to the mechanical coupling of the piezomagnetic spinel and the piezoelectric perovskite. The maximum value of the magnetoelectric effect $\Delta E/\Delta H$ obtained up till now is 5.0×10^{-2} V cm^{-1} Oe^{-1} at room temperature.

1. Introduction

The existence of the magnetoelectric effect, proposed in 1894 by P. Curie, was demonstrated first in Cr_2O_3 by Astrov [1] and subsequently in numerous other single-phase solids. Up till now Cr_2O_3 has been found to have the largest magnetoelectric effect at room temperature. Its value expressed in Gaussian units is $\alpha_{zz} = 8 \times 10^{-4}$ [2] or, using the relative dielectric constant of Cr_2O_3, $\epsilon_{zz} = 11.9$ [3], $\Delta E_z/\Delta H_z = 2.0 \times 10^{-2}$ V cm^{-1} Oe^{-1}.

The magnetoelectric effect in a composite material is one of the so-called product properties of two-phase materials described by van Suchtelen [4]. A piezomagnetic phase deforms under the influence of an applied magnetic field. If this phase is mechanically coupled to a piezoelectric phase the latter generates an electric charge. Conversely a change in the magnetization arises in the piezomagnetic phase due to elastic strain generated by the piezoelectric phase under the influence of an applied electric field. A necessary condition for such behaviour by a two-phase material is a strong mechanical coupling between the phases, transferring elastic strains without appreciable losses. Such coupling may occur between solid phases which have been grown by directional solidification from a eutectic melt [5]. An additional advantage of *in-situ* grown two-phase composites is the well-defined crystal orientation of the two phases with respect to the growth direction and with respect to each other. Physical properties of crystalline solids have a tensorial character, so that one can expect the crystallographic alignment of all crystallites constituting one phase to give optimum results for the physical properties of the composite.

It has been found that three phase equilibria exist in which a solid phase with good piezoelectric properties at room temperature and a solid phase which is piezomagnetic at room temperature simultaneously solidify from a eutectic melt [6].

Here we report on the physical properties of the composite material (barium titanate)–(cobalt ferrite-titanate) with composition in mol %: 27.83 BaO; 34.48 TiO_2; 28.62 CoO; 9.06 Fe_2O_3, without and with slight modification by a few additional weight percent of TiO_2 and exhibiting a regular eutectic structure and primary spinel dendrites, respectively.

2. Experimental

Measurements of ferroelectric and ferromagnetic Curie temperatures, electrical resistivity, permittivity and permeability have been carried out by standard techniques.

The piezomagnetic properties in the growth direction have been measured using semiconductor strain gauges, namely, total strain as a function of external field $H_{d.c.}$ as well as a.c. strain due to a constant-amplitude (20 Oe) field $H_{a.c.}$ (1 kHz), as a function of $H_{d.c.}(H_{a.c.}//H_{d.c.})$. The maximum slope of the former and the top value of the latter gave the same value of strain per unit field strength.

Samples for measurements of the magnetoelectric effect have been poled electrically by cooling from a temperature well above the

ferroelectric Curie temperature in an electric field of 500 V cm^{-1}. Fig. 1 shows the (Leitsilber) electrode configurations used, with respect to the growth direction. Cooling in a magnetic field from above the ferromagnetic Curie temperature gave no improvement of the piezomagnetic properties at room temperature.

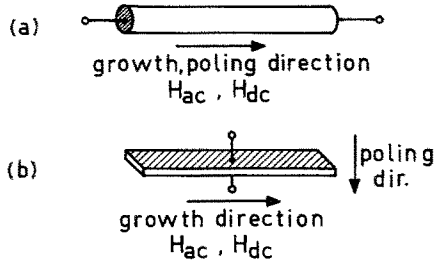

Figure 1 Electrode configurations used in measuring the magnetoelectric effect.

The magnetoelectric effect has been measured using a resonant technique. The sample was placed lengthwise (= growth direction of the bar) parallel to a 20 Oe a.c. magnetic field, $H_{a.c.}$, and a d.c. field, $H_{d.c.}$, up to 6 kOe. The frequency of $H_{a.c.}$ was such that the sample shows longitudinal mechanical resonance (fundamental mode ω_{res}). The mechanical quality factor Q, which can have values ranging from 100 to 800 and includes damping due to acoustic radiation and to the influence of contact leads, was determined from the frequency dependence of the magnetoelectric output signal in the neighbourhood of ω_{res}. The expression for the magnetoelectric effect in terms of the measured quantities is

$$\frac{\Delta E}{\Delta H} = a \frac{\pi V}{2dQH}$$

with V = electrode voltage; H = driving a.c. magnetic field; Q = quality factor; d = electrode distance; a = a factor describing the influence of a.c. demagnetization which cannot be calculated exactly and is put equal to one as a first approximation.

The use of the resonance technique allows one in the case of samples with a weak magnetoelectric effect to distinguish this effect from spurious signals. The capacitance of a sample with electrode configuration shown in Fig. 1a amounts to a few pF. At resonance (typically at 70 kHz) such a sample offers a source impedance of about 1 Mohm. For this reason and to minimize the input capacitance of the measuring circuit, the sample was connected with as short leads as possible to a field effect transistor.

For samples with a large magnetoelectric effect nonresonance measurements (for instance at 1 kHz) are also possible. The values of the magnetoelectric effect obtained in this quasi-static way are always higher than the resonance values, typically by a factor of 1.4. The mechanical resonance also allows one to determine the Young's modulus along the growth direction.

Typical sample dimensions are for the Fig. 1a configuration: length 45 mm, diameter 4.5 mm; for Fig. 1b: obtained from the former by grinding to 1 mm thickness.

3. Results

Samples with a composition in mol %: 27.,83 BaO; 34.48 TiO_2; 28.62 CoO; 9.06 Fe_2O_3 showed a magnetoelectric effect $\Delta E/\Delta H$ = (1 to 4) × 10^{-3} V cm^{-1} Oe^{-1}, a relative dielectric constant ϵ_{rel} of about 700 at 1 kHz, a relative magnetic permeability μ_{rel} of about 2 and ferromagnetic and ferroelectric Curie temperatures of about 130° C and 60° C, respectively. In general the magnetoelectric effect depends on the magnetic field $H_{d.c.}$ as is shown in Fig. 2. The

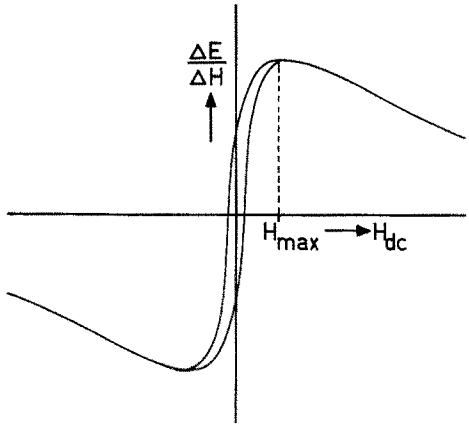

Figure 2 Magnetic field dependence of the magnetoelectric effect (arbitrary units).

maximum value occurs at fields of (0.4 to 0.6) kOe and coincides with the maximum value of the piezomagnetic strain per Oe. The width of the hysteresis loop is about 150 Oe.

A slight change of the chemical composition mentioned above by adding a few wt % of TiO_2 resulted in samples with a considerably improved magnetoelectric effect. A sample with 1.5 wt % of additional TiO_2 showed the highest value

obtained up till now: $\Delta E/\Delta H = 5.0 \times 10^{-2}$ V cm^{-1} Oe^{-1} measured at resonance at 60 kHz with the electrode configuration shown in Fig. 1a. This value of the magnetoelectric effect is a maximum, obtained in a field $H_{d.c.}$ of about 700 Oe. For $H_{d.c.} = 0$, the effect is reduced to about 0.6 times the maximum value. With a relative dielectric constant $\epsilon_{rel} = 630$ the result can be expressed in the dimensionless quantity α (Gaussian units):

$$4\pi\Delta P/\Delta H = \alpha = 0.10$$

(P = dielectric polarization) which is two orders of magnitude larger than the room temperature value of the single phase magnetoelectric material Cr_2O_3. The ferromagnetic and ferroelectric Curie temperatures of these samples containing additional TiO_2 are 115 and 85°C, respectively.

The maximum piezomagnetic strain per unit magnetic field was about $\Delta S/\Delta H = -5.0 \times 10^{-9}$ Oe for all samples.

Measurements of the reverse magnetoelectric effect, $4\pi\Delta M/\Delta E$, gave values for all samples which, expressed as the dimensionless quantity α, are slightly smaller than that for $4\pi\Delta P/\Delta H$.

The magnetoelectric effect, which has been measured using the electrode configuration of Fig. 1b, was about one half of the effect measured using the electrode configuration of Fig. 1a. This applies to all samples. The Young's modulus along the growth direction for all samples is about 1.25×10^{12} dyn cm^{-2}. All samples have d.c. electrical resistivities of about 10^9 Ω cm at room temperature and retain sufficiently high resistivities up to 150°C to accomplish the poling procedure.

4. Discussion

The magnetoelectric effect $\Delta E/\Delta H$ of the composite is the product of the piezomagnetic deformation $\Delta S/\Delta H$ and the piezoelectric charge generation $\Delta q/\Delta S$. The latter has been calculated from the results given above.

$$\Delta q/\Delta S = \epsilon_0\epsilon_{rel} \cdot \frac{\Delta E}{\Delta H} \Big/ \frac{\Delta S}{\Delta H}$$

$$= 5.6 \times 10^{-4} \text{ C cm}^{-2}$$

and

$$= (1.2 - 4.9) \times 10^{-5} \text{ C cm}^{-2}$$

for samples with and without the additional TiO_2, respectively. In the former samples the piezoelectric effect is smaller by a factor of 3.3 compared with data for ceramic $BaTiO_3$ [7]. However, in the composite the perovskite phase fills about 60% of the volume and is dispersed.

The large difference in performance of the perovskite phase in samples with and without the additional TiO_2 may partly be due to a small difference in doping level as expressed by the ferroelectric Curie temperatures, 85 and 60°C, respectively. X-ray fluorescence revealed this dope to be mainly iron. From the data given by Bogdanov *et al.* [8] it is concluded that about 1.5 at. % iron has been dissolved in the perovskite phase. However, the two kinds of samples also show a large difference in structure. The additional TiO_2 caused numerous ⟨100⟩ oriented spinel dendrites to appear which extend over several millimetres in the growth direction [6]. This structure of the composite resulted in magnetic properties which hardly deviated from those of samples without additional TiO_2. The piezomagnetic deformation $\Delta S/\Delta H$ did not improve and measurements of the magnetic moment versus magnetic field gave almost identical curves for directions parallel and perpendicular to the growth direction. The presence of the spinel dendrites thus improved the piezoelectric properties of the composite and it did so in the following way.

In all samples the perovskite phase showed numerous microcracks due to the difference in the thermal expansion coefficients of the two phases. In samples with a regular eutectic structure (samples without additional TiO_2) the distribution of the crack faces is random with respect to the growth direction. In the samples with additional TiO_2 the spinel dendrites are accompanied by a lamellar eutectic structure. The crack faces in the perovskite lamellae appeared to extend parallel to the dendrite axis. A transverse section (Fig. 3a) shows numerous cracks in the perovskite lamellae, in contrast with Fig. 3b, a section through a spinel dendrite almost parallel to the growth direction, in which the cracks are far less numerous. Now, if a sample is stressed piezomagnetically the deformation transferred from the spinel phase to the perovskite phase is partly produced by an opening and closing of the cracks whose faces are not parallel to the deformation direction. In a sample having spinel dendrites a great part of the crack surface is parallel to the deformation direction if the sample is excited longitudinally. Consequently, such a sample will show a larger magnetoelectric effect compared with a sample

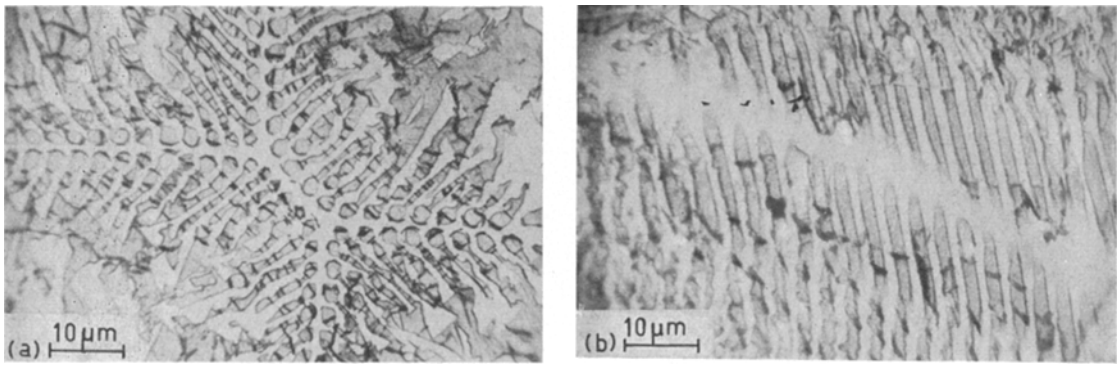

Figure 3 Transverse (a) and longitudinal (b) sections of a spinel dendrite. Etch: 15 min conc. HCl to reveal the cracks in the perovskite phase (dark grey).

devoid of spinel dendrites. This has been confirmed moreover by measuring the magnetoelectric effect with deformation parallel and perpendicular to the growth direction. For samples with a regular eutectic structure the values are almost equal, for samples with spinel dendrites the parallel effect exceeds the perpendicular effect by a factor of 4.

The piezomagnetic effect in the composite along the growth direction has the negative sign. Since the orientation of the spinel phase with respect to the growth direction is $\langle 100 \rangle$, the cobalt ferrite-cobalt titanate mixed spinel behaves similarly to pure $CoFe_2O_4$ [9]. However, no data are available in the literature concerning the piezomagnetic effect in this mixed spinel to compare with our results. The maximum value of $\Delta S/\Delta H$ and the field $H_{d.c.}$ at which it occurs, will be strongly influenced by internal demagnetizing fields and by the mechanical (compressive) stresses due to the difference in the thermal expansion coefficients of the two phases in the composite.

The influence of Fe^{2+} content on the resistivity of ferrites has been studied by several authors [10]. Apart from dopes the partial pressure under which a ferrite sample has been cooled and the rate of cooling also determine the resistivity. Moreover, grain boundaries may have a strong influence, especially at low frequencies. The d.c. resistivities of the composite samples, as grown, all had values of about 10^9 Ω cm. Measurements of the resistivity as a function of frequency revealed a gradual decrease to about 10^7 Ω at 100 kHz. A dielectric dispersion of resistivity and dielectric constant has not been observed, so it was concluded that grain boundary effects do not contribute to the d.c. resistivity. The piezoelectric phase is electrically shunted by the spinel phase, so piezoelectrically generated charges will tend to be compensated by leakage currents through the spinel phase. The perovskite phase itself will have resistivities exceeding 10^{11} Ω cm according to Bogdanov *et al.* [8]. This charge compensating can be described by a relaxation time $\tau = \epsilon_0 \epsilon_{rel} \rho_c$; ρ_c and ϵ_{rel} being the resistivity and the relative dielectric constant of the composite material, respectively. These quantities have typical values of $\rho_c = 10^9$ Ω cm and $\epsilon_{rel} = 700$ so that a negligible loss of signal due to leakage currents is to be expected if measurements are made at frequencies higher than $\nu = (2\pi\epsilon_0\epsilon_{rel}\rho_c)^{-1} = 3$ Hz.

5. Conclusions

A composite magnetoelectric material has been prepared which exceeds the best known single-phase magnetoelectric material in performance at room temperature by two orders of magnitude. The magnetoelectric effect is the result of the mechanical coupling of a piezomagnetic and a piezoelectric phase. The magnetoelectric composite constitutes a medium for which magnetic, electrical and mechanical quantities can act as input and/or output parameters.

A start has been made on quantitative comprehension of the properties of the composite magnetoelectric material in terms of the properties of the component phases and their mutual dependence. It is to be expected that additional knowledge of the chemical phase equilibria in the system and of the relations between the structure of the composite and the way in which the bulk phase properties are expressed in the composite properties, will result in an improved performance of the composite.

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References

1. D. N. ASTROV, *Sov. Phys. JETP* **11** (1960) 708.
2. T. J. MARTIN and J. C. ANDERSON, *Phys. Letters* **11** (1964) 109.
3. P. H. FANG and W. S. BROWER, *Phys. Rev.* **129** (1963) 1561.
4. J. VAN SUCHTELEN, *Philips Res. Rep.* **27** (1972) 28.
5. H. BIBRING, Proceedings of the Conference on *In-Situ* Composites (Lakeville, Connecticut, September, 1972) Vol. II, pp. 1-69 (Publ. 1973).
6. J. VAN DEN BOOMGAARD, D. R. TERRELL, R. A. J. BORN and H. F. J. I. GILLER, *J. Mater. Sci.* **9** (1974) 1705.
7. R. BECHMANN, *J. Acoust. Soc. Amer.* **28** (1956) 347.
8. S. V. BOGDANOV, K. V. KISELEVA, B. N. MATSONASHVILI, V. A. RASSUSHIN and N. N. SENTYURINA, *Bull. Acad. Sci. USSR, Phys. Ser.* **29** (1965) 994.
9. R. M. BOZORTH, E. F. TILDEN and A. J. WILLIAMS, *Phys. Rev.* **97** (1955) 1788.
10. C. G. KOOPS, *Phys. Rev.* **83** (1951) 121. L. G. VAN UITERT, *Proc. Inst. Radio Engrs.* **44** (1956) 1294. G. H. JONKER, *J. Phys. Chem. Solids* **9** (1959) 165.

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