

A sintered magnetoelectric composite material $\text{BaTiO}_3\text{-Ni}(\text{Co, Mn})\text{Fe}_2\text{O}_4$

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Magnetoelectric composite materials have been made by sintering a mixture of a piezoelectric and piezomagnetic phase. This paper deals with the preparation and some properties of the combination $\text{BaTiO}_3\text{-Ni}(\text{Co, Mn})\text{Fe}_2\text{O}_4$, and investigates the influence of the cooling rate after sintering, TiO_2 additions, the mole ratio of both phases and the crystallite size of the grains of both phases on some physical properties of the composite material. The maximum value of the conversion factor $(\delta E/\delta H)_{\text{max}}$ found for this material up till now is about $80 \text{ mV cm}^{-1} \text{ Oe}^{-1}$.

1. Introduction

The theoretical properties of composite materials [1], particularly those obtained by the combination of a piezoelectric and a piezomagnetic phase into one solid body, led to a magnetoelectric composite material of this type grown *in situ* [2–5]. The material consisted of the phases BaTiO_3 , and the mixed crystal phase $\text{CoFe}_2\text{O}_4)_x(\text{Co}_2\text{TiO}_4)_{1-x}$; in a number of cases a third phase, the mixed crystal phase $(\text{BaFe}_{12}\text{O}_{19})_y(\text{BaCo}_6\text{Ti}_6\text{O}_{19})_{1-y}$, was present.

During the investigation of this type of composite material it was also found that magnetoelectric composites can be prepared by sintering together powders of BaTiO_3 and a piezomagnetic spinel phase [5–7], particularly if both phases can co-exist from room temperature to the temperature at which they are sintered. Sintered composite materials are much easier and much cheaper to prepare than *in situ* composites. Moreover their preparation offers several advantages, such as the free choice of the mole ratio of constituent phases, the independent choice of the grain size of each of the phases in the starting mixture, the more or less free choice of the sintering temperature and the fact that the existence of a eutectic point, a eutectic gutter, or a eutectoid phase between the two desired phases is not a prerequisite. The first experiments were done with the same compositions as were used for the *in situ* composites, i.e. with the combination $\text{BaTiO}_3\text{-(CoFe}_2\text{O}_4)_{1-x}(\text{Co}_2\text{TiO}_4)_x$. The composition that gave rise to the highest con-

version in the *in situ* grown composite (i.e. $130 \text{ mV cm}^{-1} \text{ Oe}^{-1}$) exhibited a somewhat low conversion in the sintered material ($<10 \text{ mV cm}^{-1} \text{ Oe}^{-1}$).

During preliminary experiments promising results were obtained with the combination $\text{NiFe}_2\text{O}_4\text{-BaTiO}_3$ with small additions of cobalt and manganese. We therefore focused our attention on this combination and investigated it more intensively. It must not, however, be concluded that reasonable results, i.e. comparable with those obtained with the chosen combination, cannot be obtained with other combinations, including that mentioned above. Some phase relations in the quinary system Ba-Fe-Ni-Ti-O are considered in Section 2.

2. Phase relations in the Ba-Fe-Ni-Ti-O quinary system

As far as we could check in the literature, there are no uninterrupted series of mixed crystals of the $(\text{NiFe}_2\text{O}_4)_{1-x}(\text{Ni}_2\text{TiO}_4)_x$ and $(\text{BaFe}_{12}\text{O}_{19})_{1-x}(\text{BaNi}_6\text{Ti}_6\text{O}_{19})_x$ types, because compounds such as Ni_2TiO_4 and $\text{BaNi}_6\text{Ti}_6\text{O}_{19}$ appear not to exist. In NiFe_2O_4 one Ni and one Ti atom can replace two Fe atoms to some extent; the same holds for $\text{BaFe}_{12}\text{O}_{19}$. However, we confined our investigation to combinations of BaTiO_3 and NiFe_2O_4 without intentional substitution in the spinel phase and both without and with additions of TiO_2 , added for reasons which will be explained below.

With regard to the performance of the compo-

site, there has to be intimate slip-free contact between the phases. This means that they must be sintered firmly together, which is only possible if they can be in equilibrium with each other at the sintering temperature and sintering atmosphere. This point was checked by sintering pellets, pressed from the two phases for fairly long periods at temperatures between 1000 and 1350° C, followed by X-ray analysis. No phases other than BaTiO₃ and NiFe₂O₄ were found. It even proved possible to solidify both phases at the same time from a melt by a “eutectic” reaction, L → S + P [S = spinel phase (NiFe₂O₄) and P = perovskite phase (BaTiO₃)].*

The equilibrium between the phases is not the only condition that must be fulfilled in order to prepare useful magnetoelectric composite materials. Because the piezo-generated electric charges at the surface of the perovskite grains will tend to be compensated by leakage currents in the spinel phase, as the resistivity of the NiFe₂O₄ phase in the composite sintered in air is lower than that of the BaTiO₃ phase, the resistivity of the former phase must be made high in order to make the relaxation time for the charge compensation, $\tau = \bar{\rho} \bar{\epsilon}_r \epsilon_0$, as long as possible ($\bar{\epsilon}_r$ and $\bar{\rho}$ being the average values of the dielectric constant and the resistivity, respectively, of the composite material). It is known that small additions of Co and Mn to the NiFe₂O₄ phase cause a considerable increase of the resistivity of this phase [11]. However, because of cross-doping, Mn will also be present in the BaTiO₃ phase, causing a decrease of the temperature at which the transition BaTiO₃ (cubic) → BaTiO₃ (hexagonal) takes place, the cubic phase being the low temperature phase [12, 13]. It is known that the hexagonal phase, once it is formed at higher temperatures, transforms only very slowly into the cubic phase at temperatures below the transition temperature. Rase and Roy have shown that this transition temperature rises steeply with TiO₂ in excess of that in stoichiometric BaTiO₃ [11]. Although replacement of a small amount of Ba in BaTiO₃ by Ca has a similar effect [14] it has, we found, a negative influence

on the magnetoelectric conversion, as opposed to an excess of TiO₂. The influence of TiO₂ additions on the phases present in the composite material and on the magnetoelectric conversion of that material was therefore also investigated.

3. Experimental

3.1. Chemical

3.1.1. General remarks

Early on in this investigation it was found that, if the composite samples were prepared from the oxides and carbonates as starting materials (BaCO₃, NiO, TiO₂ and Fe₂O₄ with small additions of Co and Mn in the form of oxides or carbonates), the size of the crystallites in the phases in the sintered final product was always very small, even after prolonged sintering at 1300° C. Experiments in which the phases were previously prepared before combining them into a composite material revealed that there is a relation between the coarseness of the crystallites in the composite material and the efficiency of its magnetoelectric conversion. We therefore decided to prepare the sample from previously prepared phases. This gave us an opportunity to combine the single phases with different sizes of the crystallites into the composite material. This paper reports the results obtained with composites made by sintering together the previously prepared perovskite phase with composition BaTi_xO_{1+2x} (x = 1.00 to 1.10) and the previously prepared spinel phase with the composition Ni_{0.97}Co_{0.03}Mn_{0.10}Fe_{1.90}O₄. For brevity, this latter phase will be referred to as Ni(Co, Mn)Fe₂O₄.

3.1.2. Preparation of BaTiO₃

Crystallites of BaTiO₃ with a diameter less than 0.4 μm were prepared by firing a mixture of BaCO₃ and TiO₂ in the appropriate ratio for 16 h in air at 1050° C, followed by ball milling. This procedure was repeated once and the resulting powder was checked by X-ray analysis to ascertain that only BaTiO₃ was present. Coarse crystallites of this phase were prepared by the flux growth method. A mixture consisting of 95 wt % BaTiO₃,

*This is in accordance with the results of Kramer *et al.* [8], who determined the T-x cut NiFe₂O₄-BaTiO₃ in air through the phase diagram. However, their remark that the composition at the lowest melting temperature on the NiFe₂O₄-BaTiO₃ join apparently does not represent a eutectic point as might be anticipated from the work of Van den Boomgaard *et al.* [2], is not correct. In the last paragraph of Section 2 in the paper cited [2], it is stated that the composition of the liquids that may give rise to regular eutectic structures under steady state conditions must be situated on a kind of effective ternary solidus curve. As pointed out earlier [9, 10], before such a steady state is reached dendrites of one of the solid phases may be expected during the solidification of the two-phase solid. This is exactly what was found by Kramer *et al.* [8].

prepared as stated above, and 5 wt% BaCl₂ was heated in air for 6 h at a temperature between 1100 and 1200° C. After cooling to room temperature the BaCl₂ was dissolved in hot water and the coarser BaTiO₃ crystallites were roughly separated from the small ones with the aid of a hydrocyclone. Some of these coarser crystallites were used as such and those remaining were divided into groups with different average diameters, again by means of a hydrocyclone. The average diameter of the crystallites in each group was determined by a microscopic method, using Martin's diameter [15]. Although the diameters of all the crystallites present in such a fraction have to be measured in order to determine this average diameter, this was not possible because of an unknown number of crystallites with submicroscopic dimensions. This implies that the value of the average diameter thus determined is too high, but assuming the same type of distribution of the diameters in each group the real diameters will have the same sequence as those determined.

3.1.3. Preparation of BaTiO₃ with excess TiO₂

BaTiO₃ with excess TiO₂ and a crystallite diameter less than 0.4 μm was prepared in the same way as stoichiometric BaTiO₃. BaTi_xO_{1+2x} powders with *x* varying from 1.00 to 1.10 were made.

3.1.4. Preparation of Ni(Co, Mn)Fe₂O₄

Crystallites of Ni(Co, Mn)Fe₂O₄ with a diameter less than 0.4 μm were prepared in essentially the same way as the corresponding crystallites of BaTiO₃. The basic oxides were used as starting materials. Coarse crystallites of Ni(Co, Mn)Fe₂O₄ were made by a flux growth method. A melt consisting of 65 wt% PbO and 35 wt% of the ferrite, prepared as indicated above, was homogenized at 1100° C in air for 16 h and subsequently cooled to 880° C at a rate of 15° C h⁻¹. Then it was cooled fairly quickly to room temperature. The coarse ferrite crystallites were released by dissolving the PbO of the lump in concentrated HNO₃.

Owing to (magnetic?) interaction of the crystallites it was not possible to separate coarser fractions from less coarse fractions with the aid of a hydrocyclone. The average diameter was therefore determined for the whole batch and was found to be larger than 1 μm.

3.1.5. Preparation of the composite samples

Samples were made in the form of pellets. Pellets containing small crystallites of both phases (diameter < 0.4 μm) were made by moulding a chosen mixture of the phases into pellets, followed by isostatic repressing at 1000 atm. Pellets containing coarse crystallites of at least one phase were made by pressing the desired mixture into a mould. To avoid cracking of the coarser crystallites no isostatic repressing was applied.

The pellets were sintered under desired conditions of firing time, temperature and ambient. Pellets containing coarse crystallites needed careful handling before they were fired because, due to the gentle pressing, the mechanical contact between the crystallites in the pellets was poor. As a consequence of this the mechanical contact between the phases in these pellets after sintering may be worse than in the sintered pellets that were repressed isostatically.

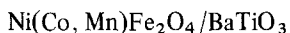
3.1.6. Parameters investigated

With the aid of pellets prepared as described above we investigated the way in which some physical properties of the composite material were influenced by variation of some important parameters.

(a) The influence of the *cooling rate after sintering* on the magnetoelectric conversion (MC) was investigated in samples with mole ratio BaTiO₃/Ni(Co, Mn)Fe₂O₄ = 60/40. The results were compared with those of samples with the same mole ratio but with TiO₂ added.

(b) The influence of *TiO₂ additions* on the amount of hexagonal BaTiO₃ and on the MC of the material was investigated in samples in which the mole ratio was BaTiO₃/Ni(Co, Mn)Fe₂O₄ = 60/40 and with *x* varying from 1.00 to 1.10 (see 3.1.3 above).

(c) The influence of the *mole ratio* of the phases on the MC and on the resistivity was investigated in samples with the following mole ratios:



$$= 2/98, 5/95, 34/66, 40/60, 50/50, 60/40, \\ 70/30, 95/5, \text{ and } 98/2$$

These three groups of experiments were confined to combinations of small (< 0.4 μm) crystallites of both phases.

(d) The influence of the *crystallite size* on the MC was investigated in samples containing small and coarse crystallites. The greater part of this investigation was carried out with samples containing small crystallites of the ferrite phase and crystallites of different average sizes of the titanate phase, because, as noted above, the coarse crystallites of the ferrite phase could not be divided into groups with a different average diameter. The influence of the mole ratio of both phases (see (c) above) was checked on samples containing titanate crystallites of two different sizes combined with small ferrite crystallites.

3.2. Physical measurements

3.2.1. Poling procedures

To enable the MC to be measured the composite had to be poled electrically and magnetically. Three electrical poling procedures are described in [5]. Because of the unstable results obtained with one of these procedures ((c) in [5]) it was abandoned. Two poling procedures were used. The first was a modification of procedure (a) in [5]. The sample is heated up to 150°C, which is about 20°C above the ferroelectric Curie temperature of the perovskite phase, in an external electric field of 10 kV cm⁻¹, and subsequently cooled to room temperature in this field at a rate of about 13°C min⁻¹. This procedure will be referred to as procedure I. The second procedure was exactly the same as procedure (b) in [5]. The sample is heated to 350°C in an external field of initially 10 kV cm⁻¹ but which, when the current through the sample is limited to 1 mA, starts decreasing at about 200°C, becoming 0.4 to 0.8 kV cm⁻¹ at 350°C. The sample is kept at this temperature for 15 min. It is then cooled to 150°C, at which temperature the external field is switched off. The sample then cools further to room temperature without external field because it is short-circuited. This procedure will be referred to as procedure II.

The samples were poled magnetically by applying an external d.c. magnetic field of 8 kOe at room temperature. This poling was carried out in the set-up in which the magnetoelectric conversion was measured using the d.c. magnetic bias field (see below). Cooling in a magnetic field from a temperature above the ferromagnetic Curie point ($\pm 550^\circ\text{C}$) did not improve the magnetoelectric properties of the samples at room temperature.

3.2.2. Measurement of the magnetoelectric conversion

The disk-shaped samples were provided with “Leitsilber” contacts. The MC was measured in terms of the variation of the coefficient $\delta E/\delta H$ as a function of a d.c. magnetic bias field up to 2.5 kOe. The coefficient itself was measured directly as the response of the sample to an a.c. magnetic input signal of 1 kHz and 10 Oe amplitude superimposed on the d.c. bias field, both parallel to the sample axis. The output signal was fed into a FET transistor as a first stage for amplification and impedance matching. Corrections were made for the shunting of the sample by the capacitance of the leads and of the input stage. In order to keep the signal-to-noise ratio at the input stage as high as possible the leads were kept short (≈ 5 cm). The maximum value of the $\delta E/\delta H$ coefficient, which occurs at a bias field of about 0.5 kOe in samples 1 mm thick, was taken as a measure of the performance of the material [4].

3.2.3. Resistivity measurements

D.c. resistivity measurements were carried out on the samples by means of a two-point method. A known constant potential was applied to the specimens that were fitted with “Leitsilber” contacts. The current through the samples was measured with a TEKELEC TE 921 nanoampere meter.

3.2.4. Determination of the ferroelectric Curie temperature

The capacitance of the samples was determined by connecting a capacitor of a known value and an a.c. voltage source (200 kHz) in series with them. The in-phase part of the voltage over this capacitor was measured with a PAR 129 A lock-in amplifier, this quantity being a measure of the capacitance of the sample. The real part of the dielectric constant of the sample, $\bar{\epsilon}_r$, can be calculated from this capacitance and the dimensions of the sample. When the capacitance of an electrically poled sample is measured as a function of the temperature from room temperature and higher, it exhibits a maximum value. The temperature at which this maximum occurs is referred to as the ferroelectric Curie temperature.

In some preliminary experiments it was found that the ferromagnetic Curie temperature of the samples was always higher than 500°C. This

means that the ferroelectric Curie temperature is the limiting temperature in testing and using the magnetoelectric composite. For this reason we did not measure the ferromagnetic Curie temperature.

3.2.5. Determination of the amount of hexagonal BaTiO₃ in the samples

It is practically impossible to determine the ratio BaTiO₃ (hex + cub)/Ni(Co, Mn)Fe₂O₄ in the sintered composite by some kind of analysis because it is not possible to dissolve one of the phases leaving the other one unattacked. It will be appreciated that it is also impossible to determine the amount of hexagonal BaTiO₃ in the final material. The intensity of one of the X-ray reflections of hexagonal BaTiO₃ was therefore used as a qualitative measure. In a series of samples, all containing the same wt % of BaTiO₃, the intensities of the (2 0 3) reflection of hexagonal BaTiO₃, ($d = 2.195\text{\AA}$) and that of the (4 0 0) reflection of the spinel phase Ni(Co, Mn)Fe₂O₄ ($d = 2.090\text{\AA}$) were determined and their ratio was taken as a measure of the relative amount of hexagonal BaTiO₃ present in the composite. Although this quantity is generally not proportional to the real amount of hexagonal BaTiO₃, it is nevertheless suitable for our purpose, namely to determine the increase or decrease of the relative amount of this phase.

4. Results

(a) The influence of the cooling rate on the MC after sintering of the composite is shown in Tables I and II.

(b) The influence of TiO₂ additives on the MC is shown in Table II and Fig. 1. The influence of these additives on the amount of hexagonal BaTiO₃ is shown in Table III. For amounts of TiO₂ larger than $x = 1.02$ (see Table III) a fourth phase M with the magnetoplumbite structure was found to occur. The amount of this phase is indicated by the ratio of the intensity of its (1 1 4) reflection

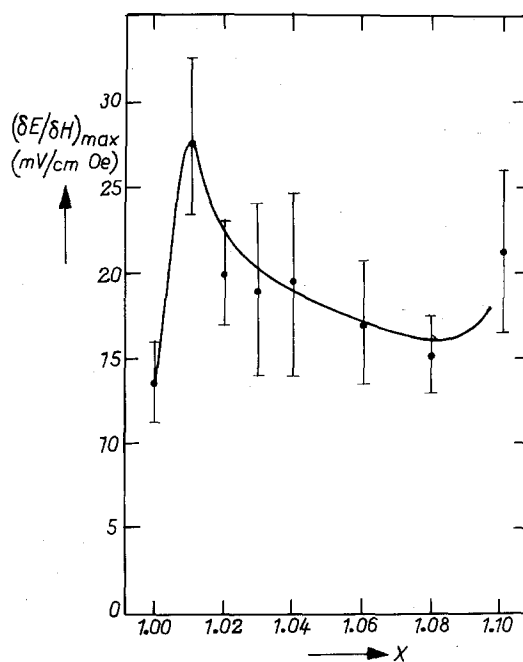


Figure 1 Dependence of the magnetoelectric conversion on excess TiO₂ in the (BaTi_xO_{2+x})-(Ni(Co, Mn)Fe₂O₄) composite (excess TiO₂ for $x > 1$).

and the intensity of the (2 2 2) reflection of the spinel phase. TiO₂ additions did not significantly change the crystallite size of the perovskite phase and the spinel phase but we observed a marked decrease in the number of pores at the grain boundaries between the two phases.

(c) The influence of the mole ratio on the magnetoelectric conversion is seen in Table IV and Fig. 2. Additional information is given in Table VI.

(d) The influence of the crystallite size of BaTiO₃ on the magnetoelectric conversion is shown in Tables V, VI and VIII and in Fig. 3.

(e) The influence of the poling procedure on the conversion is to be seen in Table VIII.

(f) Fig. 4 shows the influence of the mole percentage of BaTiO₃ in the samples on their resistivity as a function of the temperature. The crystal-

TABLE I Influence of cooling rate

Cooling rate (° C h ⁻¹)	5	10	20	50	100	200
Average value of ($\delta E/\delta H$) _{max} (mV cm ⁻¹ Oe ⁻¹)	16.2	13.3	14.6	12.4	13.8	11.5

Composition	: 60 mol% BaTiO ₃ and 40 mol% Ni _{0.97} Co _{0.03} Mn _{0.10} Fe _{1.90} O ₄ .
Pressing	: 1000 kg cm ⁻² , isostatic.
Sintering procedure	: 200° C h ⁻¹ to 1300° C; 24 h at 1300° C; x° C h ⁻¹ to room temperature.
Atmosphere	: oxygen (1 atm.)
Poling procedure	: II.

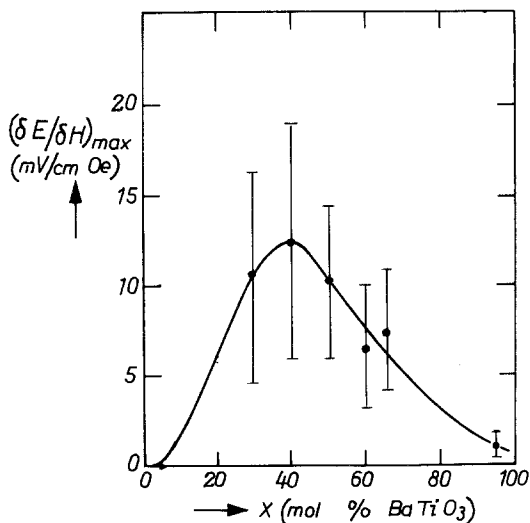


Figure 2 Dependence of the magnetolectric conversion on the mole ratio $\text{BaTiO}_3/\text{Ni}(\text{Co}, \text{Mn})\text{Fe}_2\text{O}_4$ expressed in mol% BaTiO_3 .

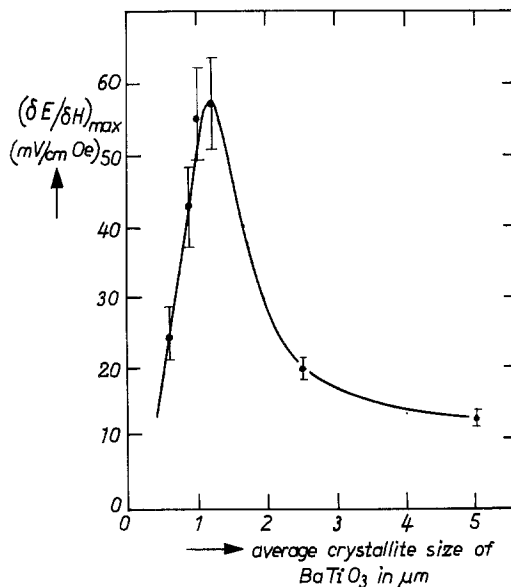


Figure 3 Dependence of the magnetolectric conversion on the average crystallite size of BaTiO_3 .

lites of both phases in the samples used were smaller than $0.4 \mu\text{m}$.

(g) The ferroelectric Curie temperature of all samples is about 128°C , as can be concluded from Fig. 5.

5. Discussion

In order to evaluate the results of this investigation it is necessary to realize that the value of the MC depends on such factors as the crystallite size of the phases, the mechanical contact between the phases, the mole ratio of the phases, excess TiO_2 , dopant etc. Small fluctuations of all these quan-

tities may be expected to give rise to a fairly large scatter in the MC of samples prepared under the same conditions and such a scatter is indeed found to depend significantly on particular parameters.

(a) From Tables I and II it can be concluded that, within the region of rates used, the MC does not depend on the cooling rate of the samples at the end of the sintering procedure.

(b) The significant dependence of the MC on excess TiO_2 as is given in Fig. 1 is a result of a number of effects. Firstly, the total amount of undesired phases passes through a minimum value as

TABLE II Influence of excess TiO_2 on magnetolectric effect

x in $\text{BaTi}_x\text{O}_{1+2x}$	Average value of $(\delta E/\delta H)_{\text{max}}$ (in $\text{mV cm}^{-1} \text{Oe}^{-1}$) after various cooling rates y ($^\circ\text{C h}^{-1}$)					
	5	10	20	50	100	200
1.00	16.2	13.2	14.6	12.4	13.8	11.5
1.01	25.0	20.2	31.1	28.9	23.6	28.6
1.02	19.3	19.8	22.6	20.4	20.2	16.1
1.03	15.7	15.6	25.9	19.9	20.6	16.9
1.04	23.1	16.4	25.1	19.3	15.8	14.3
1.06	21.8	13.7	19.7	18.2	13.6	17.6
1.08	10.9	16.1	15.4	16.7	13.5	16.8
1.10	20.6	20.3	22.5	19.9	19.5	27.4

Composition : 60 mol% $\text{BaTi}_x\text{O}_{1+2x}$; 40 mol% $\text{Ni}_{0.97}\text{Co}_{0.03}\text{Mn}_{0.10}\text{Fe}_{1.90}\text{O}_4$.
 Pressing : 1000 kg cm^{-2} , isostatic
 Sintering Procedure : 200°C h^{-1} to 1300°C ; 24 h at 1300°C ; $y^\circ\text{C h}^{-1}$ to room temperature.
 Sintering atmosphere : oxygen (1 atm.).
 Poling procedure : II.

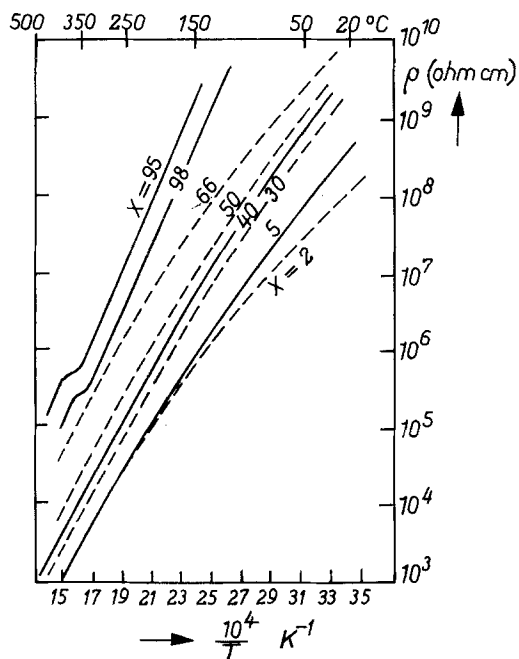


Figure 4 Dependence of the resistivity of the composite material on the temperature for different mole percentages of BaTiO_3 (x). The sizes of the crystallites of the two phases is smaller than $0.4 \mu\text{m}$.

a function of excess TiO_2 , and this gives rise to a minimum dilution of the desired phases. The excess TiO_2 at which this minimum occurs cannot be calculated from Table III. Secondly, the mechanical contact between the crystallites of the two phases changes with the excess TiO_2 because the number of pores between these crystallites decreases with increasing excess TiO_2 . Thirdly, although it dilutes the desired composite, the M-phase formed at larger amounts of excess TiO_2 is a magnetic phase which

TABLE III Amount of hexagonal BaTiO_3 and M-phase (" $\text{BaFe}_{12}\text{O}_{19}$ ") in composite specimens $(\text{BaTi}_x\text{O}_{1+2x})_{0.6}(\text{Ni}_{0.97}\text{Co}_{0.03}\text{Mn}_{0.10}\text{Fe}_{1.90}\text{O}_4)_{0.4}$ as a function of x (excess TiO_2 if $x > 1$)

x	I_H/I_{S_1}	I_M/I_{S_2}
1.00	0.38	0
1.01	0.17	0
1.02	0.17	0
1.04	0.07	0.44
1.06	0	0.83
1.08	0	1.05
1.10	0	1.60

I_H = Intensity (203) reflection of hexagonal BaTiO_3 .

I_M = Intensity (114) reflection of " $\text{BaFe}_{12}\text{O}_{19}$ ".

I_{S_1} = Intensity (400) reflection of spinel phase.

I_{S_2} = Intensity (222) reflection of spinel phase.

exhibits magnetostriction. It may contribute to the total magnetostriction but it also reduces the demagnetizing field of the spinel grains. As the M-phase is formed at the expense of the cubic BaTiO_3 phase and of the spinel phase the MC certainly will decrease at a large excess of TiO_2 . A quantitative explanation of Fig. 1, however, will be very difficult.

The phase with the magnetoplumbite structure is already observable by X-rays analysis at $x = 1.04$. The material with that composition contains about 0.8 wt% TiO_2 in excess, which indicates that the existence region of this phase is fairly large; a considerable number of Fe atoms in $\text{BaFe}_{12}\text{O}_{19}$ can be replaced by Ni and Ti atoms.

(c) The influence of the mole ratio of the two phases on the magnetoelectric conversion is difficult to explain. If there were no depolarizing fields, if the composition of both phases were independent

TABLE IV Influence of molecular ratio

$\text{Ni}_{0.97}\text{Co}_{0.03}\text{Mn}_{0.10}\text{Fe}_{1.90}\text{O}_4$ (mol%)	BaTiO_3 (mol%)	$(\delta E/\delta H)_{\text{max}}$ ($\text{mV cm}^{-1} \text{Oe}^{-1}$)		
		Lowest value	Highest value	Average value
98	2	ne*	ne	—
95	5	ne	ne	—
70	30	3.3	19.4	10.5
60	40	7.3	25.1	12.4
50	50	5.7	17.9	10.2
40	60	1.8	11.7	6.5
34	66	1.3	11.4	7.2
5	95	0.5	1.7	1.0
2	98	0.3	0.3	0.3

Pressing : 1000 kg cm^{-2} , isostatic.

Sintering procedure : at 1300°C for 24 h in oxygen (1 atm.). (cooling rates used 5 to 20 and 30°C h^{-1}).

Poling procedure : II.

*ne : no effect.

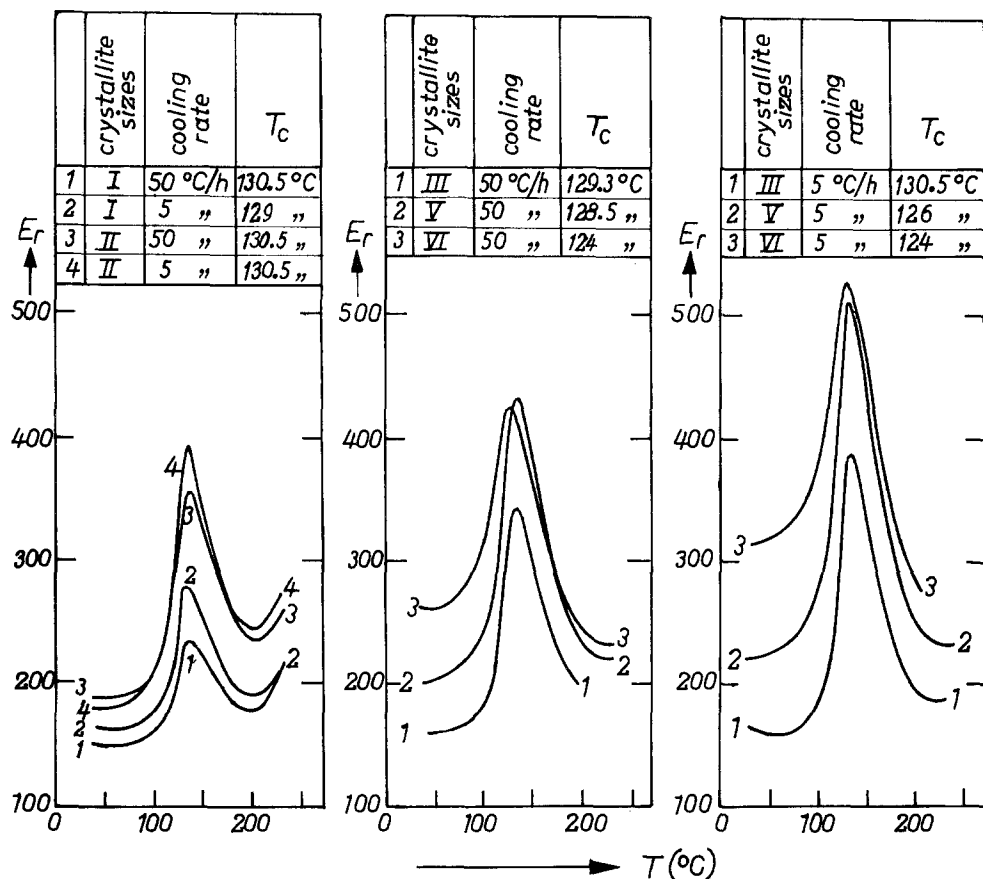


Figure 5 $\bar{\epsilon}_r$ as a function of temperature for composite samples with different crystallite sizes and at two different cooling rates. The sizes of the crystallites are given in Table VII.

TABLE V Influence of crystallite size of piezoelectric phase

Particle size (μm)	$(\delta E/\delta H)_{\text{max}}$ ($\text{mV cm}^{-1} \text{Oe}^{-1}$)		
	Highest value	Lowest value	Average value
0.6	32.0	18.5	24.7
0.9	55.4	32.8	43.0
1*	62.7	44.4	55.6
1.2	71.4	47.6	57.1
2.5	22.7	18.1	20.2
5.0	15.3	11.0	13.0

*: Size not reliable.

Composition : 60 mol% BaTiO_3 (coarse).
40 mol% $\text{Ni}_{0.97}\text{Co}_{0.03}\text{Mn}_{0.10}\text{Fe}_{1.90}\text{O}_4$ (powder).

Pressing : not isostatic.

Sintering procedure : $200^\circ \text{C h}^{-1}$ to 1300°C .
24 h at 1300°C .

Cooling rates : (5, 10, 20, 50, 100 and $200^\circ \text{C h}^{-1}$ to room temperature.

Sintering atmosphere : oxygen (1 atm.).

Poling procedure : I.

TABLE VI Influence of crystallite size and mole ratio on magnetolectric conversion

Combination of crystallite sizes	$(\delta E/\delta H)_{\text{max}}$ ($\text{mV cm}^{-1} \text{Oe}^{-1}$)	
	Mole ratio 60/40	Mole ratio 40/60
BaTiO_3 (0.9 μm)/ ferrite (0.4 μm)	43.0	61.2
BaTiO_3 (1.2 μm)/ ferrite (0.4 μm)	57.1	81.7

Sintering procedure : heating at $200^\circ \text{C h}^{-1}$ to 1300°C ;
sintering for 24 h at 1300°C ;
and cooling at $100^\circ \text{C h}^{-1}$ to room temperature.

Sintering atmosphere : oxygen (atm.).

Poling procedure : I.

of their mole ratio, if the dilatation coefficients of both phases were exactly the same and if the mechanical coupling were independent of the mole ratio, the maximum conversion would be expected to occur at a volume ratio $V_{\text{BaTiO}_3}/V_{\text{Ni}(\text{Co}, \text{Mn})\text{Fe}_2\text{O}_4} = 50/50$. This maximum, however, occurs at the

TABLE VII Influence of electrical poling on magnetoelectric conversion of samples with different crystallite sizes

Sample	Composition	Average crystallite size (μm)	Average $(\delta E/\delta H)_{\text{max}}$ ($\text{mV cm}^{-1} \text{Oe}^{-1}$)	
			Poling procedure I	Poling procedure II
A*	60 mol% BaTiO ₃ 40 mol% ferrite	1 > 1	59.9	10.0
B†	60 mol% BaTiO ₃ 40 mol% ferrite	1 < 0.4	55.6	13.5
C	60 mol% BaTiO ₃ 40 mol% ferrite	< 0.4 > 1	12.4	8.4
D	60 mol% BaTiO ₃ 40 mol% ferrite	< 0.4 < 0.4	9.0	14.0

* Mixture VII in Table VIII.

† Mixture IV in Table VIII.

Pressing : not isostatic.

mole ratio 40/60, or the volume ratio 37/63, i.e. at a higher volume percentage of Ni(Co, Mn)Fe₂O₄. In the series of samples given in Table IV (and in Fig. 2) the depolarizing fields for the BaTiO₃ phase are eliminated by the "baked in" space charge field since they are electrically poled in accordance with procedure II [6]. As for the Ni(Co, Mn)Fe₂O₄ phase, the depolarizing fields become larger the more "diluted" this phase is, i.e. the smaller its volume fraction, and hence the maximum of the conversion will be shifted in the direction of a higher volume percentage of the piezomagnetic phase, as was found experimentally in this series. There are other reasons for the maximum of the MC to occur at a higher volume percentage than 50%. The medium between the ferrite grains, BaTiO₃, has a permeability $\mu = 1$. The medium between the BaTiO₃ grains, ferrite, has a dielectric constant $\epsilon \approx 10$. Moreover, the external field of an electrically polarized BaTiO₃ grain can be compensated by charge transport through the ferrite grains. As a consequence it is to be expected that even in the case of electrical

poling in accordance with procedure I the maximum value of the MC will be situated at a volume percentage of the ferrite phase higher than 50, irrespective of the crystallite size of the two phases. The results of a few experiments given in Table VI support this hypothesis.

(d) The crystallite size of the BaTiO₃ phase has a considerable influence on the MC of the composite material, as is seen in Fig. 3 and Table V. The values of the MC for the combination of small crystallites of the two phases ($< 0.4 \mu\text{m}$) prepared by isostatic repressing are not introduced because of their different preparation. Nevertheless their value (see Table I) fits rather well in Fig. 3 and Table V. Nothing can be said about the influence of the crystallite size of the Ni(Co, Mn)Fe₂O₄ phase because the MC was determined for only two different sizes ($< 0.4 \mu\text{m}$ and $> 1.00 \mu\text{m}$). The initial increase of the MC with the size of the BaTiO₃ crystallites can be explained as follows. It is known from the literature [16–18] that BaTiO₃ crystallites have a surface layer, with a thickness d between 0.01 and 0.1 μm , which has properties that deviate from those of the bulk. The piezoelectric properties of such a surface layer can be expected to be poorer than those in the bulk of the crystallites. In the case of crystallites of BaTiO₃ in the sintered composite that are less than $2d$ in diameter no or only very low conversions will take place, but with increasing diameter the contribution of the bulk will increase, giving rise to larger magnetoelectric conversion values. Although the decrease of the MC with increasing crystallite diameter at larger values of this diameter might possibly be connected with the fact that larger BaTiO₃ crystallites can be poly-domain and smaller ones not, the exact explanation for this decrease is not known.

TABLE VIII Samples of mixtures with different average crystallite sizes, with the diameter of the BaTiO₃ crystallites $> 0.4 \mu\text{m}$. For the preparation of these samples see Tables V and VI

Mixture	Average crystallite size (μm)	
	BaTiO ₃ 60 mol%	Ni _{0.97} Co _{0.03} Mn _{0.10} Fe _{1.90} O ₄ 40 mol%
I	5	0.4
II	2.5	0.4
III	1.2	0.4
IV	1	0.4
V	0.9	0.4
VI	0.6	0.4
VII	1	1

(e) The influence of the electrical poling procedure on the MC is seen in Table VII. The magnetoelectric conversion of samples poled according to procedure II is independent of the size of the crystallites of the two phases in the sintered composite. With poling in accordance with procedure I, however, the conversion is much higher if coarse crystallites of the titanate are present in the composite material. If the diameter of the crystallites of the titanate phase is smaller than $0.4\ \mu\text{m}$ the MC measured is independent of the poling procedure. A satisfactory explanation for this behaviour has not yet been found.

(f) The resistivity of the samples increases with increasing mole fraction of the BaTiO_3 phase, as is seen in Fig. 4. The resistivity of the composite is a result of the resistivities of BaTiO_3 crystallites and $\text{Ni}(\text{Co}, \text{Mn})\text{Fe}_2\text{O}_4$ crystallites being connected in series and parallel. It can be deduced from this figure that the resistivity of BaTiO_3 in the composite is higher than that of $\text{Ni}(\text{Co}, \text{Mn})\text{Fe}_2\text{O}_4$.

It has to be appreciated that the resistivity of each of the participating phases in a sample generally differs from that of the starting phases. This is due to cross-doping and may depend on the mole ratio of the phases.

(g) From Fig. 5 it can be concluded that neither the cooling rates used nor the crystallite size of the phases has any influence on the ferroelectric Curie temperature of the composite material, which is situated at about 128°C . Within the investigated range of sizes the peak in the plot of $\bar{\epsilon}_r$ versus T increases with decreasing crystallite size. The cooling rate does not seem to have any influence on this peak height.

6. General remarks

The maximum value of the magnetoelectric conversion coefficient $(\delta E/\delta H)_{\text{max}}$ obtained with the sintered composite material is $81.7\ \text{mV cm}^{-1}\ \text{Oe}^{-1}$. Compared with the result obtained with the *in situ* grown composite $(\text{BaTiO}_3)_{0.61} - ((\text{CoFe}_2\text{O}_4)_{0.47} (\text{CoTiO}_4)_{0.53})_{0.39}$, namely $\approx 130\ \text{V cm}^{-1}\ \text{Oe}^{-1}$, this is a fairly good result. The sintered composite magnetoelectric material even compared favourably with monocrystalline material at room temperature, the best of which is Cr_2O_3 with a conversion factor of about $20\ \text{mV cm}^{-1}\ \text{Oe}^{-1}$. As previously pointed out, a better figure of merit is the quantity $4\pi (dP/dH)$ which, at room temperature, is a factor of about 120 larger for the sintered material than for monocrystalline Cr_2O_3 .

The use of the sintered magnetoelectric compo-

site is restricted to applications in which the frequency of the a.c. magnetic field is higher than the reciprocal value of the relaxation time of the internal leakage current in the material. This means roughly that an a.c. magnetic field at 3 Hz cannot be detected above 60°C .

Although the samples poled in accordance with procedure II have a smaller magnetoelectric conversion than those containing coarse BaTiO_3 ($1.2\ \mu\text{m}$) poled with procedure I, they are more suitable to be used for the detection of a.c. magnetic fields with a frequency $> 3\ \text{Hz}$ at temperatures above 60°C than samples of the second type due to their better stability at these temperatures. Because of the value of the ferroelectric Curie temperature, namely 128°C , the material should not be used above 100°C .

7. Conclusions

(1) Sintered composite material that can convert magnetic into electric fields with a fairly good conversion factor can be made by combining BaTiO_3 and $\text{Ni}(\text{Co}, \text{Mn})\text{Fe}_2\text{O}_4$ into one solid material.

(2) For the conversion of magnetic into electric fields the crystallite dimension of the BaTiO_3 phase has an optimum value ($\sim 1.25\ \mu\text{m}$).

(3) The maximum conversion is found at the mole ratio $\text{BaTiO}_3/\text{Ni}(\text{Co}, \text{Mn})\text{Fe}_2\text{O}_4 = 40/60$.

(4) Addition of TiO_2 to the BaTiO_3 phase reduces the amount of hexagonal BaTiO_3 in the final product. It is not impossible that it also causes better mechanical contact between the two phases.

(5) If coarse BaTiO_3 crystallites are used, the samples poled by the normal electrical poling procedure I have a higher magnetoelectric conversion factor, $(\delta E/\delta H)_{\text{max}}$, than those poled with the aid of a built-in space-charge field procedure II). If the diameter of the crystallites of both phases is small ($< 0.4\ \mu\text{m}$), both electrical poling procedures give rise to the same magnetoelectric conversion factor.

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