ELSEVIER

Ceramics International 30 (2004) 389–392

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis and characterization of in situ grown magnetoelectric composites in the BaO–TiO–FeO–CoO system

S. Mazumder*, G.S. Bhattacharyya

Central Glass and Ceramic Research Institute, Jadavpore, Kolkata 700032, India

Received 3 September 2002; received in revised form 6 May 2003; accepted 10 June 2003

Abstract

Magnetoelectric composite materials with mixed spinel cobalt ferrite–cobalt titanate and perovskite barium titanate as co-existing phases have been grown in situ by solid state reactions over a wide region of compositions of the BaO–TiO–CoO–FeO system. An estimate of phase formation was obtained by XRD. The magnetoelectric properties of the composites in relation to their composition and synthesis process have been assessed. The magnetoelectric (ME) conversion factor has been measured by a dynamic method as a function of magnetic field and has been found to vary from 3.0081 to 5.5886 mV/cm Oe at room temperature depending on the synthesis procedure. Typical dependance of ME conversion factor on magnetic field shows that the magnetic saturation occurs at low stimulation and the samples are best suitable in responding to relatively weak magnetic field.

Keywords: A. Powders: solid state reaction; B. X-ray methods; D. Perovskites; D. Ferrites

1. Introduction

In a magnetoelectric (ME) composite the magnetostrictive strain in the magnetic phase creates an electric polarization in the adjacent piezoelectric phase and hence is capable of converting magnetic field into electric field and vice versa. Such product property can be utilized in smart materials used in sensors, processors and feedback systems. A dense sintered mixture of perovskite barium titanate and spinel ferrite was obtained by unidirectional solidification and electrically poled to make the barium titanate phase piezoelectric [1]. When a magnetic field is applied to the composite, the ferrite grains change shape because of magnetostriction. The strain passes along the piezoelectric grain resulting in an electric polarization. The necessary condition for the ME behaviour by the two phase material is a strong mechanical coupling between the phases transferring elastic strains and ideally without loss. Such coupling may occur between the phases when solid phases are grown by directional solidification from an eutectic melt [2,3]. The major advantage of this type of in situ grown two phase composition is its well defined crystal orientation with respect its mutual growth direction. Magnetoelectric composites may be prepared [4–6] by sintering powders of piezoelectric barium titanate (PE) and piezomagnetic spinel (PM) particularly if both phases can co-exist up to room temperature from the temperature at which they are sintered. Sintered composite materials are much easier as well as cheaper to prepare than unidirectional solidified in situ composites. As regard to the ME effect it was found that [3] ME composites made by unidirectional solidification always gave a higher value than those prepared by solid state sintering of the presintered component phases for a given composition [4]. The first method of preparation is undoubtedly good, nevertheless it is commercially unviable. In situ growth of the ME composites from the respective oxides is equally difficult due to the complicated reaction kinetics, thermodynamic constraints and all sorts of possible random diffusions but can be made commercially viable when suitably processed. In this paper we report magnetoelectric properties of a few in situ grown ME composites in the the quinary oxide system of BaO–TiO–FeO–CoO.

* Corresponding author. Tel.: +91-033-2473-3469; fax: +91-033-2473-0957.

E-mail address: suj52@yahoo.co.in (S. Mazumder).

0272-8842/$30.00
doi:10.1016/S0272-8842(03)00121-4

Table 1
ME values for quinary composition as synthesized at different temperatures

Sample code	Oxides compositions in wt.%				Group-A (1000–1200)°C			Group-B (1000–1100)°C		
	BaO	Fe_2O_3	CoO	TiO_2	ρ Gohm	ϵ (RT)	ME mV/cmOe	ρ Gohm	ϵ (RT)	ME mV/cmOe
1	34.29	18.41	29.84	26.46	3.81	200	4.6667	2.95	180	3.4477
2	35.56	15.59	20.91	27.94	6.08	420	3.7667	5.93	400	3.0081
3	38.13	15.89	18.24	27.99	9.29	250	4.2107	5.94	240	3.6905
4	34.29	21.24	19.46	25.01	10.44	320	3.8413	10.19	300	3.3787
5	42.02	11.24	16.33	30.23	13.46	500	5.5886	14.95	450	5.1613
6	38.01	13.49	19.41	29.09	8.99	350	4.9376	4.46	340	3.6317
7	35.56	14.89	21.25	28.31	11.13	560	5.3188	8.03	540	4.5489
8	34.29	15.57	22.23	27.91	14.11	175	5.1711	9.19	150	4.4737
9	36.21	17.02	19.54	27.23	14.18	520	4.8891	14.07	500	4.0001

2. Experimental procedure

2.1. Preparation of the magneto electric composites

The composites were prepared by conventional solid state reactions among the constituent oxides of $BaCO_3$, Co_3O_4, Fe_2O_3 and TiO_2 (AR grade). Synthesis temperatures were assessed by analyzing the DTA for a few compositions and were varied from 1000 to 1200 °C for 3 h. followed by calcination at 1000 °C (3 h). The sintered ceramics were lapped to make the surface flat and parallel and then electroded by applying silver paste.

2.2. Electric and magnetoelectric measurements

To enable the magnetoelectric measurements the samples were poled both electrically and magnetically.

Each electroded sample was centrally mounted in a small laboratory made muffle furnace between two highly insulating ceramic blocks containing two copper electrodes which were taken from a 10 kV/cm DC power source (Model No.-DC 10 K) for electric poling. The furnace was heated up to 150 °C which was 30 °C above the ferroelectric transition temperature of perovskite phase and poling was done during cooling and continued for 30 min at room temperature.

Magnetic poling was done at a constant DC magnetic field (13 K Oe) for 30 min by mounting the samples centrally between the poles of a horse-shoe type electromagnet.

ME measurements were done by dynamic method [7–9] with an AC sweeping magnetic field of magnitude 30 Oe at a frequency of 1070 Hz with a biased variable DC magnetic field. The ME signal was registered by measuring the developed electric potential across the sample as a function of applied increasing DC magnetic field with 30 Oe AC bias. The emf generated in the sample was measured with a LOCK IN AMPLIFIER (EG&G PAR-5210) at the lock frequency of 1070 Hz.

The electrical and dielectric measurement (1 KHz) were done by two probe technique(HP-3458A multimeter, HP-4276A LCZ meter and HP 4192A impedance analyzer).

2.3. X-ray diffraction study

The crystallographic phases present in the compositions synthesized under different experimental conditions were determined by XRD analysis (XRD Model No. PW1710).

3. Results and discussions

We took a wide range of quinary oxide compositions (Table 1) in synthesizing and characterizing of the in situ grown ME composites to locate the best possible zone where both the PM and PE phases remained in equilibrium and showed the ME effect due to their mechanical coupling. The estimated composition tetrahedron for the present investigation has been identified as a solid marked area in Fig. 1 where we could get a standard ME body whose ME coefficients may vary from 3.0081 to 5.5886 mV/cm Oe depending on the synthesis procedure.

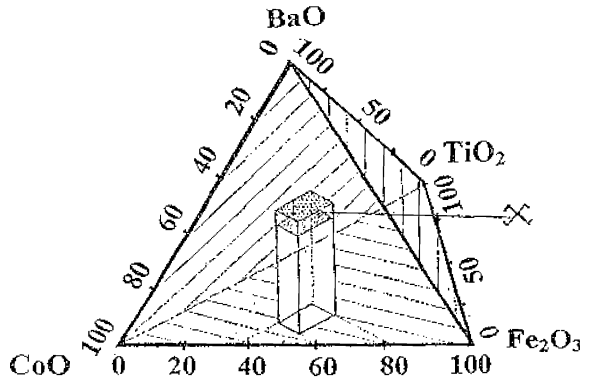

Fig. 1. A simplified tetrahedron of quinary oxides system representing the estimated composition range under study marked by a shaded area [χ].

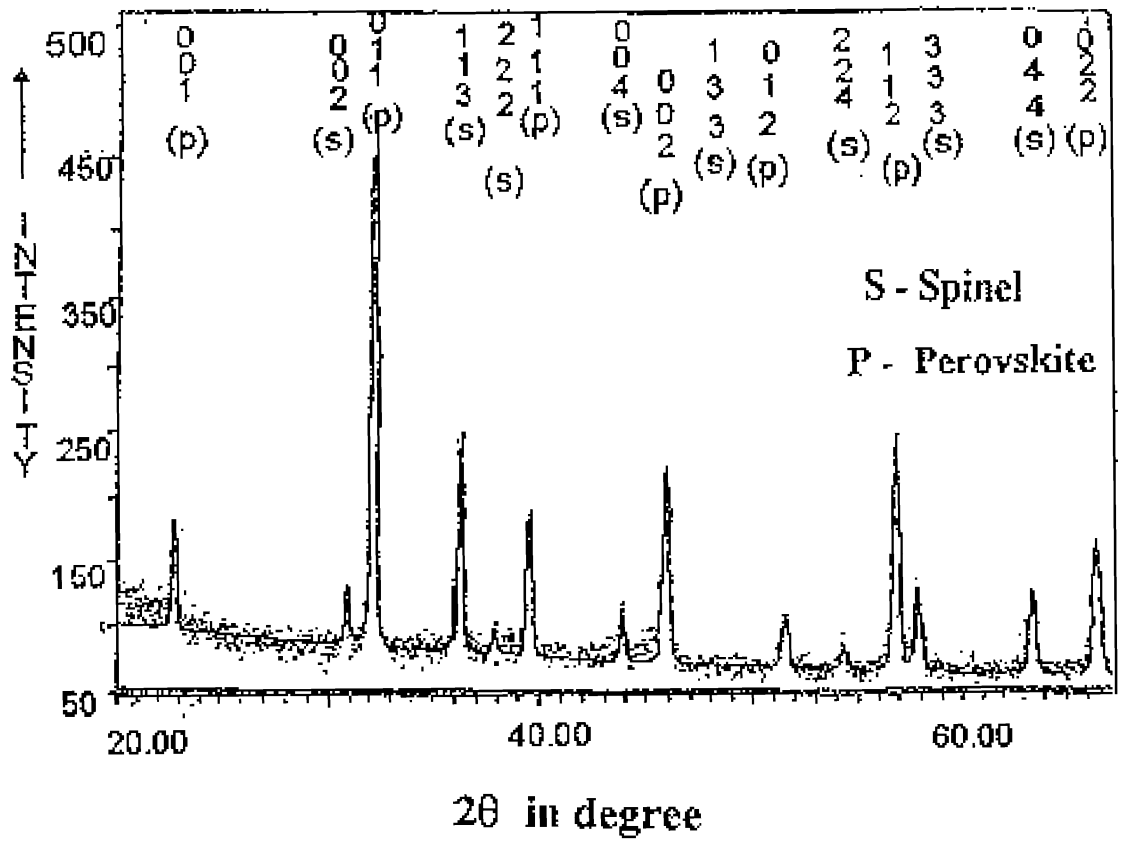

Fig. 2. X-ray diffraction pattern of ME materials. The perovskites (P) and the spinel (S) phases along with their corresponding reflection indices are marked.

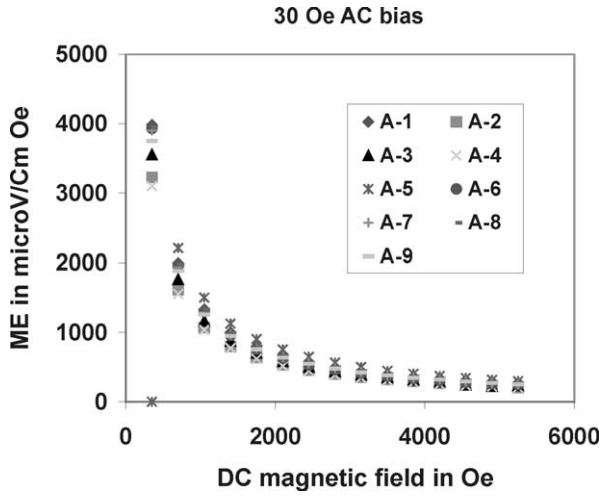

Fig. 3. Typical dependance of the ME values on magnetic field of a series of composites sintered at 1200 °C (A1–A9).

All the compositions primarily exhibit the presence of combinations of perovskite (P) and spinel (S) phases (Fig. 2). Unidentified minor phases appeared in a few cases and were found to have a metastable behaviour as the synthesis temperatures were varied. The dielectric constant (Table 1) in all the compositions has been measured from room temperature to 150 °C which exceeds the Curie temperature of ferroelectric barium titanate. The DC resistivity measurements at RT (Table 1) revealed resistivities in the order of 10^9 ohm/cm and suggest the composites to be highly resistive so that accumulated charges do not leak through the piezomagnetic phase.

The ME signal as registered by measuring the developed electric potential across a sample as a function of applied increasing DC magnetic field from 0 to 5.250 kOe (30 Oe AC bias) are listed in Table 1. Fig.3 shows the typical dependence of the ME conversion on magnetic field for a composite (Gr–A) under study. For all composites the highest ME value was obtained for 30 Oe AC biased zero DC field indicating that the magnetostrictive phase has reached a saturation value producing constant electric field in the PE phase, hence making dE/dH decrease with increasing magnetic field. This indicates that magnetic saturation occurs at low stimulation and the samples are best suitable in responding to relatively weak magnetic field.

The wide differences in the ME performance (Table 1) of the composites over the wide range of compositions may be attributed due to (1) basic composition of oxides resulting in variable amounts of PM and PE phases in the composite; (2) structural modifications in the component phases by the random diffusion during in situ

preparation as allowed by the synthesis procedure. The scattering of the intensity pattern gave a qualitative description of the structural modification in the co-existing phases (PM and PE) and their mutual dependence is reflected in the ME effect.

The highest ME value obtained in the present study is 5.5886 mV/cm/Oe at room temperature (sample code 5A). A close look at the Table 1 shows that the wt.% of BaO and TiO_2 in the compositions is highest leading to the possibility of a greater amount of stochiometric perovskite phase formation. Moreover the stoichiometric wt.% ratio (BaO/TiO_2) in pure $BaTiO_3$ (perovskite) phase is equal to 1.8974 which is much higher than the corresponding value (=1.2540) in that sample (code 5A). The dependance of the ME conversion factor on excess TiO_2 has been described in the study of magnetoelectric composite material made by sintering a mixture of a piezoelectric and piezomagnetic phase [4]. In the case of in situ preparation of ME composites, the presence of excess TiO_2 can influence both the spinel and perovskite phases favourably. Indeed if more and more TiO_2 is diffused into the spinel phase, the change of Fe^{3+} to Fe^{2} becomes possible and this may possibly be responsible for larger magnetostriction, although a complete structure analysis is needed to justify the statement. The possibility of dilution of desired perovskite phase also becomes minimum with excess of TiO_2. It is to be expected that additional knowledge on the structure of the co-existing phases of the composites and the way in which the bulk phase properties are expressed in the composite properties, will lead to an improved synthesis procedure giving improved performance of the composite.

4. Conclusions

A series of magnetoelectric composite materials from a quinary oxide system have been grown in situ and the best possible composition zone has been estimated where we could get a standard ME body whose ME coefficients may vary from 3.0081 to 5.5886 MV/cm Oe depending on the synthesis procedure. The formation of both piezoelectric and piezomagetic phases which is prerequisite of a ME composite has been confirmed. 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.

Acknowledgements

The authors would like to thank Dr. H.S. Maity (Director, C G & C R I, Kolkata), Mr. S. Baisnab (Electronic Consultant) and Mr. N. Bharti (Technical Assistant).

References

[1] J. Van Suchtelen, Product properties: a new application of composite materials, Philp Res. Rep. 27 (1972) 28–37.
[2] J. Van den Boomgaard, D.R. Terrel, R.A.J. Born, H.F.J.I. Giller, An in situ grown eutectic magnetoelectric composite material Part I, J. Mater. Sci. 9 (1974) 1705–1709.
[3] A.M.J.G. Van Run, D.R. Terrel, J.H. Schooling, An in situ grown eutectic magnetoelectric composite material Part 2, J. Mater. Sci. 9 (1974) 1710–1714.
[4] J. Van den Boomgaard, R.A.J. Born, A sintered magnetoelectric composite material $BaTiO_3$-Ni(Co, Mn)Fe_2 O_3, J. Mater. Sci. 13 (1978) 1538–1548.
[5] R.P. Mahajan, K.K. Patankar, A.N. Patil, S.C. Choudhury, S.A. Patil, Electrical properties and magnetoelectric effect in $MnFeO_4$ and $BaTiO_3$ composites, Indian J. Eng. Mater. Sci. 7 (2000) 203–211.
[6] A. Hanumaiah, T. Bhimasankaram, S.V. Suryanarayan, G.S. Kumar, Dielectric behaviour and magnetoelectric effect in cobalt ferrite–barium titanate composites, Bull. Mater. Sci. 17 (4) (1994) 405–409.
[7] S.V. Suryanarayan, Magnetoelectric interaction phenomena in materials, Bull. Mater. Sci. 17 (7) (1994) 1259–1270.
[8] M. Mahesh Kumar, A. Srinivason, S.V. Suryanarayan, G.S. Kumar, T. Vimkrisnan, Experimental setup for dynamic measurement of magnetoelectric effect, Bull. Mater. Sci. 21 (3) (1998) 251–255.
[9] M. Mercier, Magnetoelectric behaviour in garnets, in: A.J. Freeman, H. Schmid (Eds.), Magnetoelectric Interaction Phenomena in Crystals, Gordon and Breach, New York, 1975.