

Magnetolectric properties of multiferroic cobalt ferrite and soft piezoelectric PZT particulate composites

C. MICLEA*, C. TANASOIU, L. AMARANDE, C. F. MICLEA, C. PLAVITU^a, M. CIOANGHER, L. TRUPINA, C. T. MICLEA^a, T. TANASOIU^a, M. SUSU^a, I. VOICU^a, V. MALCZANEK^b, A. IVANOV^a, C. DAVID^c

National Institute for Materials Physics, Bucharest-Magurele, Romania

^a*Hyperion University, Calea Calarasilor 169, sector 3, Bucharest, Romania*

^b*Fairleigh Dickinson University, NJ, USA*

^c*Technical University of Civil Engineering of Bucuresti, Romania*

Multiferroic composite materials, consisting of piezoelectric and piezomagnetic phases, show electric polarization in the presence of a magnetic field and magnetization on applying an electric field, i.e. piezomagnetic phase causes polarization while piezoelectric phase causes changes in magnetization. The figure of merit of such multiferroic particulate composites is the magnetolectric voltage coefficient representing the amount of polarization induced by a given magnetic field. In the present investigation we prepared and studied the properties of bulk particulate composites made from cobalt ferrite (COF) and a soft piezoelectric material (PZT). Composite samples, according to the formula $x\text{COF} \cdot (1-x)\text{PZT}$ with $0 \leq x \leq 1$ were prepared by mixing the COF and PZT powders, pressing them as discs and then sintered at 1200 °C for 3 hours. Structural, magnetic, piezoelectric and magnetolectric characteristics of the sintered composites were determined as a function of the mass fraction of COF into PZT and magnetic field. The ME coefficient shows a maximum value of about 70 mV/cm-Oe for composites containing 40 % COF and 60% PZT, in a DC magnetic field of 3 kOe at a frequency of 1KHz of the ac magnetic field. Some of the dielectric and piezoelectric properties of the composite samples, as a function of the mass fraction x , were also determined.

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1. Introduction

The magnetolectric (ME) effect is considered to be a coupled two fields magnetic and electric effect in which the polarization in a material is induced by a magnetic field and vice-versa the magnetization is induced by the application of an external electric field. During the last years the number of work dedicated to this subject increased considerably [1]. ME effect was observed in some single phase crystals [2-9], but at lower intensities, as well as in composite ceramics made from a magnetostrictive ferrite and a piezoelectric material [10-17], at higher intensities, due to the higher magneto-mechanical-electrical interaction between the piezoelectric and ferrite phases. Though in many cases the measured magnetolectric coefficient proved to be smaller than the theoretical predictions, the experimental efforts are directed towards achieving ceramic materials with higher densities but still having distinct piezo and magnetic phases. In addition, care must be taken to avoid the formation of microcracks due to a large thermal expansion between the phases which may lower the density. A too high sintering temperature may possible help the interphase diffusion thus facilitating the increase of defect concentration or foreign phases formation which could lead to lower resistivities of composites making the poling more difficult.

In the present investigation we report on the results obtained with a PZT-Co ferrite particulate composite

sintered at reasonable temperature, but still having higher densities and ME coefficient.

2. Experimental

Simple CoFe_2O_4 (COF) was chosen as magnetic phase in this experiment due to its high magnetization and magnetostriction coefficient [18]. The Co ferrite was synthesized by the usual mixed oxide route using high purity raw materials from Merk. Both oxides Fe_2O_3 and Co_2O_3 are in the nanopowders form and have purities of 99.8 %.

The stoichiometric amounts of oxides were wet mixed together in a Retsch 400 PM planetary ball mill for 2 hours, then dried and calcined at 950 °C for 4 hours to complete the solid state reaction. The calcined product was manually crushed and sieved and then checked by X-ray diffraction to verify the formation of spinel phase. The X-ray patterns were assigned only to cubic spinel phase with no other foreign phase being visible.

As piezoelectric material we have chosen a soft type PZT with the chemical formula $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Nb}_{0.05}\text{Ni}_{0.06}\text{Zr}_{0.49}\text{Ti}_{0.40})\text{O}_3$ for its high piezoelectric parameters [19-22]. The usual mixed oxide route was used to synthesise the PZT material, starting from high purity (over 98 %) oxides and carbonates (from Merk). The raw oxides and carbonates were wet mixed for 2 hours in the same planetary ball mill, double calcined at

850 and 900 °C, crushed and sieved and checked by X-ray diffraction. The X-ray showed the formation of only perovskite phase.

Batches of about 50 g of composites samples, according to the formula $x\text{COF}\cdot(1-x)\text{PZT}$ with $x = 0; 0.1; 0.2; \dots 0.9; 1$ were then mixed together in the same planetary ball mill for 20 hours, in order to get intimately mixed powders in the nanometric range. The mixed samples were next uniaxially pressed as disc shaped pellets with a diameter of 15 mm and 2 mm thickness at a pressure of approximately 50 MPa. The pellets were next sintered at temperatures between 1000 and 1300 °C for 3 hours.

The phase composition and microstructure of the sintered samples were revealed by X-ray diffraction technique (D-500 Siemens diffractometer with $\text{CuK}\alpha_1$ radiation) and by electron microscopy images (Hitachi S-2600 N model electron microscope)

The density of the sintered samples was determined by the Archimede method, and for electrical measurement the samples were Ni electroded on the main surfaces and poled in a silicon oil bath at 220 °C in a field of 3 kV/mm, applied at high temperature and kept on down to 80 °C. The piezoelectric properties were determined by the resonance method using an Agilent 4294A analyzer and standard piezo d_{33} meter. The ME effect obtained by applying an ac magnetic field superimposed on a dc magnetic field was determined by the dynamic method and measuring the output signal amplified by a charge amplifier.

The dc magnetic field was of 5 kOe and was measured by a standard teslameter. The driving ac magnetic field of 20e was generated by a Helmholtz coil. The measurements were made at room temperature.

3. Results and discussion

The pressed compositions were sintered for 3 hours at different temperatures between 1000 and 1300 °C and their densities were determined as a function of the sintering temperatures. The results are shown in Fig. 1.

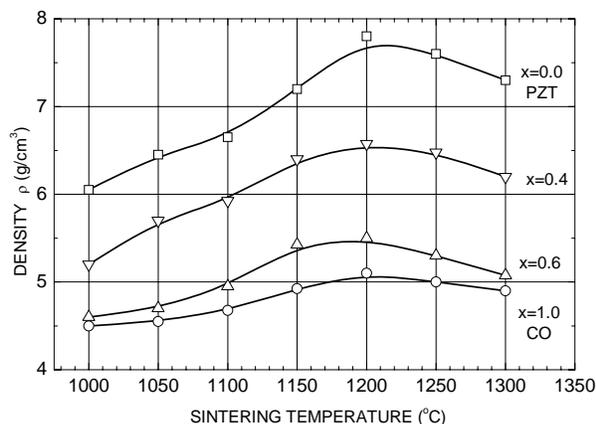


Fig. 1 The density vs sintering temperature for different composite samples

One can see that the optimum sintering temperature is situated around 1200 °C where the densification exhibits maximum values for almost all compositions. Therefore, the samples for the piezoelectric and magnetoelectric measurements were further sintered only at this temperature.

The behavior of the density as a function of the composition is illustrated in Fig. 2.

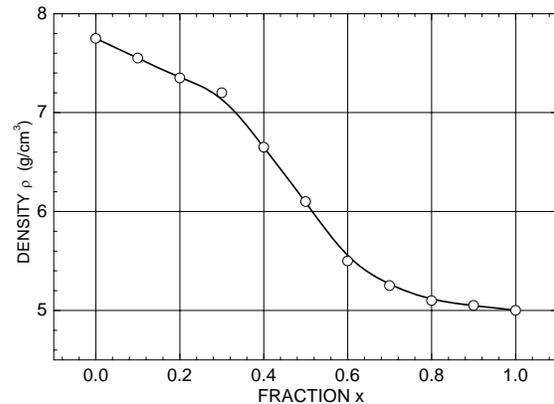


Fig. 2 The density vs composition of $x\text{COF}(1-x)\text{PZT}$.

One can see that the composites density decreased continuously with increasing x from the highest value of pure PZT to the lowest one for pure COF but the decreasing is not uniform and three regions can be distinguished. Thus for x ranging between 0 and 0.3 the decreasing rate is about 10 %, then between 0.3 and 0.7 the decreasing is more sudden of about 30 % and finally between 0.7 and 1 it is only 5 %. This behavior could be due to the different predominance of each phase. Thus in the first region PZT predominates while at the end of composition Co ferrite predominates. At the middle of the interval, there is an equilibrium between the phases and the decrease is more uniform. Figure 3 shows the X-ray patterns of the PZT/COF particulate composites.

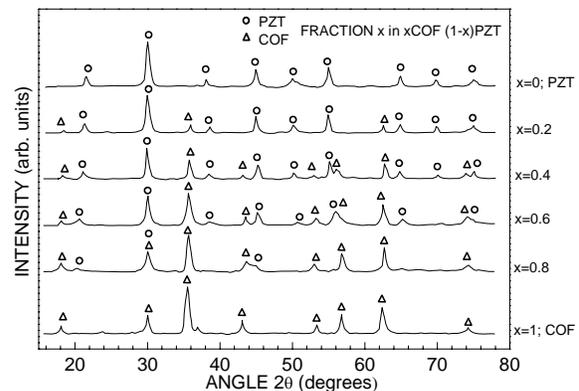


Fig. 3 XRD of composite samples with different composition in the system $x\text{COF}(1-x)\text{PZT}$

One can see that all diffraction peaks consist of those characteristics to PZT and COF.

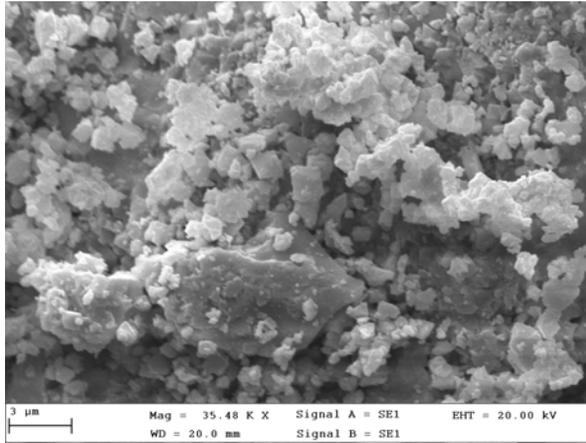


Fig. 4 A typical SEM image of the sample structure for composition with $x=0.4$.

These patterns suggest that there is no important reaction between the two phases and that during sintering the diffusion process take place only within a very thin surface layer of the crystallites. A typical SEM image of the sample structure, shown in figure 4, illustrates the two different phases quite distinctly.

The relative dielectric constant ϵ_r for different composite samples is shown in Fig. 5.

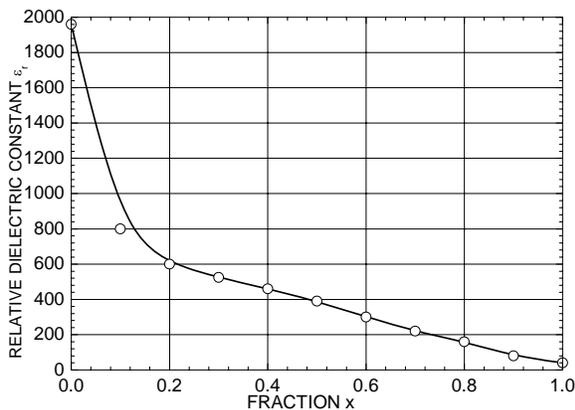


Fig. 5 The dependence of the relative dielectric constant on magnetolectric composite

The permittivity is drastically decreased by the presence of the ferrite phase and even for only 0.1 COF phase, the decrease reaches 70 %. Then the decrease is very slow up to the final concentration of COF. This may suggest a possible reaction between PZT and COF for low concentration of COF in PZT. A nearly similar behavior is also exhibited by the planar coupling factor k_p as can be seen in figure 6.

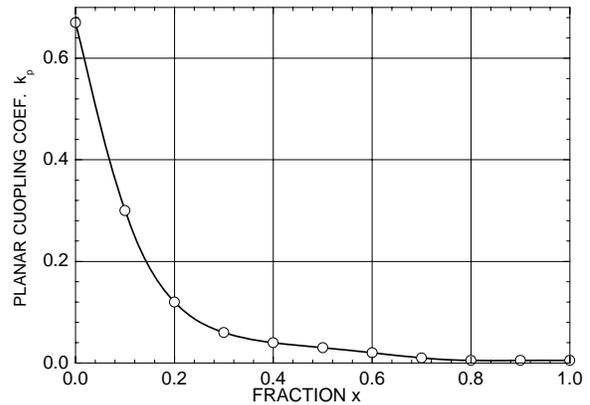


Fig. 6 The dependence of the planar coupling coefficient on magnetolectric composite

The presence of COF in PZT even in small quantities gives rise to a sudden drop of k_p with more than 80 %. After that the decreasing is very slow. The charge constant d_{33} behaves completely similar to k_p as can be seen in figure 7.

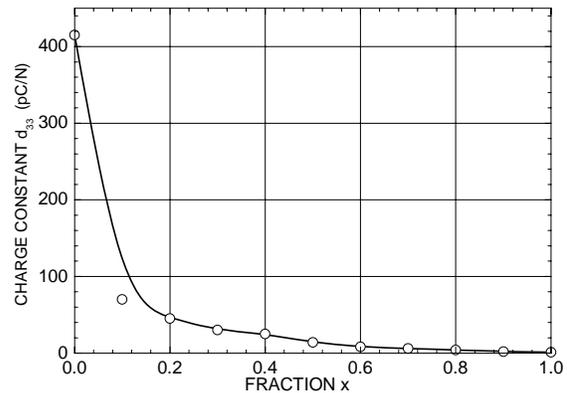


Fig. 7 The dependence of the charge constant on magnetolectric composite

It drops with nearly 90 % for COF fractions up to 0.2 and then very slowly. From such a behavior one may speculate that the introduction of COF in PZT drastically weakens the piezoelectric properties of the composites, suggesting that a reaction between Fe and possible Co in the basic composition of PZT takes place at least within the surface layer whose thickness may depend on the sintering temperature and dwelling time. The presence of larger amount of COF may drastically lower the composite resistivity making the poling process harder and thus the piezoelectric properties decrease up to the disappearance.

The magnetization of the composite samples in a DC field of 5 kOe is shown in fig. 8.

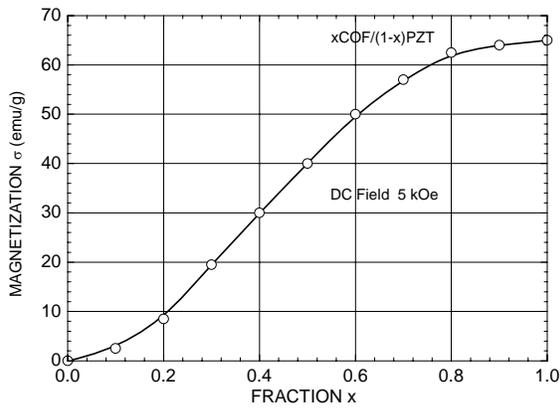


Fig. 8 Magnetisation of composite samples as a function of COF concentration in PZT

One can notice a steady increase of magnetization with increasing COF concentration up to a maximum value of about 65 emu/g.

The ME coefficient as a function of DC magnetic field is shown in figure 9.

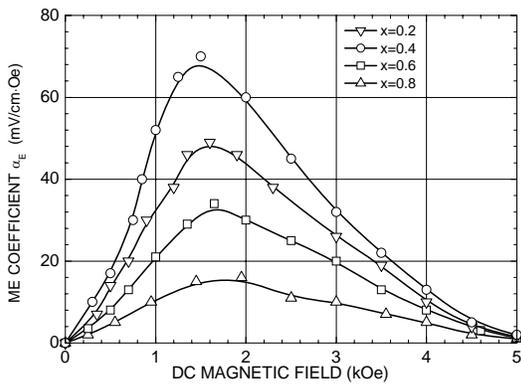


Fig. 9 The dependence of ME coefficient on the DC magnetic field for different composite samples

One can see that ME coefficients do not depend monotonically on the magnetic field regardless the concentration of COF in PZT but they shows peaks around a dc field of 3 kOe. At higher fields the magnetostriction seems to be saturated so that the electric field produced in PZT remains constant therefore the ME decreased with increased magnetic field. The dependence of the ME with composition is shown in figure 10.

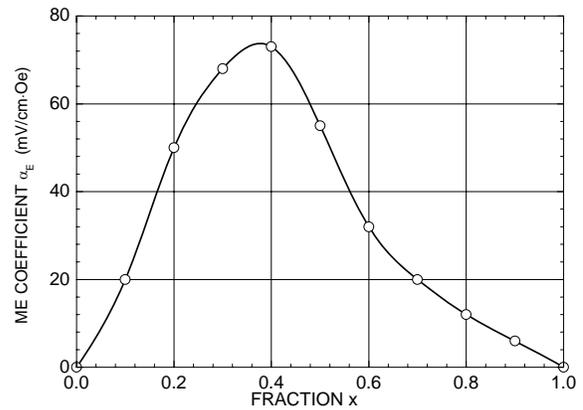


Fig. 10 The dependence of ME coefficient on composition in the system $xCOF(1-x)PZT$.

The increase of ME with increasing COF concentration is attributed to the increase of magnetoinduction for larger concentration of magnetic phase and the charge induced in PZT since ME is a product property between piezoelectricity and magnetostriction. However, when the piezoelectric phase decreases, the charge induced is lower and so does the ME effect.

The ME also depends on the ac field frequency. A typical example of such dependence is shown in Fig. 11.

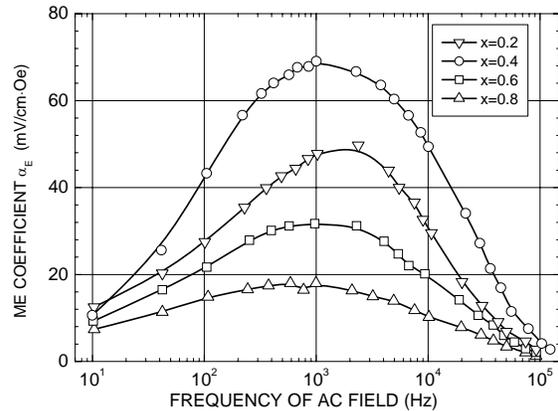


Fig. 11 The dependence of ME coefficient of different composites on the AC field frequency

One can see that all composites show maximum values around 1 kHz.

4. Summary

Dense particulate composite samples of PZT and COF with the formula $x\text{COF} \cdot (1-x)\text{PZT}$ with $0 \leq x \leq 1$ were produced by the conventional ceramic technique.

The powders of the two compositions were mixed in a high energy planetary ball mill for 20 hours in order to produce homogeneous nanometric powders. The optimum sintering temperature proved to be 1200 °C. Piezoelectric and magnetoelectric properties were determined for each composition. Optimum composition was that containing 40 % COF and 60 % PZT which exhibited maximum values of piezoelectric properties as well as magnetoelectric coefficient.

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*Corresponding author: cmic@infim.ro