MAGNETOELECTRIC PROPERTIES OF MULTIFERROIC COBALT FERRITE AND SOFT PIEZOELECTRIC PZT PARTICULATE COMPOSITES

C. MICLEA, C. TANASOIU, L. AMARANDE, C. F. MICLEA, M. CIOANGHER, L. TRUPINA, C. PLAVITU*, C. T. MICLEA*, T. TANASOIU*, M. SUSU*, I. VOICU*, V. MALCZANEK**, C. DAVID***

NATIONAL INSTITUTE FOR MATERIALS PHYSICS, Bucharest-Magurele, ROMANIA

*HYPERION UNIVERSITY, Faculty of Physics, Str. Calarasi 169, Bucharest, ROMANIA

**FAIRLEIGH DICKINSON UNIVERSITY, NJ, USA

*** TECHNICAL UNIVERSITY OF CIVIL ENGINEERING OF BUCHAREST, ROMANIA

Corresponding author: Prof. C. Miclea
cmic@infim.ro

1. INTRODUCTION

The magnetoelectric (ME) effect is considered to be a coupled two fields magnetic and electric effect in which the polarization is induced by a magnetic field and vice-versa. ME effect was observed in some single phase crystals, but at lower intensities, as well as in composite ceramics made from a magnetostrictive ferrite and a piezoelectric material, at higher intensities, due to higher magneto-mechanical-electrical interaction between the piezoelectric and ferrite phases. Though in many cases the measured magnetoelectric 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 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. OBJECTIVES

- To prepare dense composite samples from a magnetic material (cobalt ferrite - COF) and a piezoelectric material (soft lead titanate zirconate material – PZT with high properties;
- The composition of materials:
• magnetic phase $CoFe_2O_4$;
• piezoelectric phase: $Pb_{0.95}Sr_{0.05}(Nb_{0.05}Ni_{0.06}Zr_{0.49}Ti_{0.40})O_3$
- The materials were synthesized by the mixed oxide route from pure raw materials;
-The composites were in the system xCOF·$(1-x)$PZT with $x \in \{0, 0.1, \ldots, 0.9, 1\}$;
-To establish, optimum sintering temperature and composition with the highest magnetoelectric properties

3. EXPERIMENTAL

Simple $CoFe_2O_4$ (COF) and a soft type PZT with the chemical formula $Pb_{0.95}Sr_{0.05}(Nb_{0.05}Ni_{0.06}Zr_{0.49}Ti_{0.40})O_3$ were chosen as magnetic and piezoelectric phase due to their high magnetization and magnetostriction coefficient as well as for high piezoelectric parameters. The materials were synthesized by the usual mixed oxide route using high purity raw materials (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. The calcined products were checked by X-ray diffraction where the X-ray patterns were assigned only to cubic spinel phase and perovskite phase. Composites samples, according to the formula xCOF·$(1-x)$PZT with x = 0; 0.1; 0.2; …0.9; 1 were then mixed together for 20 hours, in order to get intimately mixed powders in the nanometric range. The mixed samples were pressed and sintered at temperatures between 1000 and 1300 °C for 3 hours. The samples were Ni electroded 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.

4. RESULTS

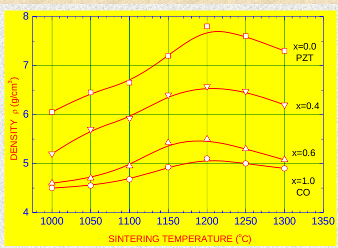

Fig. 1. The density vs. sintering temperature for different composite samples

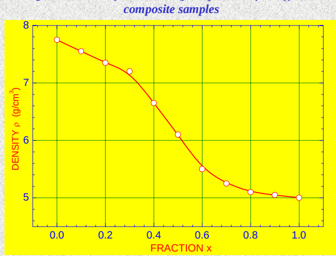

Fig. 2. The density vs. composition of xCOF(1-x)PZT

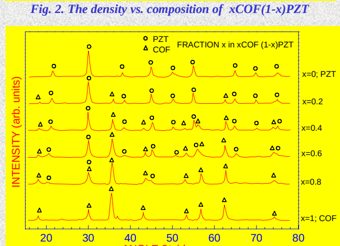

Fig. 3. XRD of composite samples with different composition in the system xCOF(1-x)PZT

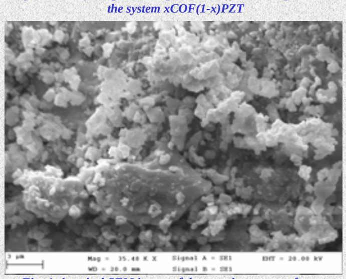

Fig. 4. A typical SEM image of the sample structure for composition with x=0.4

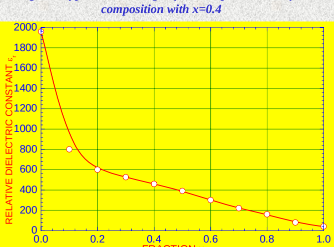

Fig. 5. The dependence of the relative dielectric constant on magnetoelectric composite

The optimum sintering temperature is situated around 1200 °C where the densification exhibits maximum values (figure 1). 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 figure 2. 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. One can see that all diffraction peaks consist of those characteristics to PZT and COF. 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 figure 5. 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 and charge constant d_{33} as can be seen in figure 6. The presence of COF in PZT even in small quantities gives rise to a sudden drop of k_p and d_{33} with more than 80 % and 90 % respectively. From such a behavior on 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 figure 7. The ME coefficient as a function of DC magnetic field is shown in figure 8. The 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 9. 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 figure 10. One can see that all composites show maximum values around 1 kHz.

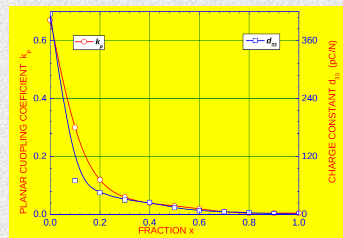

Fig. 6. The dependence of the planar coupling coefficient and of the charge constant on magnetoelectric composite.

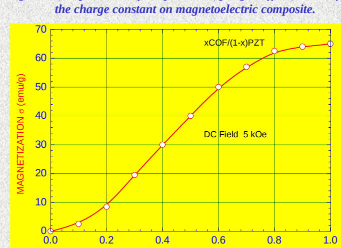

Fig. 7. Magnetization of composite samples as a function of COF concentration in PZT.

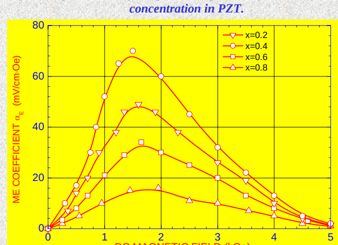

Fig. 8. The dependence of ME coefficient on the DC magnetic field for different composite samples.

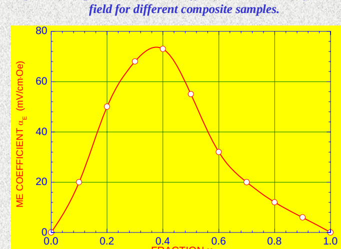

Fig. 9. The dependence of ME coefficient on composition in the system xCOF(1-x)PZT

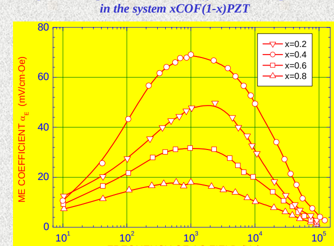

Fig. 10. The dependence of ME coefficient of different composites on the AC field frequency.

5. SUMMARY

Dense particulate composite samples of PZT and COF with the formula xCOF·$(1-x)$PZT with $0 \le x \le 1$ 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.