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 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 investigations 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 CoFe₂O₄;
  - piezoelectric phase Pb₀.₉₅Sr₀.₀₅(Nb₀.₀₅Ni₀.₀₆Zr₀.₄₉Ti₀.₄₀)O₃;
- 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 = 0; 0.1; 0.2; …; 0.9; 1;
- To establish optimum sintering temperature and composition with the highest magnetoelectric properties.

3. EXPERIMENTAL

Simple CoFe₂O₄ (COF) and a soft type PZT with the chemical formula Pb₀.₉₅Sr₀.₀₅(Nb₀.₀₅Ni₀.₀₆Zr₀.₄₉Ti₀.₄₀)O₃ were chosen as magnetic and piezoelectric phase due to their high magnetization and magnetostriiction 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 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 electrodeed and sintered at a silicon oil bath at a temperature of 1300 °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 d₃₃ meter. The ME effect obtained by applying an ac magnetic field superimposed was determined by the dynamic method and measuring the output signal amplified by a charge amplifier.

4. RESULTS

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 0.15% 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 high concentration 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 takes place only within a very thin surface layer of the crystallites. A typical SEM micrograph of the sample structure, shown in figure 4, illustrates the two different phases quite distinctly.

The relative dielectric constant εr for different composite samples is shown in figure 5. The permittivity is drastically decreased by the presence of the ferrite phase and even for 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 even in small quantities gives rise to a sudden drop of k_p and d_33 with the increase of magnetoinduction for larger concentration of magnetic phase and the charge induced 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 magnetostriiction. 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.

5. SUMMARY

Dense particulate composite samples of PZT and COF with the formula xCOF(1-x)PZT with 0 ≤ x ≤ 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.