STRUCTURE AND PROPERTIES OF CERAMIC FERROIC COMPOSITES FROM PZT AND BT SOLID SOLUTION

C. MICLEA, C. TANASOIU, C. F. MICLEA, I. SPANULESCU*, L. AMARANDE, A. IUGA,
M. CIOANGHER, L. TRUPINA, C. T. MICLEA*, M. SUSU*, T. TANASOIU
NATIONAL INSTITUTE FOR MATERIALS PHYSICS, Bucharest-Magurele, ROMANIA
*HYPERION UNIVERSITY, Faculty of Physics, Str. Calarasi 169, Bucharest, ROMANIA

1. INTRODUCTION

Multiferoic materials are those materials that posses two or three ferroic properties such as ferroelectricity, ferroelasticity and ferromagnetism. Multiferroic materials may exist either in single phase form or in two phase systems. While the former is quite limited, the latter one may be found in a large number of combinations. In the two phase systems the most used ferroic substances are barium titanate and lead-titanate zirconate. Barium titanate is a typical perovskite material with the formula $BaTiO_3$ and it was the first ceramic material to be used as transducer. The ferroic material lead titanate-zirconate known as PZT material crystallize in the perovskite form and practically all ions of the basic composition can be partially replaced. In spite of their separate virtue, they were not mixed together to form new materials with new properties except in the last few years when the interest for such mixed material arose. In the present investigation we prepared mixtures of nanopowders of piezoelectric compositions from a soft type piezoceramic material and the classic piezoelectric barium titanate within the whole compositional interval.

2. OBJECTIVES

- To prepare solid solution from two representative piezoelectric materials namely: PZT and BT with the chemical composition $Pb_{0.98}Sr_{0.02}Zr_{0.50}Ti_{0.45}Nb_{0.05}O_3$ (PZT) and $BaTiO_3$ (BT);
- The mixed proportion were (1-x)PZT·xBT with x=0, 0.1, … 0.9, 1;
- To investigate the structural and piezoelectric properties of the mixed compositions in order to determine whether or not are there some intermediate compositions with enhanced properties compared with the initial ones;
- The main properties investigated were the dielectric (ε_r) and piezoelectric (k_p, d_{31}, g_{31}) ones.

3. EXPERIMENTAL

The composition chosen for the experiment was the following: $Pb_{0.98}Sr_{0.02}Zr_{0.50}Ti_{0.45}Nb_{0.05}O_3$ and $BaTiO_3$. Bouth Sr and Nb were added in order to imprint the composition a soft character. The ferroic PZT-BT mixed powder samples were processed to correspond to a generic formula of this type: (1-x)PZT·xBT with x=0; 0.1; 0.2 …… 0.9; 1. The stoichiometric amounts of each nanopowder were mixed for 4 hours in the planetary ball mill, in methanol. The dried mixed powders were moistened with about 5 % wt. distilled water by spraying and uniaxially pressed in a cylindrical steel die at a pressure of about 50 MPa. The pressed samples were next sintered on platinum closed boats at temperatures between 1100-1400 °C for 5 hours. Silver electrodes were applied on their faces and then the electroded samples were poled for 5 minutes in a silicon oil bath, heated at 200 °C under an electric field of 3 kV/mm.

4. RESULTS

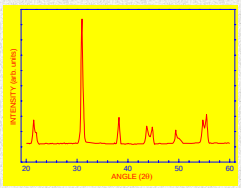

Fig. 1a. X-Ray patterns of PZT powder, after calcining and milling for 24 hours

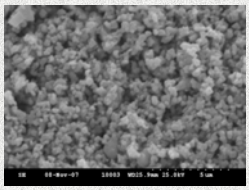

Fig. 1b. The morphostructure of the PZT calcined powder after milling. The average grain size is about 250 nm.

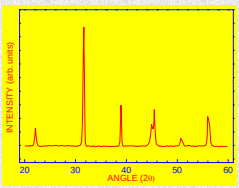

Fig. 2a. X-Ray patterns of BT powder, after calcining and milling for 24 hours.

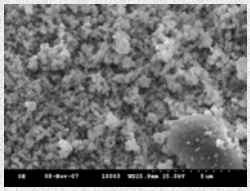

Fig. 2b. The morphostructure of the BT calcined powder after milling. The average grain size is about 213 nm.

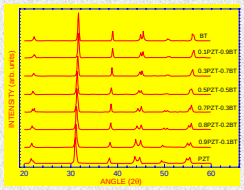

Fig. 3. X-Ray patterns of sintered mixed samples of PZT and BT for some compositions. Only perovskite phase is evident and no other foreign phase was detected.

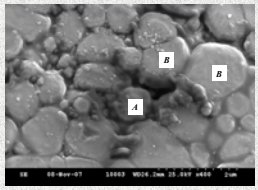

Fig. 4. SEM micrograph of the composition with x=0.6 sintered at 1350 °C. One can see a PZT particle (A) surrounded by about 5 particles of BT being practically "melted" and incorporated into BT matrix. A well defined neck between BT particle can be observed (BB).

4. STRUCTURAL PROPERTIES

Figures 1a and b and 2a and b illustrate the X-ray patterns and morphology of PZT and BT nanopowders after calcining and milling for 24 hours. The X-ray patterns for both powders show only the well known perovskite structure. The morphostructures shown in the SEM images of fig. 1b and 2b seems extremely similar for both powders. An estimate of the average grain size for both powders showed about 250 nm for PZT and to 213 nm for BT. These differences could be explained by the different mechanical properties of the two materials. The X-ray diagrams of the mixed and sintered samples of PZT and BT are shown in figure 3. There are no noticeable differences between the X-ray patterns of all these compositions. All of them show only the perovskite phase regadless the amounts of PZT and BT. The sintering process of the two different mixed powders is not as simple as in the case of one single phase, because the optimum sintering temperature for each separate powder is different: lower for PZT (about 1200 °C) and higher for BT (about 1400 °C). Any polycrystalline compact sinters by diffusion transport matter which takes place by two main mechanisms, namely: surface diffusion and volume diffusion. In the initial stage of sintering the interparticle necks growth rapidly by diffusion. The volume diffusion takes place by the movement of point defects in which the vacancies play the most important role. These processes in which coalescence of neighboring grains are well illustrated in the SEM image of figure 4 taken for the composition with x=0.6 and sintered at 1350 °C where one can see in the middle, a particle of PZT surrounded by about 5 particles of BT which practically "swallow" it by diffusion. In the upper right side one can also see how BT particles formed a large neck and finally they will unite in to a single larger particle if the sintering time or temperature increases. Figures 6 a, b and c illustrate the mechanical fracture behavior of composites. For compositions reacher in BT the fracture is mainly transgranular while for those reacher in PZT, is mainly intergranular.

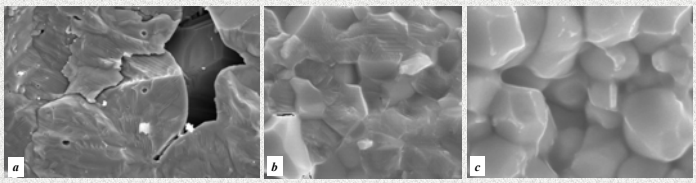

Fig. 6. SEM fracture micrograph of sintered composites between PZT and BT: (a) composite with x=0.8 sintered at 1400°C; (b) composite with x=0.5 sintered at 1300 °C; (c) composite with x=0.1 sintered at 1200 °C

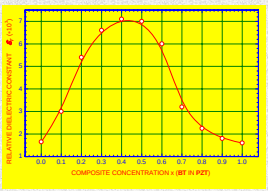

Fig. 7. The dependence of the relative dielectric constant on composite concentration x for sintered mixed PZT and BT samples

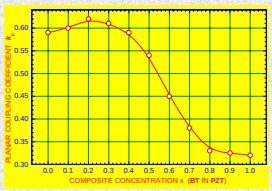

Fig. 8. The dependence of the electromechanical planar coupling factor on composite concentration x for sintered mixed PZT and BT samples

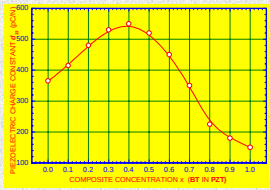

Fig. 9. The behaviour of piezoelectric charge constant d_{33} as a function of composite concentration for sintered mixed PZT and BT samples.

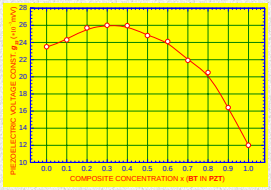

Fig. 10. The behaviour of piezoelectric voltage constant g_{33} as a function of composite concentration x for sintered mixed PZT and BT samples.

5. DIELECTRIC AND PIEZOELECTRIC PROPERTIES

The permittivity is an important parameter for ferroic composites regarding the material selection for application because materials with higher permittivity will experience lower activating electric fields compared to those with lower permittivity. This improves the electrical efficiency. The relative permittivity ε_r, was calculated by the capacitance (C) measurements making use of the basic equation: $C = \varepsilon r \varepsilon 0 A/h$, where A is the active sample area, h is the sample thickness and ε_0 the permittivity of free space. Figure 7 shows the behavior of the relative dielectric constant ε_r as a function of compositions. The middle compositions exhibit a rather sharp maximum with the highest value of 7000. This behavior could be associated with the crystallite size. At both ends there is a nonuniform distribution of the crystallite due to inhomogeneity of the compositions involved. At the middle of the compositional interval the distribution is more uniform and probably the crystallite size is an optimum for high dielectric constant. It is known that the dielectric constant is strongly dependent on the grain size. Coarse grain ceramics show lower dielectric constant than fine grain ones. But there is an optimum grain size where the dielectric constant shows a maximum value Figure 8 shows the dependence of the planar coupling coefficient k_p on composition. For pure PZT the k_p is 0.59 and, the presence of BT up to about x=0.4, enhances slightly the coupling coefficient up to about 0.64 and then constantly decreases up to 0.33 for pure BT. This behavior is rather unusual because the presence of BT should diminish a little the electromechanical factor k_p and not increase it.. A qualitative explanation for this behavior could be based on the fact that for smaller amounts of PZT particles into the BT matrix, the solving process of PZT is more complete as it take place at higher temperatures. When the amounts of PZT and BT starts to echilibrate, the PZT phase become preponderent and k_p increases. A similar behavior was also recorded for the piezoelctric charge constant d_{33}, as shown in figure 9. A similar trend may be observed for the piezoelectric voltage constant g_{33} as well as can be seen in figure 10.

6. CONCLUSION

Sintered samples in the ferroic system (1-x)PZT·xBT with x = 0; 0.1; 0.2 … 0.9; 1 were investigated both structurally by X-ray diffraction and SEM microscopy and also from the piezoelectric point of view. The morphostructure of the samples is different, though X-ray patterns are similar for all compositions. This is due to the sintering process which depends on compositions taking place at different temperature for each composition. The dielectric properties showed a rather unusual behavior which was explained in terms of different grain size of the samples.