

# PIEZOELECTRIC PROPERTIES OF CERAMIC PZT-BT SOLID SOLUTION

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## 1. INTRODUCTION

The PZT materials centered around the basic composition  $PbZr_{0.5}Ti_{0.5}O_3$  exhibit highest values for all piezoelectric properties. All ions of the basic composition can be partially replaced by isovalent and/or aliovalent ions giving rise to a rather endless number of new compositions with enhanced properties. The structure of all these compounds is the classic perovskite structure with the formula  $ABO_3$ .

Another typical piezoelectric material is the barium titanate (BT), with the formula  $BaTiO_3$ . It is also a typical perovskite material with tetragonal structure.

In spite of their separate virtue, they were not mixed together to form new materials with new properties. The first trials in this direction was made some years ago and quite recently the subject was revival.

## 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  $x=0, 0.1, \dots, 0.9, 1$ ;
- 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 ( $\epsilon_r$ ) and piezoelectric ( $k_p$ ,  $d_{31}$ ,  $g_{31}$ ) ones.

## 3. EXPERIMENTAL

There are several ways to synthesize PZT & BT materials. Mixed oxide combined with mechanochemical activation produce nanoscale powders.

The PZT powder was the following:  $Pb_{0.98}Sr_{0.02}Zr_{0.50}Ti_{0.45}Nb_{0.05}O_3$ . High purity oxides (over 99.2 %) from Merck, Fluka and Riedel de Haen were used as raw materials. The stoichiometric amounts of oxides was calcined at 900 °C for 3 hours and then subjected for a prolonged milling in a high energy planetary ball mill Retsch PM 400. The milling time was 24 h.

The BT powder corresponding to the formula  $BaTiO_3$  was synthesized from pure barium carbonate  $BaCO_3$  and titanium dioxide  $TiO_2$  from Merck having purities of 99.95 and 99.97 % respectively. Stoichiometric amounts of each raw material were mixed and calcined at 1100 °C for 3 hours. After calcining it was milled for 24 hours in the same high energy planetary ball mill.

The PZT-BT mixtures powder samples with the formula:  $(1-x)PZT-xBT$  with  $x=0; 0.1; 0.2; \dots, 0.9; 1$  were mixed for 2 hours in the planetary ball mill in methanol in order to make a physical mixture as homogeneous as possible. The pressed samples were next sintered on platinum closed boats at temperatures between 1100-1400 °C for 5 hours.

## 4. RESULTS

Figures 1a and 1b illustrate the X-ray patterns and morphology of PZT (fig. 1a) and BT (fig. 1b) nanopowders after calcining and milling. The X-ray patterns for both powders show only the perovskite structure and no other foreign phase.

The X-ray diagrams of the mixed and sintered samples of PZT and BT are shown in figure 2 for several compositions. One can see that there is no noticeable difference between the X-ray patterns of all these compositions. All of them show only the perovskite phase regardless the amounts of PZT and BT.

Fig. 3 shows the evolution of the sample density as a function of composition and sintering temperature. Each composition has an optimum sintering temperature where the density reaches the maximum value.

Figure 4 shows the graph with the maximum density as a function of composition. The dependence is nearly linear, the existing deviations being due to the structural inhomogeneities.

Figure 5 shows the behavior of the relative dielectric constant  $\epsilon_r$  as a function of compositions. Both end members show nearly the same values around 1500, while the middle compositions exhibit a rather sharp maximum of 7000. This behavior could be associated with the crystallite size.

Figure 6 shows the dependence of the piezoelectric planar coupling coefficient  $k_p$  on composition. The presence of PZT up to about  $x < 0.4$ , make the coupling coefficient slightly to decrease and then it shows a sudden increase up to 0.6 for pure PZT.

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 the new solid solutions formed are not within a morphotropic phase boundary and thus the poling cannot be entirely efficient. When the amounts of PZT and BT starts to echilibrate the PZT phase become preponderant and  $k_p$  increases. Similar behavior was also recorded for the piezoelectric charge constant  $d_{31}$ , and voltage constant  $g_{31}$  shown in figs 7 and 8.

The sintering process between PZT and BT is a complex one and it can be clarified by structural investigations.

## 5. CONCLUSION

Sintered samples in the system  $(1-x)PZT-xBT$  with  $x = 0; 0.1; 0.2 \dots 0.9; 1$  were investigated both structurally by X-ray diffraction and 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.

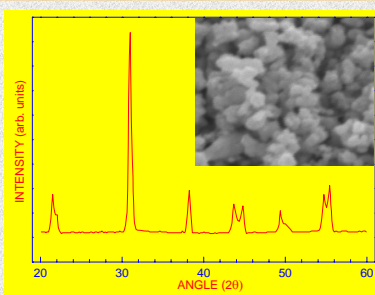


Fig. 1a. X-Ray patterns of PZT powder, after calcining and milling for 24 hours in a high energy planetary ball mill. The morphostructure of the powder is shown in the inset of the figure. Average grain size is about 250 nm.

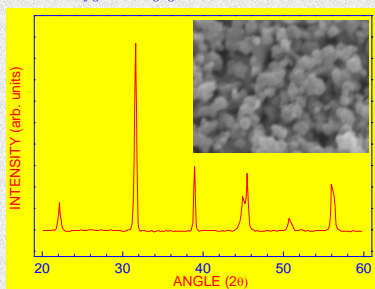


Fig. 1b. X-Ray patterns of BT powder, after calcining and milling for 24 hours in a high energy planetary ball mill. The morphostructure of the powder is shown in the inset of the figure. Average grain size is about 213 nm.

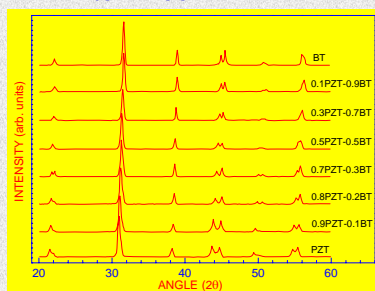


Fig. 2. X-Ray patterns of sintered mixed samples of PZT and BT for some compositions. Only perovskite phase is evident and no other foreign phase was detected.

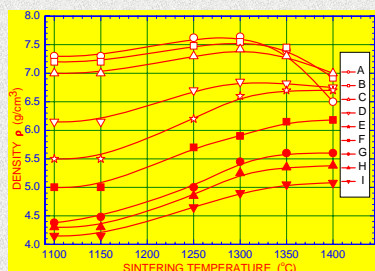


Fig. 3. The evolution of density as a function of temperature and composition for sintered mixed samples of PZT and BT. A to I refers to compositions with  $x$  from 0 to 1 respectively.

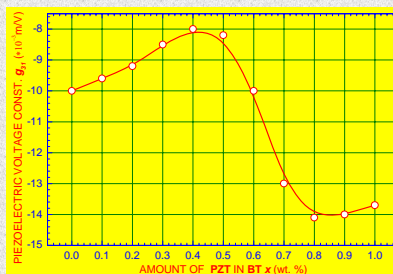


Fig. 8. The behaviour of piezoelectric voltage constant  $g_{31}$  as a function of composition for sintered mixed PZT and BT samples.

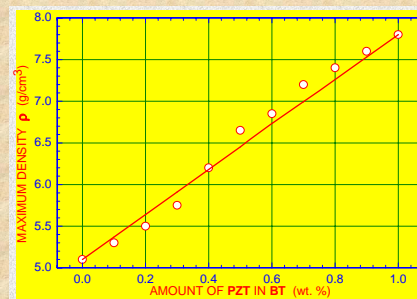


Fig. 4. The dependence of the maximum density on composition for mixed PZT and BT samples.

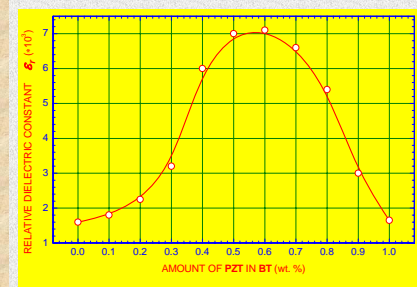


Fig. 5. The dependence of the relative dielectric constant on compositions for mixed PZT and BT samples

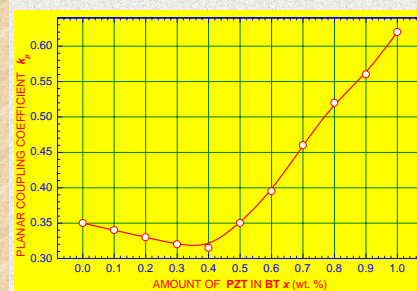


Fig. 6. The dependence of the electromechanical planar coupling factor  $k_p$  on composition for mixed PZT and BT mixed samples.

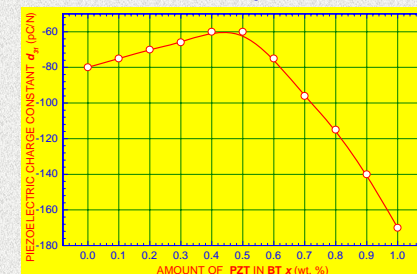


Fig. 7. The behaviour of piezoelectric charge constant  $d_{31}$  as a function of composition for sintered mixed PZT and BT samples.