

## Synopsis

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Ferroelectrics are important class of functional materials that finds application in transducers, actuators, memory devices, electro-optics and position sensing devices. Until recently, the high performance piezoelectrics were based on lead-based alloys such as  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT),  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PMN-PT) and  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PZN-PT). However, the presence of ~60% of toxic lead(Pb) in PZT based commercial piezoelectric materials has raised serious health and environmental concerns and legislation are being framed world wide to free industrial products from toxic elements. As a consequence, there is now greater emphasis on research on lead free electronic materials.  $\text{BaTiO}_3$ ,  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  and  $\text{KNbO}_3$  are the well known lead-free ferroelectrics compounds which can be used for designing a lead free materials with improved piezoelectric properties. It is interesting to note that among pure ferroelectric compounds,  $\text{BaTiO}_3$  shows the highest piezoelectric response with the longitudinal piezoelectric coefficient ( $d_{33}$ ) ~190 pC/N and transverse piezoelectric coefficient ( $d_{31}$ ) ~ -79 pC/N in ceramic form. It also shows a significant larger relative permittivity ~ 1700 as compared to other ferroelectric compounds.  $\text{BaTiO}_3$  is therefore an attractive compound for design of lead-free piezoelectric material by suitable chemical substitutions. Apart from the general objective to design lead-free ferroelectric compositions with the enhanced piezoelectric response, it still remains an interesting question as to what makes  $\text{BaTiO}_3$  exhibit far superior dielectric and piezoelectric properties at room temperature. Davis *et al* (J. Appl. Phys, **101**, 054112, 2007) have highlighted that the large piezoelectric response of  $\text{BaTiO}_3$  is related to considerably large dielectric anisotropy ( $\chi_{11}/\chi_{33}$ ) leading to enhancement in the shear piezoelectric coefficient  $d_{15}$ . The mechanism contributing to large  $d_{15}$  is associated with the polarization rotation and field-induced low symmetry phases. In order to gain better insight, in the present work, we looked for a structural basis to understand the anomalously large electromechanical properties exhibited by  $\text{BaTiO}_3$  ceramic. With this in view we have carried out a detailed high resolution synchrotron XRD and aberration corrected TEM study on the polycrystalline  $\text{BaTiO}_3$  specimen. A careful analysis of the higher order weak Bragg reflections with d-values less than 0.6 Å (e.g . 600 reflection) in the synchrotron XRD pattern, which otherwise are not accessible in normal laboratory XRD and neutron diffraction patterns, revealed the presence of a subtle monoclinic

distortion ( $\beta \sim 90.03^\circ$ ) coexisting with the conventional tetragonal phase. Additionally, we also verified the presence of orthorhombic regions of very small coherence length in BaTiO<sub>3</sub> at room temperature. In this work, we also developed a new “powder poling technique” that enabled us to apply very strong electric field to free ferroelectric crystallites and capture the nature of the electric field induced phase transformation in this system. Using this technique we have shown the evidence of increased phase fraction of the orthorhombic phase after poling confirming that BaTiO<sub>3</sub> at room temperature have the tendency for polarization switching. These interesting results helps in providing a rational explanation for the anomalous piezoelectric properties exhibited by BaTiO<sub>3</sub> ceramics at room temperature.

In the next step, we use this understanding to improve the piezoelectric property of BaTiO<sub>3</sub> by suitable chemical substitutions. The presence of subtle monoclinic distortion and small orthorhombic regions at room temperature was interpreted as the precursor effect associated with the ferroelectric (tetragonal) -ferroelectric (orthorhombic) phase transition which occurs near 0 °C in pure BaTiO<sub>3</sub>. It was therefore anticipated that those chemical substitutions which can raise the tetragonal-orthorhombic transition temperature towards room temperature would further enhance the system’s response. A survey of literature revealed that chemical substitution of Zr, Hf and Sn in BaTiO<sub>3</sub> increases both the tetragonal-orthorhombic and also the orthorhombic-rhombohedral transition temperatures from below room temperature. Accordingly, in this work, we carried out a detailed structure property correlation study on Zr, Hf and Sn modified BaTiO<sub>3</sub> ceramics. The success of this modest approach was proved when we found that  $d_{33}$  increased to  $\sim 425$  pC/N by only 4% of Sn substitution. Likewise, in Zr and Hf modified BaTiO<sub>3</sub>  $d_{33}$  increased to  $\sim 350$  pC/N by just 2% of substitution. We also found that very dilute substitution of Zr(1%) and Sn(1-3%) increased the electric field-strain response to double (0.2%) at field strength of  $\sim 40$  kV/cm, a value double in comparison to what could be achieved in pure BaTiO<sub>3</sub> (0.1%). Using our innovative powder poling technique we found that the composition exhibiting large piezostain response exhibit a large fraction of field induced orthorhombic phase as compared to the rest of the compositions. The mechanism for such large piezoelectric strain response is explained on the basis of the polarization rotation model.

Having succesfully exploited the results of the powder poling technique towards understanding the mechanism associated with high piezoelectric response in pure and modified BaTiO<sub>3</sub>, we

employed this innovative technique to understand the mechanism associated with the anomalous piezoelectric response on a high performance soft-PZT (La modified  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ) exhibiting longitudinal piezoelectric coefficient of  $\sim 650$  pC/N. We carried out a comparative structural study of the structural states of this system in the annealed (equilibrium) and the powder poled state using high resolution synchrotron XRD. Rietveld analysis revealed that the poling of the free crystallites led to increase in the monoclinic fraction and also a considerable increase in the tetragonality of the coexisting tetragonal phase. The results were interpreted in terms of the twin mechanism of *polarization rotation and polarization extension* with electric field. We also found that the relative permittivity of the pellet increases with increasing the poling field. This was suggestive of the decrease in the coherence length of polarization on poling, a phenomenon which seems counterintuitive at the outset.

The powder poling technique also offered a unique opportunity to study separately the effect of electric field and stress with regard to the nature of phase transformation exhibited by ferroelectrics exhibiting morphotropic phase boundary (MPB). For the first time we could prove that moderate stress brings about the same phase transformation as the electric field. Since stress/electric driven phase transformation has a close relationship with the anomalous piezoelectric behavior in MPB based systems, we have indicated that the equivalence of the stress and electric field with regard to the structural changes in MPB could be linked with the thermodynamic equivalence of the direct (stress as stimulus) and converse (electric field as stimulus) piezoelectric coefficients.

The thesis is divided into five chapters. The first chapter of the thesis provides a brief introduction to the basic concepts related to ferroelectrics and the perovskite structure. A brief exposure to the conventional high performance lead based piezoelectrics and then on lead free piezoelectrics is presented. A detailed overview of the existing models to explain the phenomenon of enhanced piezoelectric response is discussed. The details of the experimental procedures and the characterization techniques used have been given in Chapter 2.

The third chapter deals with understanding the mechanism of high piezoelectric response of  $\text{BaTiO}_3$  in comparison to other compounds available. The piezoelectric response of  $\text{BaTiO}_3$  ( $d_{33} \sim 190$  pC/N) is relatively large compared to other compounds such as  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  ( $d_{33} \sim 66$  pC/N) and  $\text{KNbO}_3$  ( $d_{33} \sim 57$  pC/N). In order to understand the origin of high piezoelectric

response in BaTiO<sub>3</sub>, initially Rietveld refinement was carried out on laboratory x-ray and high resolution neutron powder diffraction data using a tetragonal *P4mm* model. Neutron diffraction data at a higher angles ( $120^\circ < 2\theta < 145^\circ$ ) shows the inadequacy of the single phase tetragonal model. Thus to resolve the issue more accurately, high resolution synchrotron powder diffraction was data collected at ESRF, France. The excellent signal-to-noise ratio data even at the higher angle clearly reveals additional reflections along with tetragonal reflections like  $\{600\}_C$ . The careful structural analysis along with a novel powder poling technique developed to understand the electric field effect on powder specimen reveals that, at room temperature the unpoled state of BaTiO<sub>3</sub> is characterized by the coexistence of metastable monoclinic *Pm* and orthorhombic *Amm2* phases along with the tetragonal *P4mm* phase and the application of a strong electric field (poled state) leads to switching of polarization direction from  $[001]_C$  direction towards  $[101]_C$  direction.

The fourth chapter deals with the development of lead free BaTiO<sub>3</sub>-based high performance piezoceramics. Three lead free BaTiO<sub>3</sub> based solid solutions Ba(Ti<sub>1-x</sub>Zr<sub>x</sub>)O<sub>3</sub>, Ba(Ti<sub>1-x</sub>Sn<sub>x</sub>)O<sub>3</sub> and Ba(Ti<sub>1-x</sub>Hf<sub>x</sub>)O<sub>3</sub> respectively were investigated. The addition of these elements improved the piezoelectric response drastically, longitudinal piezoelectric coefficient ( $d_{33}$ ) increased from ~190 pC/N for pure BaTiO<sub>3</sub> to a maximum of ~355 pC/N in Zr substitution, to ~425 pC/N in Sn substitution and to ~360 pC/N in Hf substitution. These  $d_{33}$  values are more than the existing value of hard PZT ( $d_{33}$  ~225 pC/N) and nearly competing to soft PZT ( $d_{33}$  ~500 pC/N). To understand the origin of this high piezoelectric response in these systems, structural characterization was carried out using x-ray and neutron powder diffraction techniques. Structural refinement suggested that the composition exhibiting high piezoelectric response contains a coexistence of phases. Coexistence of phases is either tetragonal (*P4mm*) and orthorhombic (*Amm2*) or orthorhombic (*Amm2*) and rhombohedral (*R3m*) phases respectively. Stabilization of two phases becomes possible because of i) first order nature of phase transitions which ensures coexistence of phases persists ii) possible increase in the temperature interval corresponding to the phase coexistence due to random elastic strain induced by substitution of bigger sized cations (Sn<sup>+4</sup> or Zr<sup>+4</sup> or Hf<sup>+4</sup>), iii) critical temperatures associated with phase transitions approaching near room temperature with increasing cation concentration. A very dilute concentration of substitutional elements (1% in Zr and 1-3% in Sn) has doubled (0.2%) the electric field- strain response in comparison to 0.1% of BaTiO<sub>3</sub> at field strength of ~ 40 kV/cm.

In-situ/ex-situ electric field dependent structural study revealed a one-to-one correspondence between the high strain response and enhanced propensity for polarization switching.

In Chapter 5 we have made use of the innovative powder poling technique to understand the mechanism associated with high piezoelectric response in a high performance conventional soft-piezoceramic, La modified PZT (PLZT) exhibiting longitudinal piezoelectric coefficient  $d_{33} \sim 650$  pC/N. Comparative structural studies of annealed and poled powder specimens revealed an increased fraction of the monoclinic phase after poling. The chapter reports the phenomenon of increase in the dielectric constant after poling of the ceramic thereby suggesting a counterintuitive phenomenon of decrease in polarization coherence on application of electric field. We have used the results to comment on the plausibility of the two contending theories regarding anomalous piezoelectric behavior: adaptive phase theory vis-à-vis polarization rotation via a genuine monoclinic phase. Summary and Scope for further work is given in chapter 6.