

## *BaTiO<sub>3</sub>-PbTiO<sub>3</sub> solid solution*

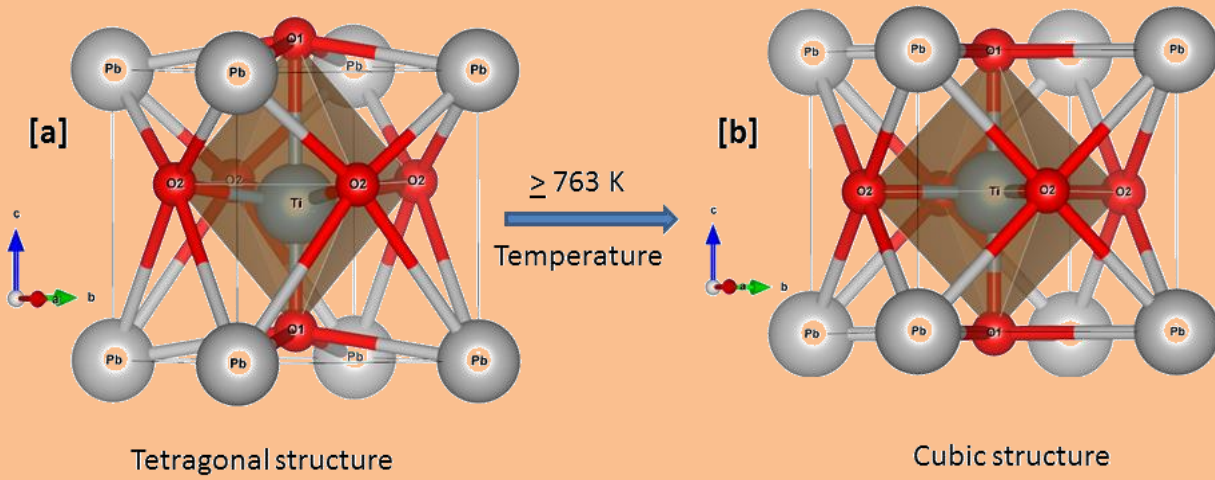
Barium titanate is studied for decades by the researchers and still there is lot of potentials to be explored and to be used in the industry because of its noble properties owing to its perovskite structure. BT is the first discovered ferroelectric as well as piezoelectric material. These properties are connected with structural phase transition from tetragonal to cubic structure. Different aspects of BT ceramics are studied in last decade, and BT becomes one of the most studied perovskite in the field of electro-ceramics. Because of high permittivity, outstanding ferroelectric and piezoelectric properties, BT is widely used in multilayer ceramic capacitors, positive temperature coefficient of resistivity thermistors, dynamic random access memory and piezoelectric sensors.

At room temperature BaTiO<sub>3</sub> has tetragonal structure. The phase changes from tetragonal to cubic at  $T_c \sim 121$  °C. BaTiO<sub>3</sub> is discovered firstly as piezoelectric ceramic material but the application in the high temperature environment is limited due to low  $T_c$ .

Perovskite PbTiO<sub>3</sub> also has the tetragonal symmetry at room temperature and highest  $c/a$  ratio ( $\sim 1.064$ ) among the all perovskites. Tetragonal to cubic phase transformation of the PT ceramics takes place at  $\sim 590$  °C.

Pure PbTiO<sub>3</sub> belongs to a perovskite ABO<sub>3</sub> type family. At room-temperature, PbTiO<sub>3</sub> is a ferroelectric material with tetragonal structure  $\mathcal{C}_{4v}^1 - P4mm$  space group as shown in **Figure 1.1a**. Pure PbTiO<sub>3</sub> is not commercially used as a piezoelectric material due to practical problems of making a sintered pellet or single crystal. However, it can be modified to form solid solutions with other elements for obtaining materials with excellent piezoelectric properties. PbTiO<sub>3</sub> undergoes structural first order phase transition at 763 K into cubic  $\mathcal{C}_{3v}^1 - Pm3m$  paraelectric structure as shown in **Figure 1.1 (a-b)**. The phase transition behaviour is of displacive nature as the central Ti atom and the oxygen atoms are displaced from their centro-symmetric position of the cubic form [1]. One of the perovskite, BaTiO<sub>3</sub> is widely studied among ferroelectric materials. Although PbTiO<sub>3</sub> is isomorphous at room temperature with BaTiO<sub>3</sub> ceramic, there are important differences between these ferroelectric materials. The lattice constant of PbTiO<sub>3</sub> at

room-temperature are  $a = b = 3.902 \text{ \AA}$  and  $c = 4.156 \text{ \AA}$ . This gives a  $c/a$  ratio of 1.06 whereas for  $\text{BaTiO}_3$ ,  $c/a$  ratio is 1.01. Hence,  $\text{PbTiO}_3$  has more tetragonal distortion than  $\text{BaTiO}_3$ . In tetragonal  $\text{PbTiO}_3$  phase, the position of the ions may be described by keeping the  $Pb$  ion at the origin  $(0, 0, 0)$ ,  $Ti$  ions  $(0.5, 0.5, 0.5+dz1)$ ,  $O1(0.5, 0.5, dz2)$ , and  $O2(0.5, 0, 0.5+dz3)$  for Rietveld refinement. Displacement of  $Ti$  and  $O$  atoms from the ideal cubic position is denoted by  $dz$ . The shifting of  $Ti$  and  $O$  in the  $\text{PbTiO}_3$  system is in the same direction whereas  $\text{BaTiO}_3$  is in the opposite direction from the cubic system.



**Figure 1.1:** Schematic diagram of  $\text{PbTiO}_3$  structures where (a) Tetragonal, and (b) Cubic structures are shown after phase transition at 763 K temperature.

The covalent character of  $Pb$  and its significant feature in ferroelectric/piezoelectric properties have been widely discussed in literature of  $\text{PbTiO}_3$  and based compounds. Cohen [2] has elaborated the difference in  $\text{PbTiO}_3$  and lead-free perovskites ( $\text{BaTiO}_3$ ,  $\text{KNbO}_3$ ) properties. It has been shown that in  $\text{PbTiO}_3$ , the hybridization between  $Ti-O$  and  $Pb-O$  are important contributions towards ferroelectricity by weakening short-range repulsions. A weakening of this hybridization reduces the ferroelectricity in the  $\text{PbTiO}_3$ .  $Pb(6s^2)$  states hybridize with the  $O(2p)$  and  $Ti(3d)$  to  $O(2p)$  states. This hybridization makes  $\text{PbTiO}_3$ -based materials important as ferroelectrics. Since it is difficult to grow single crystals of  $\text{PbTiO}_3$  of a size suitable for measurements; there have been relatively few attempts to systematically study dielectric, elastic, and piezoelectric properties of this crystal. A few complicated, experimental studies exhibit large conductivity, possibly related to a high concentrations of  $Pb$  vacancies. The most relevant

difference between  $\text{PbTiO}_3$  and other perovskite ferroelectrics is a low anisotropy of permittivity and relatively low shear piezoelectric coefficients in  $\text{PbTiO}_3$ .  $\text{PbTiO}_3$  has many important technological applications in electronics and microelectronics due to its high spontaneous polarization, Curie temperature, and pyroelectric coefficient [3, 4]. Ferroelectric  $\text{PbTiO}_3$  films deposited onto various substrates has proven advantageous in memory applications, field effect devices and pyroelectric detectors which have hence stimulated technological interest in this field of study.

In our present work, we aim to study the structure of solid solution of  $\text{Ba}_{1-x}\text{Pb}_x\text{TiO}_3$  ( $x=0-1$ ) and also to characterize its dielectric, ferroelectric and piezoelectric behavior as both of the ceramic (BT and PT) are promising in the above fields.