A.10: Effect of defects states within the band gap in reduced $BaTiO_3$

Barium titanate ($BaTiO_3$) having a perovskite structure is a classical ferroelectric insulator at room temperature and has been most widely studied material due to its various functionalities and fundamental scientific interests related to phase transition. High dielectric constant and low losses are its characteristic features that enable its use in applications like capacitors, energy storage devices etc. By increasing oxygen vacancies in the system, itinerant electrons are introduced leading to increase in conductivity of the system. It may exhibit insulator-metal transition at a certain critical doping level. The electric conduction through the oxygen vacancies in $BaTiO_3$ has been used in many applications such as ceramic capacitors and positive temperature coefficient thermistors. In earlier studies on reduced $BaTiO_3$, direct consequences of the oxygen vacancy on the dielectric properties and its effect on structural phase transformation have not been demonstrated. Thus, keeping this in mind; Hard X-Ray Application Laboratory (HXAL) of Synchrotrons Utilization Section (SUS) RRCAT has undertaken the present study on the structural, spectroscopic and dielectric properties of $BaTiO_3$ samples, where different amount of oxygen vacancy has been purposefully created in different set of samples. Disappearance of ferroelectric loop and the anomaly in the temperature variation of dielectric constant has been observed; however the structural phase transition corresponding to ferroelectric phase transitions still persists. Presence of Ti^{3+} states in the band gap appears to modify the electronic structure and hence ferroelectric and dielectric properties of the samples.

The samples were synthesized via conventional solid state synthesis route, where the calcination of thoroughly mixed raw materials followed by sintering of pellets was performed at 1250 °C for 24 hrs. Samples with varying oxygen concentrations were obtained by post annealing treatments at different temperatures and with different ambient conditions. In the present study, one of the pellet is treated with oxygen at 900 °C for 24 hrs followed by slow cooling, named as 'Oxygen treated'. Many samples were prepared by heating the different pellets of the $BaTiO_3$; at different temperatures along with a piece of titanium metal in vacuum sealed ($4x10^{-6}$ Torr) quartz ampoules. However, only two samples 'oxygen treated' and the samples kept at 800 °C, named as Ti_800C have been discussed here. X-ray diffraction (XRD) measurement confirms the tetragonal structure with no significant difference between the two samples. Polarization measured as a function of electric field shows well defined ferroelectric loop for the 'oxygen treated' sample, whereas no loop is observed for Ti_800C sample.

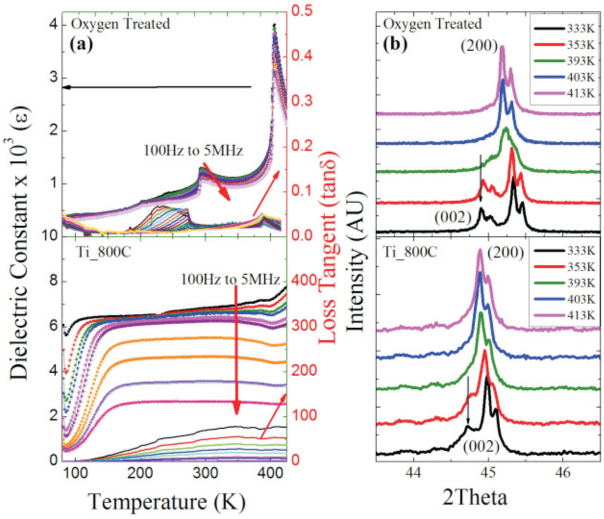

Fig. A.10.1: (a) Dielectric constant and loss tangent vs temperature at various frequencies from 100 Hz-5 MHz for oxygen treated and Ti_800C samples. (b) Merging of (002) and (200) peak in temperature dependant XRD, is a signature of tetragonal to cubic transition, for the two samples.

Dielectric measurements (Figure A.10.1(a)), shows anomaly in the dielectric permittivity data measured as a function of temperature at different frequencies in the 'oxygen treated' sample. At 403 K the structure of $BaTiO_3$ which is cubic at high temperatures, transforms to tetragonal phase. Corresponding to this transition, anomaly is observed in the dielectric permittivity. However, no anomaly is observed in the dielectric permittivity data of Ti_800C sample. In order to check the structural transition, temperature dependant XRD measurements have been performed. Temperature dependant XRD as shown in Figure A.10.1(b) shows that the structural phase transition, typical of $BaTiO_3$ system, persists even though the ferroelectric loop has not been observed and anomaly in the temperature dependant dielectric constant disappeared for the sample which are anticipated to have oxygen vacancy. The optical band gap of this sample has been probed using diffuse reflectance measurements and it has been observed that for oxygen deficient sample (Ti_800C), extra states appears below fundamental band gap i.e. at lower energies in the Kubelka-Munk plot. These extra states are speculated to be Ti^{+3} levels. The presence of Ti^{3+} oxidation state is confirmed by XANES measurements. The Ti^{3+} states are expected to give a conducting path to the otherwise insulating samples, which in turn are masking the ferroelectric and dielectric properties of the redued $BaTiO_3$ samples. For more details, please see *J. Appl. Phys. 123, 161424 (2018).*

Reported by:
Archna Sagdeo (archnaj@rrcat.gov.in)