

# Structural and Optical properties of poly-crystalline BaTiO<sub>3</sub> and SrTiO<sub>3</sub> prepared via solid state route

**Kanaka M. Jarabana, Ashutosh Mishra, Supriya Bisen**  
School of Physics, Devi Ahilya University, Indore-452001, India

E-mail: jkanaka.hvp@gmail.com

**Abstract.** Polycrystalline BaTiO<sub>3</sub> (BTO) and SrTiO<sub>3</sub> (STO) were synthesized by solid state route method and properties of made polycrystalline were characterized by X-Ray diffraction (XRD), Raman Spectroscopy & FTIR Spectroscopy. XRD analysis shows that samples are crystalline in nature. In Raman Spectroscopy measurement, the experiment has been done with the help of JOBIN-YOVN HORIBA LABRAM HR800 single monochromator, which is coupled with a “peltier cooled” charge coupled device (CCD). Raman Spectroscopy at low temperature measurement shows the phase transition above & below the curie temperature in samples. Fourier transform Infrared spectroscopy was used to determine the Ti-O bond length position.

## 1. Introduction

Barium titanate (BaTiO<sub>3</sub>) is one of the best known Perovskite ferroelectric compounds (A<sub>2</sub>B<sub>4</sub>O<sub>3</sub>) that have been extensively studied [1, 2] due to the simplicity of its crystal structure, which can accommodate different types of dopant. Barium titanate (BaTiO<sub>3</sub>) is another type of ABO<sub>3</sub> perovskite, which has not only large ferroelectric response, but also very large nonlinear optical and electro-optic coefficients, which is attractive to designing nonlinear optical devices [3]. These properties can be dramatically enhanced when they are doped with transition metals. It is well known that BaTiO<sub>3</sub> has a paraelectric to ferroelectric transition at about 120 °C with a very high dielectric constant. Thus, considerable attentions were paid to the doped BaTiO<sub>3</sub> [4-5] to modify the performance of the materials. Strontium titanate (SrTiO<sub>3</sub>) with a perovskite-type structure is an important ceramic material having wide uses in the catalysis, sensors, actuators, electrooptical devices, random access memory devices, and multilayer capacitor. Because SrTiO<sub>3</sub> have a lot of physical and chemical properties, such as, high thermal and chemical stability, low coefficient of thermal expansion, large dielectric constant, low dielectric loss, high nonlinear optical coefficient, it is widely accepted that the practical performances of product are strongly influenced by its phase, morphology, particle size, crystal defects, surface properties, etc., which ultimately depend on its preparation method and condition.

## 2. Synthesis of Iron & cobalt doped barium titanate

Both samples barium titanate and strontium titanate were synthesized via solid state route. We started from highly pure fine powdered samples of BaCO<sub>3</sub>, SrCO<sub>3</sub> and TiO<sub>2</sub> for bulk samples of BaTiO<sub>3</sub> and SrTiO<sub>3</sub>. All these were mixed in the calculated percentage ratio. Samples were grinded for 8-hours and calcinations were done at 900 °C and than sintered at 1100 °C & 1350 °C for 24 hours.



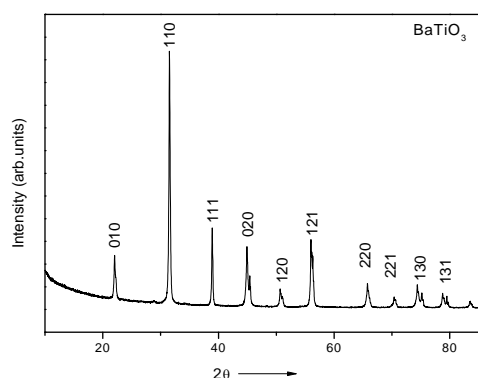
### 3. Experimental Technique

#### 3.1. X-ray Diffraction

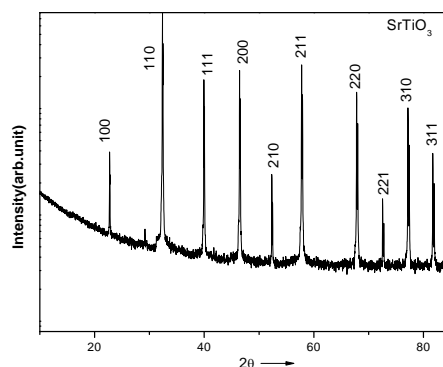
The synthesized powders were characterized by X-ray diffraction using a D8 Advanced X-ray diffractometer. X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals the detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD pattern for polycrystalline BaTiO<sub>3</sub> and SrTiO<sub>3</sub> respectively was carried out using CuK $\alpha$  radiation in the 2 $\theta$  range of 10 to 85<sup>0</sup> shown in figure 1(a) and 1(b). The XRD patterns of samples do not show any impurity peaks which indicates that the samples are single phase in nature. From the diffraction pattern, the lattice parameter for both the samples has been calculated. The lattice parameters calculated for BaTiO<sub>3</sub> are (a=0.3994nm, b=0.3994nm, c=0.4022nm) which are in accordance with the tetragonal structure of the BaTiO<sub>3</sub>. The lattice parameters calculated for SrTiO<sub>3</sub> is a=0.3910nm.

#### 3.2. Raman Spectroscopy Measurement

In Raman Spectroscopy measurement, the experiment has been done with the help of JOBIN-YOVN HORIBA LABRAM HR800 single monochromator, which is coupled with a “peltier cooled” charge coupled device (CCD). The spectra have been recorded in unpolarized mode in the full range starting from 200 to 850 cm<sup>-1</sup>. The temperatures have been recorded in unpolarized mode in the range from 80K to 350K. Spectra have the broad features characteristics of titanium disorder in the unit cell at all temperatures. During the continuous heating from 80 to 350 K, three phase transitions take place: R→O, O→T and T→C is shown in fig 2(a). At low temperature in phase rhombohedra (80 K), the spectrum shows the following main lines: a broad peak near 262.6 cm<sup>-1</sup> [A<sub>1</sub>(TO)], a sharp peak at 311.1 cm<sup>-1</sup> [B<sub>1</sub>, E(TO+LO)], a weak peak at 486.4 cm<sup>-1</sup>, [E(LO), A<sub>1</sub>(LO), E(TO)], asymmetric and



**Figure 1(a).** XRD pattern of BaTiO<sub>3</sub> at 900<sup>0</sup>C.



**Figure 1(b).** XRD Pattern of SrTiO<sub>3</sub> at 900<sup>0</sup>C.

**Table 1.** Particle size of pure BaTiO<sub>3</sub> & SrTiO<sub>3</sub> at 900<sup>0</sup> C.

Sample	Particle size(nm)
BaTiO <sub>3</sub>	26.4
SrTiO <sub>3</sub>	87.9

broad peak near  $530.8\text{ cm}^{-1}$  [E(TO),  $A_1(\text{TO})$ ], and a weak peak at  $714.8\text{ cm}^{-1}$  [E(LO),  $A_1(\text{LO})$ ], where the phonon assignment is given inside square brackets. When the temperature is increased until 175 K, the Raman peaks disappeared or were shifted. The peak intensity at  $486.4\text{ cm}^{-1}$  decreases when the temperature increases, this behavior is due to the rhombohedral to orthorhombic phase transition. The next phase transition, orthorhombic to tetragonal, is carried out at 290K, the mode [E (LO),  $A_1$  (LO), E (TO)] disappears and modes [ $B_1$ , E (TO+LO)] and [E (TO),  $A_1$  (TO)] are shifted to  $307.1$  and  $517.3\text{ cm}^{-1}$ , respectively. For phase transition  $T \rightarrow C$ , at 350K, the several Raman modes have disappeared or diminished considerably.

A systematic low temperature Raman spectroscopy study has been done on polycrystalline  $\text{SrTiO}_3$  is shown in fig 2(b). On cooling below 300K, no drastic change occurs till 90K. As the sample temperature comes closer to the transition temperature (105K) the band at  $\sim 250\text{K}$  starts to be very sharp. Since there is difference in the actual sample temperature and the temperature displayed on temperature sensor, thus the real phase transition occurs 2-3K lower than the actual  $T_c$ .

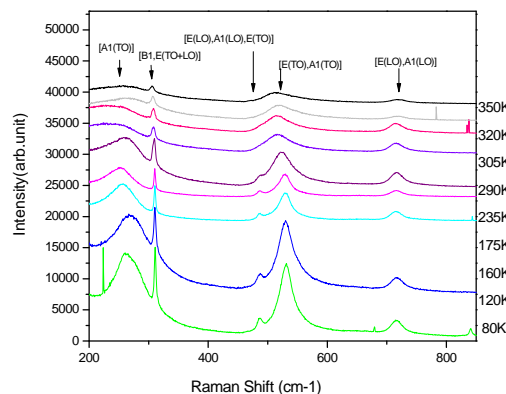
As we further lower the temperature from 105K one new sharp peak starts developing at 90K with the peak positions at  $\sim 144\text{ cm}^{-1}$ . This gives a clear evidence of the occurrence of phase transition, as we don't expect sharp peaks in cubic structure. The strength of the peak increases with further lowering of the temperature. The peak at  $\sim 144\text{ cm}^{-1}$  is assigned as  $E_g$ , at  $173.8\text{ cm}^{-1}$  as  $B_{2g}$ .

### 3.2. Fourier Transform Infrared Spectroscopy (FTIR)

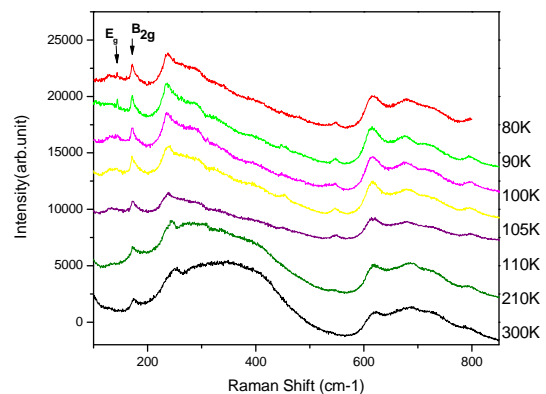
Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". FTIR is simply a technical variant of a common infrared spectrometer, which yields an intensity signal as a function of wavelength or 'spectral color'. The FTIR spectrum was measured at room temperature. The measurement of FTIR spectra was carried out by Perkin-Elmer FTIR spectrometer. Figure 3(a) shows the FTIR spectra of  $\text{BaTiO}_3$ .

The spectra of the powder calcined at  $900^\circ\text{C}$  showed a wave number range from  $400 - 4000\text{ cm}^{-1}$  attributed to the Ti-O vibration, the carbonate peaks ( $\text{CO}_3^{2-}$ ) at  $857\text{ cm}^{-1}$ ,  $1745\text{ cm}^{-1}$  and  $2441.8\text{ cm}^{-1}$  and hydroxyl (O-H) group at  $1058.9\text{ cm}^{-1}$ ,  $1634.6\text{ cm}^{-1}$ . Bands corresponding to the carbonate and hydroxyl group were noted due to the intermeate  $\text{BaCO}_3$  phase and water. Peaks corresponding to carbonate ( $\text{CO}_3^{2-}$ ) bands have been noted  $857\text{ cm}^{-1}$  (out of plane deformation),  $1745\text{ cm}^{-1}$  (symmetric stretching) and  $2441.8\text{ cm}^{-1}$  (combined symmetry).

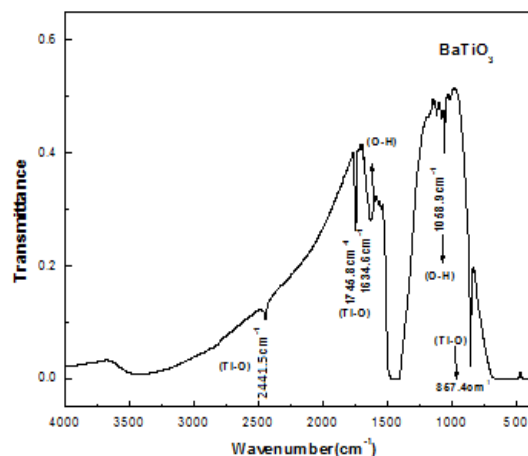
The FTIR spectrum of  $\text{SrTiO}_3$  calcined at  $900^\circ\text{C}$  is shown in fig 3(b), which exhibits a peak at  $577.6\text{ cm}^{-1}$  corresponding to Ti-O<sub>1</sub> stretching.



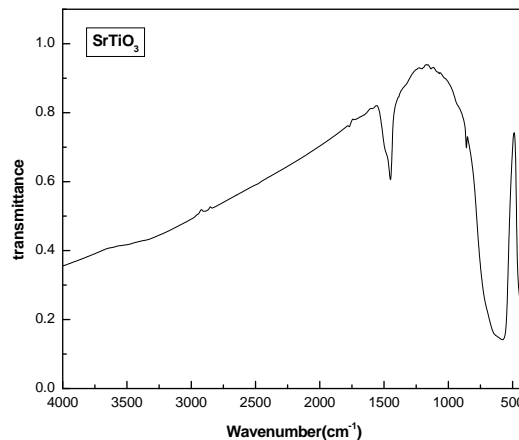
**Figure 2(a).** Unpolarized Raman spectra of polycrystalline  $\text{BaTiO}_3$  recorded at selected temperatures.



**Figure 2(b).** Unpolarized Raman spectra of polycrystalline  $\text{SrTiO}_3$  recorded at selected temperatures.



**Figure 3(a).** FTIR spectrum of pure BaTiO<sub>3</sub>.



**Figure 3(b).** FTIR spectrum of pure SrTiO<sub>3</sub>.

#### 4. Conclusion

Samples of polycrystalline BaTiO<sub>3</sub> and SrTiO<sub>3</sub> were synthesized by solid state method. The XRD patterns of samples do not show any impurity peaks which indicates that the samples are single phase in nature. We have carried out a systematic low temperature spectroscopy study of SrTiO<sub>3</sub> & BaTiO<sub>3</sub> single crystal using a micro-Raman setup. In SrTiO<sub>3</sub> we observed only broad humps in Cubic phase that is above 105K. Sharp peaks corresponding to normal modes in tetragonal symmetry are observed below this transition temperature. In BaTiO<sub>3</sub> we observed in two phase transition R→O, O→T when we increase the temperature Raman peaks disappeared or were shifted to upper frequency and Raman peak intensity decreases. But For phase transition T → C, at 350 K, the several Raman modes have disappeared or diminished considerably. The FTIR spectra reveal that they affect the vibration of crystal lattices. When a smaller ion replaces Ti<sup>4+</sup>, the cell becomes smaller; resulting in the distance between Ti and O becomes shorter. This enhances the interaction between these ions.

#### Acknowledgments

The authors are thankful to Prof. Ajay Gupta, Dr. Mukul Gupta, UGC-DAE CSR for XRD, Dr. Vasant Sathe, UGC-DAE CSR for Raman measurement and Dr. Uday Deshpandey for FTIR measurement, Indore for providing the experimental facilities and for the precious guidance. One of the authors (Supriya Bisen) is thankful to UGC-DAE CSR Indore for providing the research fellowship.

#### References

- [1] Makovec D, Samadmija Z and Drofenik M J Am 2004 *Ceram. Soc.* **87** 1324
- [2] Maga D, Igor P and Sergei M Mater J. 2000 *Chem.* **10**
- [3] Jana A, Kundu T.K , Pradhan S.K and Chakravorty D J 2005 *Appl. Phys.* **97**
- [4] Smolenski G.A, Isupov A.V, Dokl. Akad. Nauk. 1954 *SSSR* **9**
- [5] Ismailzade I.H, Ismailov R.M 1980 *Phys. Stat. Sol.* **59** K