High temperature Raman study of \( \text{BaTi}_{0.96}\text{Fe}_{0.04}\text{O}_3 \) and \( \text{BaTi}_{0.96}\text{Co}_{0.04}\text{O}_3 \) synthesized via solid state route

Ashutosh Mishra, Niyati Mishra, Supriya Bisen and Kanaka M. Jarabana
School of Physics, Devi Ahilya University, Khandwa Road, Indore-452001, India
E-mail: nmishra.sop@gmail.com

Abstract. A finest possible sample of 4% Iron and Cobalt doped ceramics of \( \text{BaTiO}_3 \) (BTO) with possible tetragonal structure via a solid-state route was prepared. Prepared sample was characterized by X-ray diffraction (XRD) using Bruker D8 Advance XRD instrument, the value of \( 2\theta \) is in between \( 20^\circ \) to \( 80^\circ \). Rietveld refinement of both samples shows the information about direct cell parameters, direct cell volume and phase. High temperature Raman spectroscopy was performed using JOBIN-YOVN HORIBA LABRAM HR800 single monochromator and the region of wave number is from 200 cm\(^{-1}\) to 800 cm\(^{-1}\) from the temperature range of 27 to 207 \(^{\circ}\)C.

1. Introduction
Barium titanate (\( \text{BaTiO}_3 \)) is a ferroelectric oxide that undergoes a transition from a ferroelectric tetragonal phase to a paraelectric cubic phase upon heating above \( 120^\circ \)C. In cubic perovskite \( \text{BaTiO}_3 \), titanium atoms are octahedrally coordinated by six oxygen atoms. Ferroelectricity in tetragonal \( \text{BaTiO}_3 \) is due to an average relative displacement along the \( c \)-axis of titanium from its centrosymmetric position in the unit cell and consequently the creation of a permanent electric dipole. The elongation of the unit cell along the \( c \)-axis and consequently the deviation of the \( c/a \) ratio from unity are used as an indication of the presence of the ferroelectric phase [1–3]. Ferroelectric properties and a high dielectric constant make \( \text{BaTiO}_3 \) useful in an array of applications such as multilayer ceramic capacitors [4, 5] gate dielectrics [6] waveguide modulators, IR detectors and holographic memory.

2. Synthesis
Both samples of Fe and Co doped barium titanate were synthesized via solid state route. We started from highly pure fine powdered samples of \( \text{BaCO}_3 \), \( \text{TiO}_2 \), \( \text{Fe}_2\text{O}_3 \) and \( \text{Co}_3\text{O}_4 \) for bulk sample of doped \( \text{BaTiO}_3 \). All these were mixed in the calculated percentage ratio. Samples were grinded for around 16-hours and calcinations were done at 900 \( ^\circ\)C and 1100 \( ^\circ\)C than sintered at 1200 \( ^\circ\)C for 24 hours.

3. Experimental techniques
3.1. X-ray Diffraction
D8 Advance XRD: The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The x-rays were produced using a sealed tube and the wavelength of x-ray was 0.154 nm (Cu K-alpha). The x-rays were detected using a fast counting detector based on Silicon trip technology (Bruker Lynx Eye detector).
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. In Figure 1 (A) and Figure 1(B) XRD patterns reports the single phase tetragonal crystal system of the space group P4mm (99) and pattern matched with the standard pattern JCPDS no. 79-2265.

| Sample          | Direct cell parameters | Direct Cell Volume | Phase |
|-----------------|------------------------|--------------------|-------|
| BaTi$_{0.96}$Fe$_{0.04}$O$_3$ | a: 3.9882, b: 3.9882, c: 4.0043 | 63.6510            | 1     |
| BaTi$_{0.96}$Co$_{0.04}$O$_3$ | a: 3.9923, b: 3.9923, c: 4.0013 | 63.7744            | 1     |
3.2 Raman Spectroscopy

The Raman spectrum of Fe and Co doped BaTiO$_3$ has been done over a range of temperatures from room temperature up to around 210 °C.

![Raman Spectra](image)

**Figure 3.** Unpolarised Raman spectra of 4% Fe doped BTO recorded at selected temperature range.

![Raman Spectra](image)

**Figure 4.** Unpolarized Raman spectra of 4% Co doped BTO recorded at selected temperature range.
The BaTiO$_3$ Raman The study of Raman spectroscopy was carried out by means Jobin-Yvon Horiba Labram HR800 single monochromator. The spectra have been recorded in unpolarized mode in the full range starting from 200 to 800 cm$^{-1}$. Spectra have the broad features characteristics of titanium disorder in the unit cell at all temperatures.

In the bulk 4% Fe doped BaTiO$_3$ spectra in Figure 2(A), the intensities of the [E (LO+TO), B1] peaks at ~307 cm$^{-1}$ and [E (LO), A1 (LO)] peaks at ~ 717 cm$^{-1}$ decrease rapidly as the temperature, increase through the bulk $T_c$. In the bulk 4% Co doped BaTiO$_3$ spectra in Figure 2(B) the intensities of the [E (LO+TO), B1] peaks at ~308 cm$^{-1}$ and [E (LO), A1 (LO)] peaks at ~ 713 cm$^{-1}$ decrease rapidly as the temperature, increase through the bulk $T_c$.

The first is an increase in peak width at the phase transition temperature and the second is the loss of peak intensity with increasing temperature. For BaTiO$_3$, the line width for the [E (LO+TO), B1] peak increases with increasing temperature. It is to be noted that bulk BaTiO$_3$ near the cubic-to-tetragonal phase transition displays a Raman line width.

4. Discussion
The BaTi$_{0.96}$Fe$_{0.04}$O$_3$ and BaTi$_{0.96}$Co$_{0.04}$O$_3$ ceramics was prepared via solid state route. The XRD data has concluded that all major peaks of Fe and Co doped BTO are matching with reported XRD data of pure BTO, and sample is in single phase, which shows that doping is perfect. The measurement of Raman spectroscopy shows that in the Fe doped BTO ceramic, the intensities of the [E (LO+TO), B1] peaks at ~307 cm$^{-1}$ and [E (LO), A1 (LO)] peaks at ~ 717 cm$^{-1}$ decrease rapidly as the temperature, increase through the bulk’s $T_c$. We interpret the disappearance of the 307 cm$^{-1}$ peak as an indicator of the tetragonal phase and use two characteristics as an indication of the phase transition. And, in the 4% Co doped BaTiO$_3$ ceramic, the intensities of the [E (LO+TO), B1] peaks at ~308 cm$^{-1}$ and [E (LO), A1 (LO)] peaks at ~ 713 cm$^{-1}$ decrease rapidly as the temperature, increase through the bulk’s $T_c$. We interpret the disappearance of the 308 cm$^{-1}$ peak as an indicator of the tetragonal phase and use two characteristics as an indication of the phase transition. The first is an increase in peak width at the phase transition temperature and the second is the loss of peak intensity with increasing temperature.

Acknowledgements
The authors are thankful to Dr. Ajay Gupta, Dr. Mukul Gupta (XRD Lab) and Dr. Vasant Sathe (Raman Lab), UGC-DAE CSR, Indore for providing the experimental facilities and for their precious guidance. One of the author (Niyati Mishra) is thankful to UGC-DAE CSR Indore for providing the CRS project fellowship.

References
[1] Jaffe B, Cook W R and Jaffe H 1971 Piezoelectric Ceramics, Vol. 3 (New York: Academic Press)
[2] Lines M E and Glass A M 1977 Principles and Applications of Ferroelectrics and Related Materials, (Oxford: Clarendon Press)
[3] Strukov B A and Levanyuk A P 1998 Ferroelectric Phenomena in Crystals, (Berlin: Springer-Verlag)
[4] Wang S F and Dayton G O 1999 J. Am. Ceram. Soc. 82 2677
[5] Hennings D, Klee M and Waser R 1991 Adv. Mater. 3 334
[6] Yildirim F A, Ucurum C, Schliewe R R, Bauhofer W, Meixner R M, Goebel H and Krautschneider W 2007 Appl. Phys. Lett. 90 083501