Influence of Copper doping on physical properties of Barium Titanate

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Abstract. A finest possible sample of Copper (Cu) doped micro particles of BaTiO$_3$ (BTO) with possible tetragonal structure via a solid-state route was prepared. Prepared samples of BaTi$_{1-x}$Cu$_x$O$_3$ ($x=0.05$) were structural characterized by X-ray diffraction (XRD). Fourier Transform Infrared spectroscopy (FTIR) technique used for determines the Ti-O bond shifting as an influence of Cu in BTO. Finally Dielectric Constant measurements of the sample above and below the Curie temperature were carried out.

1. Introduction
Barium titanate (BaTiO$_3$) is one of the best known Perovskite ferroelectric compounds (A$^{2+}$B$^{4+}$O$_3$) that have been extensively studied [1, 2] due to the simplicity of its crystal structure, which can accommodate different types of dopant. This has led to the possibility of tailoring the properties [3] of doped BaTiO$_3$ for specific technological applications, such as capacitors, sensors with positive temperature coefficients of resistivity, piezoelectric transducers and ferroelectric thin-film memories. Because of the intrinsic capability of the Perovskite structure to host ions of different size, a large number of different dopants can be accommodated in the lattice [4]. The mechanism of dopant incorporation into BaTiO$_3$ has been extensively investigated and the behaviour of some transition metal ions has been well elucidated. The ionic radius is the main parameter that determines the substitution site [5]. Ferroelectrics are materials which have the outstanding property of possessing spontaneous electric polarization, the reversibility of the permanent polarization by an electric field. Due to their possessing large piezoelectric values, make them more attractive in different piezoelectric application. BaTiO$_3$ has been a ferroelectric and piezoelectric with an extensive application. It can be used as a capacitor, thermistor, transducer or accelerometer [6]. BaTiO$_3$ chemically and mechanically more stable, which exhibits ferroelectrics properties at and above room temperature and it can be prepared and used in the form of ceramic polycrystalline samples [7]. Modified BaTiO3 is suitable for pyroelectric applications [8] as their infrared response can be adjusted over a wide range of operating temperatures. [9] Our present focus is to develop Cu modified BaTiO3 materials to get a maximum IR response near room temperature, as room temperature IR sensors are attractive for a wide range of civilian and military applications.[10, 11] The sample of Cu doped BaTiO$_3$ (Cu-BTO) by solid-state route has been synthesized. This sample was then characterized by X-ray diffraction. Also, different techniques as FTIR and dielectric constant measurement were carried out. The purpose of this paper is to throw some light on the influence of Copper impurity on the structural and Dielectric properties of BaTiO$_3$. 

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2. Experimental

2.1. Preparation of Copper doped Barium Titanate (Cu-BTO).
Sample of Copper doped Barium Titanate were prepared via Solid State Route. The starting materials were analytical reagent grade BaCO₃, TiO₂ and CuO. Weighed mixtures of the three components were homogenized by grinding and preheated at 900°C for 12 h. They were then grounded, pressed into pellets and heated at 1250°C for 12 hours in air followed by a furnace cooling.

2.2. Physical Measurement

2.1.1. X-Ray Diffraction. 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). X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker Lynx Eye detector).

2.1.2. Fourier Transform Infrared Spectroscopy. Infrared spectra (KBr disc) of the sample were obtained using Perkin-Elmer FTIR spectrometer in the 400-4000 cm⁻¹ spectral range.

2.1.3. Dielectric Constant Measurement. In Dielectric constant measurement, Dielectric-constant of the sample was recorded on hp- Hewlett Packard 4192 A, LF Impedance 5 Hz – 13 Hz Analyzer.

3. Result and Discussion

3.1. X-ray Diffraction:
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. Figure1 shows that the 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. Diffraction data of Cu doped BaTiO₃ has concluded that all major peaks of Cu- BTO are matching with reported XRD data of pure BTO and sample is in single phase. Which shows doping is perfect. The value of 2θ is in between 20 to 80°. There is a comparison of XRD peaks of samples sintered at 900°C and 1250°C.

![FIGURE1. XRD data of Cu doped BaTiO₃ at 900°C & 1250°C. Insert shows the peak width broadening after sintering.](image-url)
3.2. Fourier Transform Infrared Spectroscopy:
Figure 3 indicates FTIR spectra of the 5% Copper doped Barium Titanate (Cu-BTO) particles, synthesized at 1250 °C for 12 Hours. A broad absorption band in the range of 400-4000 cm⁻¹ suggests the presence of considerable amount of H₂O and OH in the particles [12, 13]. KBr has been used as a binder for background fit, Hydroxyl group occurs because of moisture in KBr. In particular the sharp absorption band at 3600 cm⁻¹ was assigned to the stretching vibration of the Hydroxyl group with an intermolecular hydrogen bond, which shows the presence of hydroxyl group in Barium Titanate lattice. Also the sharp absorption band observed at around 532 cm⁻¹ was attributed to the bending vibration of O₆ octahedra deformation mode which was assigned by Slater [14] and confirmed by Spitzer [15].

3.3. Dielectric Measurement:
Barium titanate is a cubic paraelectric above 120°C. Below this temperature, it is ferroelectric, with a tetragonal structure down to 5°C. Considerable effort has been devoted to understanding the behaviour of the dielectric constants of Cu-BTO. In Dielectric-constant measurement, the transition temperature Cu-BTO is occurring at 125°C. The reported value of transition temperature (Curie- temperature) of pure BTO is 120°C.

Table 1. Comparison of the lattice parameters of un-doped BaTiO₃ and Cu doped BaTiO₃

| Direct cell parameters | a    | b    | c    | Direct cell volume |
|------------------------|------|------|------|--------------------|
| BaTiO₃                 | 3.9900 | 3.9900 | 4.0302 | 64.2800            |
| BaTi₀.₉₅Cu₀.₀₅O₃ (At 900 °C) | 3.9895 | 3.9895 | 4.0077 | 63.7848            |
| BaTi₀.₉₅Cu₀.₀₅O₃ (At 1250 °C) | 3.9830 | 3.9839 | 4.0139 | 63.6791            |

In FIGURE 4 one can see that after doping Cu in pure BTO, on increasing the temperature on higher side, the transition temperature was shifted from 120°C to 125°C. While on cooling the sample, the transition temperature was shifted to 110°C.
4. Conclusion

4.1. The BaTi_{0.95}Cu_{0.05}O_3 ceramics was prepared by the solid state reaction method. XRD patterns report the single phase tetragonal crystal system of the space group P4mm (99) and pattern matched with the standard pattern JCPDS no. 79-2265.

4.2. FTIR Spectra shows that bending vibration of O_6 octahedra deformation mode, which confirms its ferroelectric behaviour.

4.3. Finally the dielectric constant measurements of the sample above and below the Curie temperature were carried out at 1 MHz, the Transition temperature is found shifted towards higher side from that of pure BaTiO_3. The Thermal Hysteresis is indicative of the fact that the transition is indeed of First Order.

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