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Structural Analysis and Dielectric Properties of Cobalt Incorporated Barium Titanate

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Abstract

The polycrystalline samples of Co2+ doped $BaTiO_3$ (BTO) with compositional formula $BaTi_{1-x}Co_xO_3$ (x = 0, 0.05 and 0.10) were prepared by solid-state reaction route. The phase composition, perovskite structural parameters have been obtained by X-ray diffraction (XRD), Raman spectroscopy as a function of chemical composition at room temperature. XRD analysis indicates the formation of single-phase tetragonal structure for all the prepared samples. Tetragonal structure with space group P4mm of all samples is further approved by Rietveld refinement and Raman spectroscopy. Four Raman modes of vibration are observed in all the samples under investigation at room temperature. The intensity of vibrational modes decreases with increasing Co doping. Small shift in Raman modes and increment in the line width has been observed due to introduction of cobalt doping ions. A high dielectric constant ~12000 and very low dielectric loss is obtained for $BaTi_{0.90}Co_{0.10}O_3$ sample.

Keywords: X-Ray Diffraction, Tetragonal, Raman Spectroscopy, Dielectric,

Introduction

Barium titanate($BaTiO_3$) is a ferroelectric compound with the perovskite type structure and is an important material for dielectric applications. Doping of $BaTiO_3$ based ceramics is of great importance in the fabrication of electric and electronic devices (multilayer capacitors, heaters and sensors with positive temperature coefficients of resistivity, piezoelectric transducers, ferroelectric thin film memories, etc.). 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 $BaTiO_3$ lattice[1].

Bulk $BaTiO_3$ has the classical ABO_3 (Ba2+ as A and Ti4+ as B) perovskite structure. Above the Curie temperature, TC ~ 130°C, it has a centrosymmetric cubic crystal (c) structure (Pm3m space) with A at the corners, B at the center, and the O^{2-} at the face centers. The ferroelectric properties of $BiTO_3$ can be efficiently controlled by doping with different elements. It has been known that a high dielectric constant and good temperature stability can be achieved through addition of dopants. It is reported that the TiO_6octahedra are disturbed with B-site doping resulting in broadening of the transition at TC [2]. When the temperature is lowered to ~ 400 K, the ionic displacement of the titanium (Ti)-ion changes the crystal structure to tetragonal from cubic $BaTiO_3$ and it goes to a ferroelectric state. Many studies developing new processing techniques in order to avoid the problems that arose through the conventional ceramic techniques were carried out[3, 4].

Motivated from the earlier observations, we aimed at studying the structural, vibrational and dielectric properties $BaTi_{1-x}Co_xO_3$ (x = 0, 0.05and 0.10) using X-ray diffraction (XRD). Solid state reaction route was employed to synthesize all the samples because of its reproducibility and sufficient final product for its various measurements. We further study the phonon structure in Co doped $BaTiO_3$ to seek the role Co doping. We obtained a high dielectric constant of all the doped samples than parent $BaTiO_3$.

Experimental Techniques

A conventional solid state reaction method was used to prepare the $BaTiO_3$ and Co doped $BaTiO_3$ samples. The general formula for the samples is $BaTi_{1-x}Co_xO_3$ (x = 0, 0.05 and 0.10). Appropriate amounts of BaO (BDH, England), TiO_2 (Merck, Germany) and CoO (Merck, Germany) were grounded for 8 hours in a wet medium. The homogeneous mixture was then calcined at 1200 K for 12 hours and disc-shaped samples of height 1.26mm and diameter 10.24mm were formed at a pressure of 8MPa. Finally, the samples were sintered at 1250 K for 12 hrs using a Carbolite 2132 furnace. The sintering is repeated twice.

The phase analysis of powder samples was carried out using Bruker D8 Advance X-ray diffractometer with CuKα1 radiation. The data was collected with a step size of 0.02° over the range 2□ (10 □ 2□□□ 80). The Raman spectra were carried out by Jobin-Yovn Horiba Labram HR800 Raman spectroscopy with 632.8 nm radiations from a He-Ne laser. For dielectric measurements, both the large surfaces of the samples were electroded with silver paint. Dielectric measurements were performed using Novocontrol Alpha-A high performance impedance analyzer over the frequency range of 1Hz to 1MHz at room temperature.

Results And Discussion:

The diffractions pattern of the $BaTi_{1-x}Co_xO_3$ (x = 0, 0.05 and 0.10) is shown in Figure 1. It can be indexed with a tetragonal structure, space group *P*4*mm* which isclearly evident from the splitting of (110) peak The obtained XRD pattern is in good agreement with the literature (JCPDS No. 81-2204). The peaks are slightly broad indicating the nanocrystalline nature of the sample. It is observed that with increase in Cobalt doping, $BaTiO_3$ loses its tetragonality and starts to transform into the cubic structure.

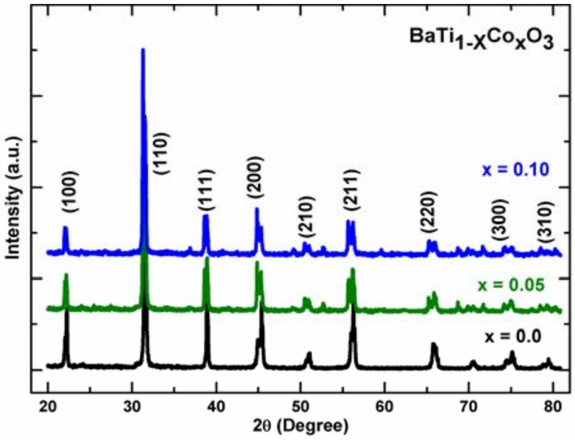

Figure 1. Xrd Pattern For $Bati_{1-x}co_xo_3$ (X = 0, 0.05 And 0.10)

The average crystallite size was calculated from Scherrer's formula where λ is wave length of X-ray used (1.5406Å), K is a constant (shape factor ≈ 0.9), θ is the angle of diffraction, β is the FWHM and the obtained values are mentioned in Table 1. It is observed that the average particle size for the doped samples increases with increase in Co doping. The strongest reflection comes from (110) plane thatindicates the growth of the crystal in 110 Plane. The XRD patterns show a slight shift in (110) peak position towards higher diffraction angle (2□).

The complete details of effect of Co doping on barium titanate could be done by analysing the influence on the structure of barium titanate in broad. The Rietveld method was used for refining structural parameters (fractional coordinates, atomic displacement parameters, occupation factors and lattice parameters) using the software FullPROF 2000 directly from whole powder diffraction patterns[5]. Rietveld refined plots are shown in Figure 2.

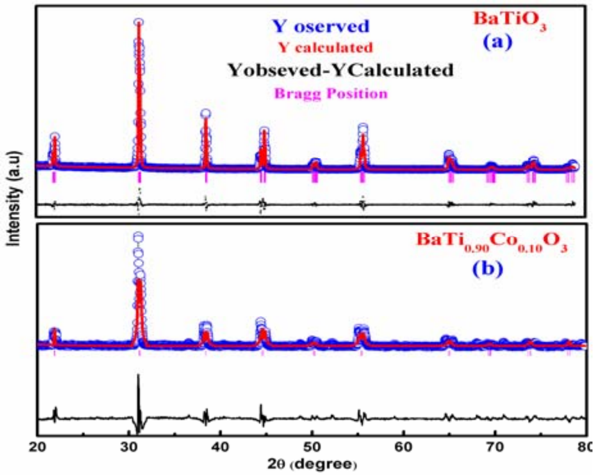

Figure 2. Retvield Refined Plots For Bati$_{1-X}$co$_x$o$_3$ (X = 0 And 0.10).

Retvield refinement also confirms space group P4mm and structural parameters. Unit cell refinement showed that the tetragonality of BaTiO3 was changed by introducing the Co doping. The Table 1 presents the structural parameters obtained by Retvield refinement. It can be seen that tetragonality factors c/a for 10% Co doped BaTiO3 is less than pristine and becomes close to one which indicates the loss of tetragonality with increase in cobalt doping. Further volume is increasing with increase in Co doping.

Table 1: Details of Rietveld refined XRD parameters $BaTiO_3$ and $BaTi_{0.90}CO_{0.10}O$ samples.

Samples	**$BaTiO_3$**	**$BaTi_{0.90}CO_{0.10}O$**
a (Å)	4.0323	4.052
c (Å)	4.0662	4.066
V (Å^3)	66.1	66.7
R_F	3.6	10
R_{Bragg}	5.60	12.6
R_{wp}	21.3	40.6
R_{exp}	12.9	37.3
R_p	20.9	71.7
χ^2	2.7	4.0
GOF	1.6	1.9
D *(nm)*	0.35	0.33

The Raman spectra BaTi$_{1-x}$Co$_x$O$_3$ (x =0.05 and 0.10) series with excitation wavelength of 488 nm obtained at room temperature are shown in Figure. 3. According to the crystallography, Raman spectroscopy suggests eight Raman active modes for tetragonal BaTiO$_3$ (P4mm) which are 4E (TO+LO) + 3A1 (TO+LO) + 1B1 (TO+LO) having a sharp band at 308 cm^{-1} and three broad bands at 260, 525, and 720 cm^{-1} [6]. The band at 308 cm^{-1}, absent in the cubic BaTiO$_3$, is considered as the signature of the tetragonal phase at room temperature. However, in this study, only four Raman active phonon modes of vibration were observed in doped samples and are found to be around at 261, 306, 516 and 716 cm^{-1}. We have compared these results with our earlier results obtained for BaTiO3[7]. These modes of vibration are in good agreement with earlier reported bulk BaTiO$_3$[8].

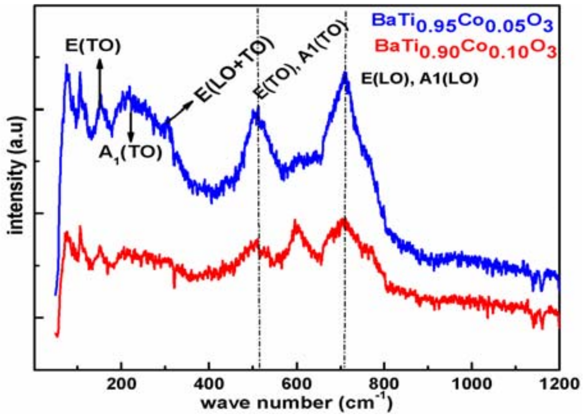

Figure 3. Raman Spectra Of Bati$_{1-x}$co$_x$o$_3$ (X = 0, 0.05 And 0.10).

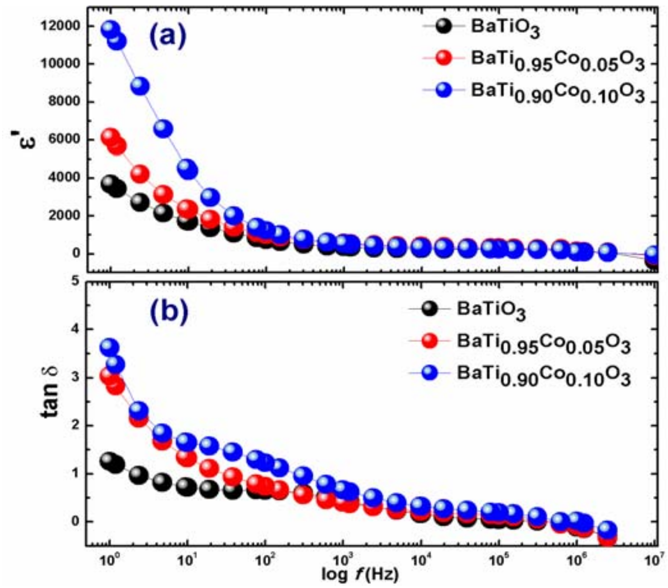

Figure 4. Room Temperature Variation Of (A) Dielectric Constant (B) Dielectric Loss As A Function Of frequency and composition for BaTi$_{1-x}$Co$_x$O$_3$ (x = 0, 0.05 and 0.10).

The dielectric constant as a function of frequency for all Co doped BaTiO3 particle is shown in the Figure 4. It is confirmed from the figure that Co doped BaTiO$_3$ has strong frequency dependence in the lower frequency region. The dielectric constant decreases with the increase in frequency and becomes constant at high frequencies for all compositions. This type of behavior can be explained on the basis of

Maxwell-Wagner model[9]. According to this model, a dielectric medium is supposed to be made of well conducting grains, which are separated by weakly conducting (or resistive) grain boundaries. Under the application of external electric field, the charges carriers can easily migrate between the grains but are accumulated at the grain boundaries. This process can produce large polarization and high dielectric constant. The small conductivity of grain boundary contributes to the high value of dielectric constant at low frequency. Further dielectric constant and loss is found to increase with increase in cobalt concentration. A high value of dielectric constant almost three times greater than that of pristine $BaTiO_3$ is obtained for $BaTi_{0.90}Co_{0.10}O_3$ sample.

Conclusions

The single phase $BaTi_{1-x}CoxO_3$ (x = 0.0, 0.05 and 0.10) series is obtained by solid state reaction. XRD and Retvield refinement confirms the tetragonal structure for all samples which is further supported by Raman spectroscopy. Dielectric constant increases with increase in cobalt concentration.

Acknowledgments

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