

Structural and Dielectric Properties of Co Substituted Multi Ferroic Ceramics

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Abstract—Tungsten Bronze (TB) type structure having a general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_4O_{30}$ consist of a complex array of distorted BO_6 octahedra sharing corner in such a way that three different type of interstices are available for cation substitutions in which a wide variety of substitution can be made for different applications. $Ba_5CaTi_2Nb_8O_{30}$ is one of the most promising ferroelectric materials well known for its excellent fatigue endurance, high Curie temperature, high remnant polarization, low coercive field and low leakage current. It is well known fact that there is a drastic change in same physical properties of materials on suitable substitution at different atomic sites of TB structure.

The polycrystalline multiferroic sample of $Ba_5CaTi_{2-x}Co_xNb_8O_{30}$ $x = 0.0, 0.02$ specimen is prepared by high-temperature solid state reaction method and studied for their structural and dielectric properties. X-ray diffraction (XRD) analysis reveals the formation of single-phase compound structure at room temperature. Microstructural analysis by scanning electron microscope (SEM) and EDS show that the compound has well defined grains, which are distributed uniformly throughout the sample. Detailed dielectric properties of the compound as a function of frequency and temperature are investigated.

1. INTRODUCTION

Ferroelectric compounds of tungsten bronze (TB) structure have a number of ferroelectric materials which are found to be very useful in various electronic application such as transducers, actuators, capacitors, and random access memory. Ferroelectrics ceramics associated with various properties like piezoelectric, pyroelectric and non linear optical properties¹. The TB structure consist of a skeleton frame work of distorted BO_6 octahedral sharing corners in such a way that variety of cations can be substituted at three different types of interstices (A, B, and C) of general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_4O_{30}$ ². In this TB structural formula A_1 and A_2 sites usually filled by divalent and trivalent cations, B_1 and B_2 sites by tetravalent or pentavalent cations and C site being small, often remains empty giving formula $(A_6B_{10}O_{30})$. Among them some of the members of TB structural family, such as lead barium niobate, barium sodium niobates, potassium lanthanum

niobate etc. have been found to be promising and useful for many devices³⁻⁷. A number of rare earth based compound including $Ba_5RTi_3Nb_7O_{30}$, $Ba_4R_2Ti_4Nb_6O_{30}$, $Ba_3R_3Ti_3Nb_7O_{30}$ [R= Gd,Sm,Nd,Eu,Dy,Y] of this family have been studied in order to find out TB niobate type of ceramics which show diffuse phase transition temperature above the room temperature. Effect of partial substitution of calcium in $Ba_5SmTi_3Nb_7O_{30}$ (BSTN) has been studied by Ganguly et al. However, the unavailability of sufficient literature on the effect of the substitution of Co in $Ba_5CaTi_2Nb_8O_{30}$ (BCTN) has led us to carry out the present work.

2. EXPERIMENTAL PROCEDURE

Sample of compositions $Ba_5CaCoTi_{2-x}Nb_8O_{30}$ with ($x=0.0,0.02$) were synthesized by solid state reaction method taking high purity $CaCO_3$, $BaCO_3$, CoO TiO_2 , Nb_2O_5 (all from M/s Aldrich,USA) in their stoichiometric proportions. The materials were thoroughly ground in an agate mortar and passed through sieve of appropriate fine mesh size. This powder mixture was then calcined at $1100^\circ C$ for 20 h in an alumina crucible. The calcined mixture was ground, and admixed with 5 weight % polyvinyl alcohol (M/s Aldrich,USA) as a binder and then pressed at 300 MPa into disk shaped pellets. These pellets were then sintered at $1300^\circ C$ for 10 hr. This is optimized sintering condition found from the extensive studies reported elsewhere⁸.

3. CHARACTERIZATION

X-ray diffraction of the sintered pellet was recorded by using Bruker diffractometer (model D8 Advance) in the range $10^\circ < 2\theta < 70^\circ$ with $CuK\alpha$ radiation ($\lambda = 1.5406$). The granular morphology of the sample was investigated using Scanning Electron Microscope (Jeol, JSM – 840), operated at 20 kV. Raman spectra of sample was recorded at room temperature and Raman Measurement was performed using Horiba Jobin-Yvon Lab RAM HR model equipped with a laser of 514.5 nm wavelength in the scan range of 100 to 1600 cm^{-1} .

4. RESULTS AND DISCUSSION

The Structure analysis

The tolerance factor was first suggested by Megaw to determine the stability of the perovskite structure⁹. The tolerance factor for tetragonal tungsten-bronze (TTB) structure has been deliberated by Wakiya et al. A₁¹⁰. As reported in Ref.¹¹, when the value of *t* is greater than 0.95, stable Tetragonal Tungsten Bronze (TTB) structure composite such as Ba₃La₃Ti₅Nb₅O₃₀ have been formed According to the general formula, there are two kinds of A sites for TTB: one is the A₁ site with 12-fold harmonization, which is identical to that in perovskite structure; and the other is A₂ site with 15-fold coordination. Therefore two kinds of tolerance factor for A sites can be given by the following equations:

$$t_{A1} = \frac{RA_1 + R_O}{\sqrt{2}(RB + R_O)}$$

$$t_{A2} = \frac{RA_2 + R_O}{\sqrt{(\sqrt{23} - 12\sqrt{3})(RB + R_O)}}$$

where, R_A, R_B, and R_O are the ionic radii of the A, and B-site ions and the O²⁻ ion, respectively. In order to find better relationship between stability and tolerance factor of tungsten bronze structure, combination of these two types of tolerance factor can be expressed as:

$$t = \frac{t_{A1} + 2t_{A2}}{3}$$

Using above relation and oxidation state ionic radii reported by Shannon¹² the calculated value of tolerance factor is 1.02, which show BCTN has stable TB structure.

Fig. 1 shows the XRD patterns of the studied samples. It is observed that single phase tungsten-bronze structure is obtained in both the samples. All peaks are indexed and there is no evidence for secondary phase present. In cobalt doped BCTN ceramic sharp and single diffraction peaks indicate better homogeneity and crystallization.

SEM micrographs of the sample shown in Fig. 2 Both compound has homogenous microstructure.

The average crystallite size was calculated using the Debye-Scherrer method from the broadening of the diffraction line using the expression

$$d = 0.9 \lambda / \beta \cos\theta$$

where λ is the wavelength of the CuK α radiation, β is the FWHM of the diffraction peak and θ is the Bragg diffraction angle. It is observed that the average particle size increases with cobalt doping. The grain size of Co doped BCTN ceramic in range 5 μ m and 10 μ m increases as compared to cobalt free BCTN ceramic. Also, there is presence of both spherical and

cylindrical grains in cobalt substituted compound as compared to only spherical grains in cobalt free specimen.

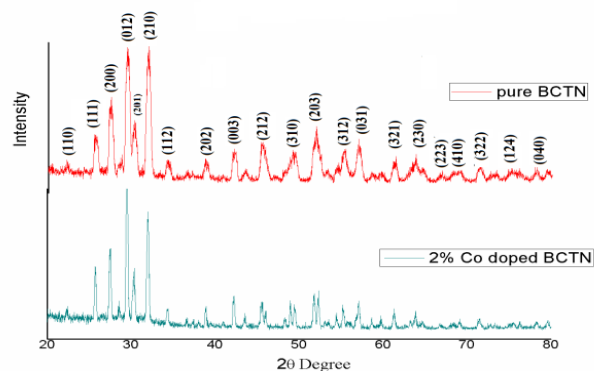


Fig. 1: X-ray diffraction patterns of Ba₅CaTi_{2-x}Co_xNb₈O₃₀ (x=0.0,0.02) compounds

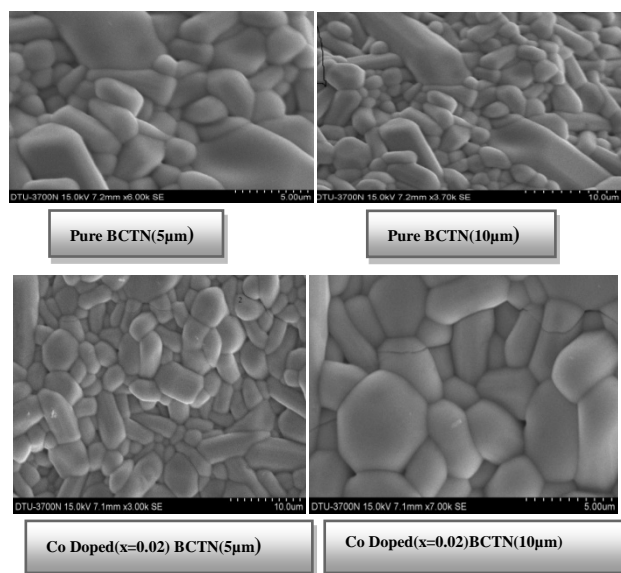


Fig. 2. SEM micrographs of Ba₅CaTi_{2-x}Co_xNb₈O₃₀ (x=0.0, 0.02) samples for 5 μ m and 10 μ m

Room temperature Raman spectra for BCTN and BCCTN sintered at 1300°C is observed at wavelength 514.5 nm.

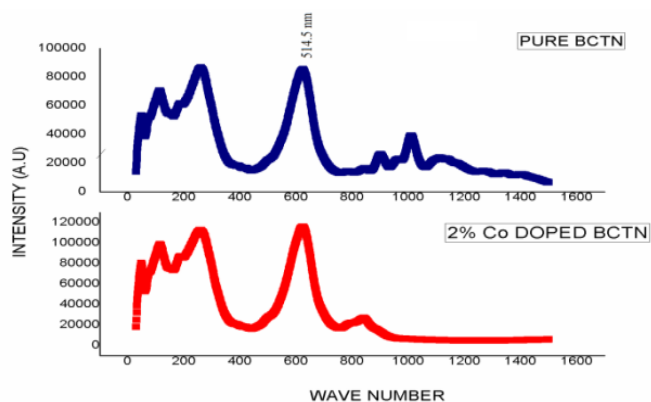


Fig. 3: Raman spectra of $\text{Ba}_5\text{CaTi}_{2-x}\text{Co}_x\text{Nb}_8\text{O}_{30}$ ($x=0.0, 0.02$) samples at 514.5nm

5. CONCLUSION

X-ray diffractograms confirm the formation of single phase and stable TB structure in BCTN and BCCTN compound. Microstructural studies reveal that there is an increase in grain size on substitution of cobalt and room temperature raman spectra is observed at wavelength 514.5 nm.

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