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### **Synthesis and Structural Behavior of Co Doped Ba(Ti<sub>0.85</sub>Sn<sub>0.15</sub>)O<sub>3</sub>**

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#### **ABSTRACT**

Effect of cobalt (Co) substitution on structural behavior of Ba(Ti<sub>0.85</sub>Sn<sub>0.15</sub>)O<sub>3</sub> has been studied. Compositions with  $x = 0.01$  and  $0.03$  in the system Ba(Ti<sub>0.85-x</sub>Co<sub>x</sub>Sn<sub>0.15</sub>)O<sub>3</sub> were prepared by solid state ceramic method. X-ray Diffraction studies confirmed the formation of cubic single phase solid solutions at room temperature. Crystallite size determined by X-ray line broadening and by Scanning Electron Micrographs show good agreement.

**KEY WORDS:** High Dielectric Constant, Diffuse Phase Transition, Scanning Electron Micrograph, X-ray Diffraction, Solid State Ceramic Route

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## **INTRODUCTION**

Ferroelectric relaxors have many potential applications as materials having high dielectric constant,  $\epsilon_0$ , as hysteresis free actuators and high performance sensors etc.<sup>1, 2</sup>. Relaxor ferroelectrics exhibit a diffuse i.e. a broad peak at a particular temperature  $T_m$  in their  $\epsilon_0$  vs  $T$  plots. Its position shifts to higher temperature with increasing frequency of measurement. Pronounced variation in the value of  $\epsilon_0$  is observed around peak maxima  $T_m$ . Lead-based perovskite oxides having more than one type of ions occupying the equivalent six co-ordinated crystallographic sites are well known for exhibiting relaxor properties<sup>3</sup>. But these oxides are toxic in nature. Therefore at present there is lot of interest in developing lead free compositions having lower temperature coefficient of dielectric constant near the peak temperature, which should be preferably around ambient conditions for above mentioned applications. Barium tin titanate  $Ba(Ti_{1-x}Sn_x)O_3$  is one such potential system which has been studied extensively<sup>4-7</sup>. Diffuse Phase Transition (DPT) behavior is different from both the normal ferroelectrics and relaxor ferroelectrics<sup>8</sup>. It is characterized by a broad maxima in  $\epsilon_0$  vs  $T$  plots whose position is independent of frequency of measurement.

$Nb_2O_5$ ,  $CoO$ ,  $NiO$ ,  $MnO$  and some rare earth oxides have been doped in  $BaTiO_3$  to improve its temperature stability<sup>9, 10</sup>. These additives broaden/diffuse the sharp dielectric constant peak at  $120^\circ C$  observed in  $BaTiO_3$ <sup>11-15</sup>. Dopant like  $CoO$  inhibits the grain growth during sintering and form a so called "core-shell" structure inside the grain to limit the movement of domain walls<sup>16</sup>. Keeping in mind the significant change in the properties of  $BaTiO_3$  due to substitution of  $Sn$  and  $Co$  independently, it was considered worthwhile to study the effect of their codoping on  $Ti$  site on the structural behavior of  $BaTiO_3$ . For this purpose, the most technologically potential composition,  $Ba(Ti_{0.85}Sn_{0.15})O_3$ , having highest dielectric constant in the system  $Ba(Ti_{1-x}Sn_x)O_3$  is chosen<sup>18-19</sup>. Results of these investigations have been reported in this paper.

## **EXPERIMENTAL PROCEDURE:**

Samples were prepared by solid state ceramic method using  $BaCO_3$  (Thomas Baker, India),  $TiO_2$  (Reidel Chemicals, India),  $SnO_2$  (Himedia, India) having purity  $> 99.5\%$  and cobalt oxalate (Himedia, India) with purity  $> 99.99\%$  as raw materials. Appropriate amounts of these chemicals were mixed in a ball mill for six hours using agate jars & agate grinding media and acetone as a mixing medium. For calcination the mixed powders were dried, ground for half an hour and then kept at  $1523K$  for 6 hours in a platinum crucible. Calcined powders were ground and mixed uniformly with a few drops of 2% solution of polyvinyl alcohol as a binder. Cylindrical pellets

having thickness in the range 1-2 mm and diameter 12 mm were prepared by pressing the uniformly mixed powder in a hydraulic press under an optimum load of 65 kN. These pellets were kept on a platinum foil and heated at a rate of 2K/min upto 773 K and kept at this temperature for about two hours to burn off the binder completely. Thereafter the temperature was raised at a rate of 4K/min to the sintering temperature 1623 K. At this temperature, the samples were sintered for 6 hours, where both sintering as well as solid state reaction amongst various constituents take place.

Powder X-ray diffraction patterns were recorded by X-ray Diffractometer (Rigaku Rotaex RTP 300) employing  $\text{CuK}_1$  radiation with a Ni filter using grounded powder of sintered pellets. Archimedes principle was used for determination of density of the sintered pellets.

For Scanning Electron Micrograph (SEM) sintered pellets of each composition were polished using emery papers of grade 0/0, 1/0, 2/0, 3/0, 4/0 and 5/0 successively. One of the polished pellet is further polished on a velvet cloth with diamond paste of the order of  $1\mu\text{m}$  and  $1/4\mu\text{m}$ . For microstructural studied the pellets were cleaned using distilled water followed by methanol. Then they were chemically etched. Chemically etched pellets were coated with gold using “Hummer” sputtering coating unit and micrographs were taken using “Hitachi-S-4700, Field Emission SEM (FESEM)”

## **RESULTS AND DISCUSSION**

### ***(a) Crystal Structure and Density***

Attempts were made to prepare compositions with  $x = 0.00, 0.01, 0.03$  and  $0.05$ , abbreviated as BTS, BTCS1, BTCS3 and BTCS5 in the system  $\text{Ba}(\text{Ti}_{0.85-x}\text{Co}_x\text{Sn}_{0.15})\text{O}_3$ . Powder XRD patterns of the samples show that compositions with  $x = 0.00, 0.01$  and  $0.03$  are single phase solid solution (Figure 1). XRD pattern of the composition with  $x = 0.05$  contains lines of constituent oxides. Solid solution forms for  $x \leq 0.03$  among the studied compositions. XRD data of the compositions with  $x = 0.00, 0.01$  and  $0.03$  could be indexed on the basis of a cubic unit cell. Powder XRD data of these compositions were compared with JCPDS Card 31-0174. Lattice parameters were calculated by means of the UNITCELL-97 program<sup>20-21</sup>. Lattice parameter for all the three compositions is given in Table 1.

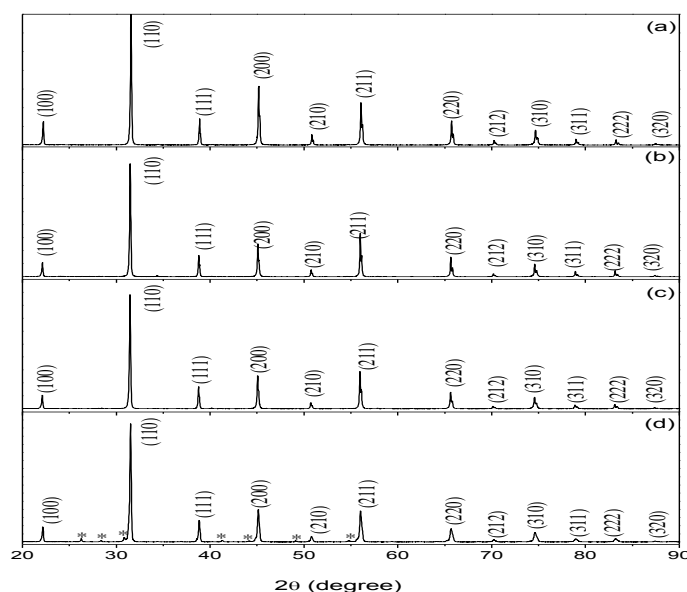


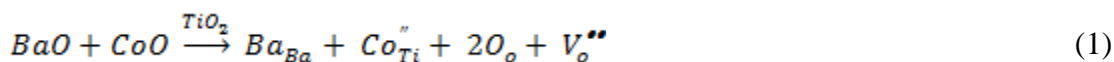
Figure No.1: XRD patterns for various compositions with x (a) 0.00 (b) 0.01 (c) 0.03 and (d) 0.05 in the system  $\text{BaTi}_{0.85-x}\text{Sn}_{0.15}\text{Co}_x\text{O}_3$  prepared by solid state ceramic route

Table1: Composition, lattice parameter, theoretical density, experimental density and percentage porosity for samples in the system  $\text{Ba}(\text{Ti}_{0.85-x}\text{Co}_x\text{Sn}_{0.15})\text{O}_3$

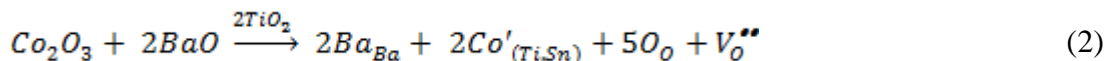
Composition	Lattice Parameter( $\text{\AA}$ )	Theoretical Density ( $\text{gm/cm}^3$ )	Experimental Density( $\text{gm/cm}^3$ )	% Porosity
BTS	4.0197	6.23	5.53	11.0
BTCS1	4.0206	6.24	5.79	7.0
BTCS3	4.0219	6.23	5.61	10.0

Lattice parameter is slightly larger for cobalt doped samples than that of BTS. This indirectly shows that cobalt ions exist mostly in  $\text{Co}^{2+}$  state. (Ionic radius of  $\text{Co}^{2+}$  and  $\text{Ti}^{4+}$  are  $0.735 \text{ \AA}$  and  $0.605 \text{ \AA}$  respectively<sup>22</sup>. Presence of cobalt in +3 oxidation state in slight amount cannot be ruled out. Oxidation state of Co needs to be confirmed by using XPS which is planned to do in near future. Theoretical density determined from the unit cell volume and molecular weight of the compound. Theoretical density, experimental density and percentage porosity are given in Table 1. Porosity present in the three compositions is around 10%. Densification of samples improves with increasing

Co doping i.e. x. On doping  $\text{Co}^{2+}/\text{Co}^{3+}$  at  $\text{Ti}^{4+}$  site, oxygen vacancies are produced according to the reaction



Or



where all the species are written in accordance with Kröger Vink notation of defects<sup>23</sup>. Presence of  $\text{V}_o^{\prime\prime\prime}$  increases diffusion of  $\text{O}^{2-}$  which seems to promote densification.

Crystallite size for the powder samples was determined from the X-ray line broadening using Scherrer's formula

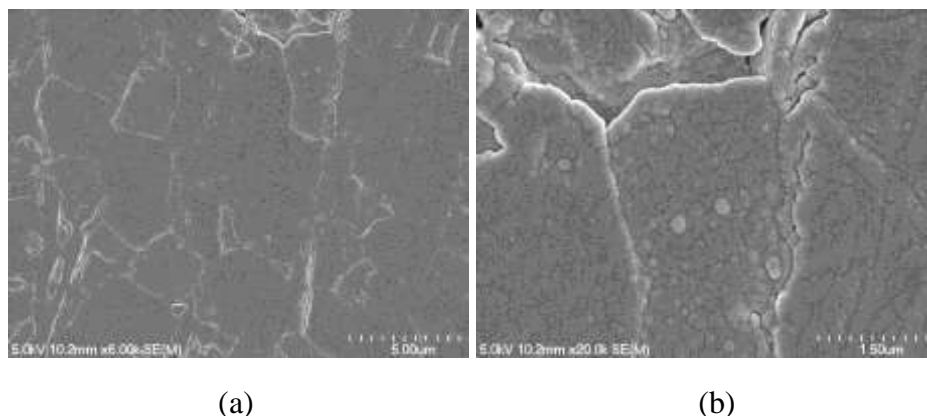
$$W = \frac{0.9\lambda}{d \cos \theta} \quad (3)$$

Where W is the width at half maximum intensity of a Bragg reflection excluding instrumental broadening,  $\lambda$  is the wavelength of the X-ray radiation and  $\theta$  is the Bragg angle. W for this sample is taken for strongest Bragg's peak corresponding to  $2\theta = 31.45$  and  $31.44$  for BTCS1 and BTCS3 respectively. The average particle size was found to be  $\sim 570$  and  $550$  nm for BTCS1 and BTCS3 respectively.

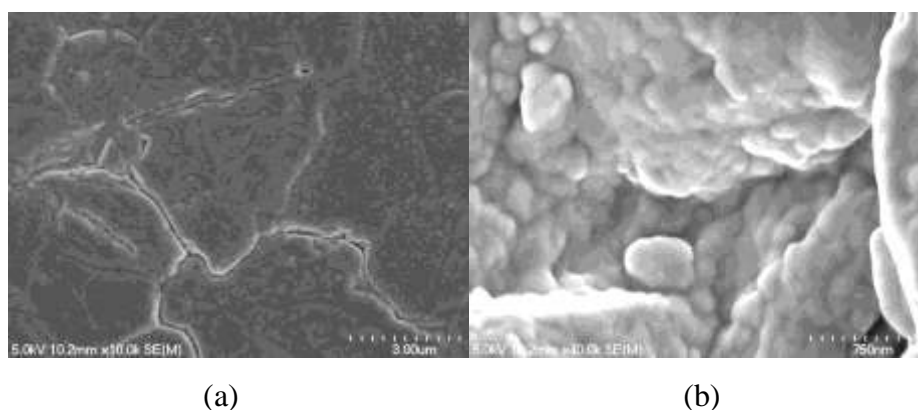
**(b) Microstructure:**

Scanning Electron Micrograph for the samples BTCS1 and BTCS3 at different magnifications are shown in figures respectively. It is noted from the figures that dense microstructure is obtained. Upto a magnification in the range 6-10 k pores, grains with size ranging from 2-5  $\mu\text{m}$  and distinct boundaries are observed. When the magnification of the microscope is increased above 20k subgrain microstructure within bigger grains is observed. Each grain is composed of large number of smaller grains(subgrains). Average subgrain size determined by linear intercept method from scanning electron micrograph has been found to be in the range 220-310 nm for BTCS1 and 100-120 nm for BTCS3 respectively. This shows reasonably good agreement with size determined from the X-ray line broadening using equation (3). From the microstructure study it appears that during the initial stage of sintering few hundred nm size grains formed through reaction

among the constituent compounds. At later stage during sintering there is no or negligibly small grain growth. However these grains agglomerate to form larger grains. Because of the process of agglomeration the sintering efficiency is less and porosity does not decrease. Percentage porosity of these samples is in the range 7-10.



**Figure2: Scanning Electron Micrographs for BTCS1 at different magnifications**



**Figure3: Scanning Electron Micrographs for BTCS3 at different magnifications**

## **CONCLUSION:**

Compositions BTS, BTCS1 and BTCS3 are single phase solid solutions having cubic crystal structure. Densification has improved due to Co doping. Scanning Electron Micrographs also show dense microstructure for these compositions.

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