

# Studies of structural, morphological and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ powders synthesized via cost-effective co-precipitation method

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## Abstract

The experimental results on the studies of structural, morphological and dielectric properties of  $Ba_{1-x}Sr_xTiO_3$  powders synthesized via cost-effective co-precipitation method were presented herein. Strontium doped  $BaTiO_3$  powders ( $Ba_{1-x}Sr_xTiO_3$  where  $x = 0, 0.25, 0.5, 0.75$  and  $1$ ) prepared by co-precipitation method were sintered at  $1000\text{ }^\circ\text{C}$  for 6 hours at the rate of  $5^\circ\text{C min}^{-1}$ . The structural and morphological properties were studied using x-ray diffraction and scanning electron microscopy respectively. Moreover, the variation of dielectric constant with frequency at room temperature for different compositions of Sr was studied using the LCR precision meter bridge. There is a phase change from tetragonal ( $x=0, 0.25$ ) to cubic ( $x=0.5, 0.75$  &  $1$ ) in  $Ba_{1-x}Sr_xTiO_3$  powders with increasing Sr content as confirmed from X-ray diffractograms. The crystallite size in  $Ba_{1-x}Sr_xTiO_3$  powders was estimated using Scherrer's equation and found to vary with strontium addition.

**Keywords:**  $Ba_{1-x}Sr_xTiO_3$ , co-precipitation, XRD, SEM, dielectric property

## 1. Introduction

Recently, perovskite materials are of wide importance due their unique ferroelectric, piezoelectric and thermoelectric properties. Amongst all these materials, barium titanate ( $BaTiO_3$ ) in particular attracts a significant attention because of their outstanding properties, viz. low dielectric loss, high permittivity

and dielectric tunable properties. It exhibits the rhombohedral, orthorhombic, tetragonal and cubic crystal structure at different temperatures. Tetragonal phase possesses room temperature stability and exhibits ferroelectric, piezoelectric and thermoelectric properties, while cubic phase has high-temperature stability with paraelectric property [1]. Barium titanate ( $BaTiO_3$ ) and its related compounds have been extensively used in the preparation of high dielectric capacitors, positive temperature coefficient (PTC) resistors, transducers and ferroelectric memories [2]. It has been observed that that the curie point of barium titanate is decreased linearly by the substitution of strontium for barium and desirable properties can be obtained such as high dielectric permittivity and low loss factor at room temperature [2, 3]. This is possible only due to the nearly same ionic radii of  $Ba^{2+}$  and  $Sr^{2+}$  as  $1.49$  and  $1.32\text{ \AA}$  respectively. Therefore, barium-strontium titanate ( $Ba_{1-x}Sr_xTiO_3$ ) has been widely studied for various device applications because of its high dielectric constant and composition-dependent Curie temperature [4]. In general,  $Ba_{1-x}Sr_xTiO_3$  powders were prepared using the solid-state reaction followed by calcinations at high temperatures in the range of  $1300\text{-}1450^\circ\text{C}$  [5, 6]. Further, other preparation routes for the synthesis of  $Ba_{1-x}Sr_xTiO_3$  such as the hydrothermal [7], co-precipitation [8], the metal organic solution deposition (MOSD) [9] and the sol-gel methods [10, 11] have been reported by elsewhere. It is widely recognized that chemical synthesis methods are able to provide high chemical purity, precise composition, uniform microstructure and a lower formation temperature of the perovskite

phase based on molecular scale mixing in the preparation of the precursor. Amongst all the chemical routes, the co-precipitation method is a simple eco-friendly method and has advantages like, single heat treatment, low cost starting materials and solutions, no need of using complexing or chelating agent. Therefore, in this work attempts were made to synthesize  $Ba_{1-x}Sr_xTiO_3$  powders via co-precipitation method and to study the influence of strontium substitution i.e.  $x=0, 0.25, 0.5, 0.75, 1$  on their structural, morphological and dielectric properties.

**2. Materials and Methods**

The starting materials used for the present synthesis of  $Ba_{1-x}Sr_xTiO_3$  were AR purity barium nitrate [ $Ba(NO_3)_2, 99.9\%$ ], strontium nitrate [ $Sr(NO_3)_2, 99.9\%$ ] and titanium-isopropoxide [ $Ti\{OCH(CH_3)_2\}_4$ ]. Nitric acid ( $HNO_3$ ) and ammonia ( $NH_3$ ) were used for obtaining the precipitate. All these chemicals

were purchased from SD Fine. Deionized (DI) water and methanol (MeOH) were used as solvents.

All compositions in the series  $Ba_{1-x}Sr_xTiO_3$  (with  $x = 0.0$  to  $1$  in steps of  $0.25$ ) were synthesized by the co-precipitation method. For the preparation of  $Ba_{1-x}Sr_xTiO_3$  powders, stoichiometric solutions of barium nitrate and strontium nitrate dissolved in water, titanium-isopropoxide dissolved in methanol with few drops of nitric acid (to obtain clear solution), were initially prepared. Both the solutions were mixed together (1:1 molar ratio) again and a clear solution was obtained. All cations were then co-precipitated using  $NH_3$  solution as a precipitating agent. The precipitation was washed with water and dried for 8 hours to get white shining powder. The white powder formed by drying the precipitate was calcined at  $1000^\circ C$  for 6 h with  $5^\circ C\ min^{-1}$  heating rate to decompose into well crystalline phase.

For the structural studies of  $Ba_{1-x}Sr_xTiO_3$  powder, the powder X-ray diffraction (XRD) (Philips Model PW 3710) using  $Cr\ K_\alpha$  radiation ( $\lambda = 2.2879\ \text{\AA}$ ) was performed. The crystallite size was determined from the measured full width half maxima (FWHM) for the most intense peak by using the Debye Scherrer formula [12];

$$\text{Crystallite size} = 0.9\lambda/\beta\cos\theta \quad \dots (1)$$

Where, the wavelength of  $Cr\ K_\alpha$  radiation  $\lambda = 2.2879\ \text{\AA}$ ,  $\beta$  is the integral width in radians.

The X-ray density ( $D_x$ ) or theoretical density was estimated by using the relation [11],

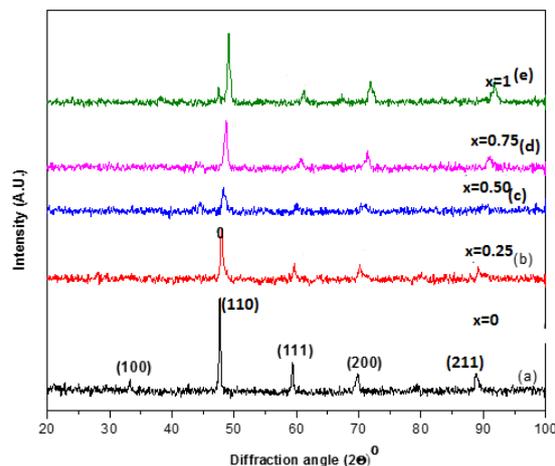
$$X\text{-ray density } (D_x) = \frac{\sum A}{N \times V} \quad \dots (2)$$

Where, A is the sum of the atomic weights of the atoms in the unit cell, V is the volume of the unit cell and N is the Avogadro's number.

The morphological analyses of  $Ba_{1-x}Sr_xTiO_3$  samples were carried out using scanning electron microscope (SEM: Model JEOL-JSM 6360). From SEM micrographs the grain size (D) was calculated by using the line intercept method. Also, the dielectric constant of these samples was measured as a function of frequency at room temperature using the LCR precision meter bridge (Model HP 4284A).

**3. Results and Discussion**

Figure 1 depicts the X-ray diffractograms of  $Ba_{1-x}Sr_xTiO_3$  samples ( $x=0, 0.25, 0.5, 0.75$  &  $1$ ) synthesized by co-precipitation method. The samples with  $x \leq 0.25$  and  $x \geq 0.5$  exhibit tetragonal and cubic crystalline structures respectively. These are confirmed from the JCPDS data card number as  $BaTiO_3$  – PDF #79-2265 (for  $x=0$ ),  $Ba_{0.5}Sr_{0.5}TiO_3$  - PDF #39-1395 (for  $x=0.5$ ) and  $SrTiO_3$ - PDF #79-0176 (for  $x=1$ ). The change in phase from tetragonal to cubic is due increasing content of Sr. The presence of  $Sr^{2+}$  in the  $Ba^{2+}$  site induced a new equilibrium denoting a shrinkage of both axis parameters in which the c-axis shrink more than a-axis. The shrinkage of the axis can be due to the smaller ionic radius of  $Sr^{2+}$  ( $1.32\ \text{nm}$ ) than that of  $Ba^{2+}$  ( $1.49\text{nm}$ ). This signifies that the more the  $Sr^{2+}$  incorporated in  $Ba^{2+}$  sites, the more cubic the structure [13]. Furthermore as strontium doping increased, the diffraction peaks slightly shift toward higher angles as seen from fig.1. The  $BaTiO_3$  lattice is contracted by incorporation of Sr and then a lattice distortion would be induced [14].



**Fig. 1** X-ray diffractograms of  $Ba_{1-x}Sr_xTiO_3$  samples Table 1 represents the Crystallite size, lattice parameters and X-ray density of various of  $Ba_{1-x}Sr_xTiO_3$  samples. The crystallite size was determined from the measured FWHM for the most intense peak by using the Debye Scherrer formula (equation 1) and the X-ray density using the formula given in equation 2. From the table 1, it is clear that the average crystallite size decreased with increase of  $x \leq 0.5$  and then increased for  $x \geq 0.75$ . X-ray density decreases

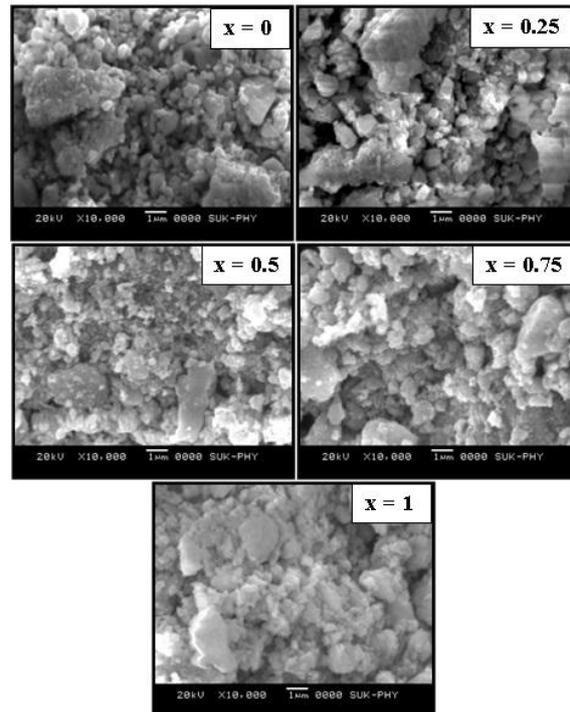
with increasing Sr content due to smaller ionic radius of Sr<sup>2+</sup> (1.32 nm) than that of Ba<sup>2+</sup> (1.49nm). So with increasing Sr content the volume of unit cell decreases which cause to reduce the X-ray density.

**Table 1** Crystallite size, lattice parameters and X-ray density of various of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> samples

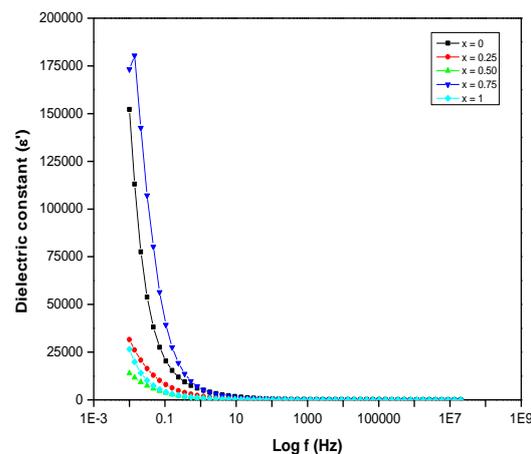
Sr content x	Crystallite size (nm)	Lattice Parameters		X-ray Density 'Dx' (gm/cm <sup>3</sup> )
		a=b (Å)	c (Å)	
0	41.76	3.999	4.009	6.03
0.25	26.83	3.973	3.983	5.81
0.5	19.41	3.958	3.958	5.57
0.75	25.16	3.924	3.924	5.38
1	28.86	3.899	3.899	5.13

The surface morphologies of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> powders with x = 0, 0.25, 0.50, 0.75, 1 sintered at 1000°C for 6h are shown in fig.2. The micrograph show agglomerated grains with different shapes and sizes. The average grain size was calculated by line intercept method. The grain size increases with increasing strontium concentrations appreciably from 0.4µm(x = 0.0) to 1.75µm(x = 1). The increasing grain size with increasing strontium may be attributed to higher grain growth rates from the more rapid diffusion of the Sr<sup>2+</sup> ion, which has a smaller ionic radius than Ba<sup>2+</sup> [15].

Fig.3 shows the variation of dielectric constant (ε') with the frequency. It is observed that with increasing frequency the dielectric constant decreased rapidly and remained constant at higher frequencies. The high value of dielectric constant observed at low frequencies is explained on the basis of space charge polarization due to inhomogeneous structure i.e. porosity, grain structure and impurities. At higher frequencies dielectric constant remains independent of frequency due to inability of dipoles to follow the applied field. The electronic exchange between Ti<sup>4+</sup> and Ti<sup>3+</sup> ions give rise to n-type carriers, however, the mobility of p-type carrier is smaller than that of n-type carriers. At higher frequencies, dielectric loss is reduced and dipole contributes to the polarization [16].



**Fig. 2** SEM micrographs of various of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> samples



**Fig. 3** Variation of dielectric constant with frequency of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> samples

#### 4. Conclusions

The influence of strontium concentration on the structural, morphological and dielectric properties of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> was studied successfully. The average crystallite size and the X-ray density decreased with increase of strontium concentration (x≤0.5). The dielectric constant reduced with increment in frequency and remained constant at higher frequencies. The SEM images clearly manifested the agglomerated grains with various shapes and sizes.

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