

## Systematic Study Of Structural, Transport and Dielectric Properties of $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$ Synthesized by Chemical Method

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### Abstract

$\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$ , where  $x=0.00, 0.25, 0.75$  and  $1.00$  have been synthesized by high temperature ( $1100^\circ\text{C}$ ) solid state reaction technique. The structural information has been obtained using XRD technique. Investigations of XRD indicates the formation of single phase tetragonal perovskite for  $x=0.00, 0.25$  and cubic phase for  $x=0.75$  and  $1.00$ . When  $x=0.5$ , it is observed that perovskite structure is not very clean at  $1100^\circ\text{C}$ , may be due to lower sintering temperature. For pure  $\text{BaTiO}_3$  the measurement of dielectric constant as a function of temperature shows broad maximum amplifying a diffuse phase transition. The dielectric constant 'k' decreases systematically with increase in strontium content. The substitution of  $\text{Sr}^{2+}$  ion at  $\text{Ba}^{2+}$  site decreases the unit cell size and hence the polarization is reduced. Reduction in ionic mass of  $\text{Ba}^{2+}$  site lowers the anharmonicity in the potential energy of the mean separation between ion which is responsible for loss factor. The loss factor  $\tan\delta$  decreases with increase in strontium content.

**Key words:** Solid State reaction, Perovskite, XRD, Dielectric studies.

### Introduction

The study of mixed-metal-oxide systems has been very popular for many reasons. Firstly, they are easy to prepare in the atmosphere. Secondly, many transition metal oxides exhibit multiple valencies, e.g.  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{KMnO}_4$  etc., where the valency of the manganese ion varies from II to VII. Besides, metal oxides assume a variety of structures such as fluorite, rutile, spinel, perovskite etc. Because of the adaptability of the metal oxides to different valencies and structures, it is possible to tune the properties of metal oxides and their combinations.

The fabrication of perovskites (oxides with the formula  $\text{ABO}_3$ ) is of great scientific and technological interest for their ferroelectric, pyroelectric, piezoelectric and catalytic properties[1]. The major use of these oxides, in electric[2], magnetic[3] circuit elements, in various catalysts in the prevention of corrosion[4] in tunable microwave applications[5], solid oxide electronic devices[6], important for numerous technological applications in electro-optics, waveguides laser frequency doubling, high capacity computer cells, etc.[7] have emphasized the necessity for a fundamental understanding of their properties.

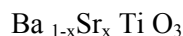
The present work is concerned with the study of  $\text{BaTiO}_3$ - $\text{SrTiO}_3$  system for their structural, electrical and dielectric behavior. The literature survey reveals that, perovskite structure titanate are frequently used as high permittivity dielectrics. Alkaline earth titanates like  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  are widely

used in microelectronic devices due to their excellent dielectric properties and high thermal stabilities[8]. BaTiO<sub>3</sub> based ceramics gave clear evidence of high resistance. Here we have synthesized Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub>, by using ceramic method, where x=0.00, 0.25, 0.50, 0.75, 1.00. Investigation on their structural, transport and dielectric properties was carried.

## Experimental

Ba<sub>x</sub>Sr<sub>(1-x)</sub>TiO<sub>3</sub> is prepared by well known ceramic method. This method is probably the easiest to use with little knowledge of chemistry required and hence is the widely used one. Moisture-free and high-purity oxide materials in the proportions required by the final product were mixed with the help of agate mortar and pestle for many hours together. The mixture is pressed into a suitable shape before presintering (calcining).

It was aimed to prepare compounds having formula Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> Where x is chosen as 0.00, 0.25, 0.50, 0.75, 1.00. Samples were prepared by conventional ceramic method. Fine powders of BaCO<sub>3</sub>, SrCO<sub>3</sub>, TiO<sub>2</sub> of high purity (A.R. grade) was taken as the starting material. All powders were dried for two hours at 200°C to remove possible traces of moisture. BaCO<sub>3</sub> + TiO<sub>2</sub> and SrCO<sub>3</sub> + TiO<sub>2</sub> were calcined at 600°C resulting in BaTiO<sub>3</sub> and SrTiO<sub>3</sub>. These powders were mixed in the following proportions,



Where x takes values 0.00 (19.735 g BaCO<sub>3</sub> + 7.99 g TiO<sub>2</sub>), 0.25 (2.5 g SrTiO<sub>3</sub> + 7.5 g BaTiO<sub>3</sub>), 0.50 (5 g SrTiO<sub>3</sub> + 5 g BaTiO<sub>3</sub>), 0.75 (7.5 g SrTiO<sub>3</sub> + 2.5 g BaTiO<sub>3</sub>), 1.0 (14.763 g SrCO<sub>3</sub> + 7.99 g TiO<sub>2</sub>). In order to ensure the homogeneous mixture, the powders were mixed thoroughly in the agate mortar for several hours in the acetone medium. The mixtures were presintered at 600 °C for 6 hrs. Presintered mixtures were then crushed in to fine powder and second presintering was given at 900°C for 6 hrs. Once again mixtures were crushed in to fine powders and mixed in Polyvinyl acetate binder. The pellets of 13 mm diameter and 1 to 2 mm thickness were prepared under 5 ton pressure. The pellets were finally sintered at 1150°C in the programmable micro wave furnace (Phoenix CEM innovators USA) with ramp time 4 hrs and constant temperature 1150°C for 2 hrs. The cooling was done slowly & steadily to the room temperature. These samples were characterized by XRD for structural analysis. By measuring capacitance and impedance by LCR meter, transport and dielectric properties were studied.

## Result Discussion

### XRD Studies

X-ray diffraction (XRD) is a well-known technique for the structural characterization of the materials. The x-ray diffraction data of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> were obtained with microcomputer controlled JEOL-JDX 8030 X-ray diffractometer. Fig. 1-5 Shows XRD patterns of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub>

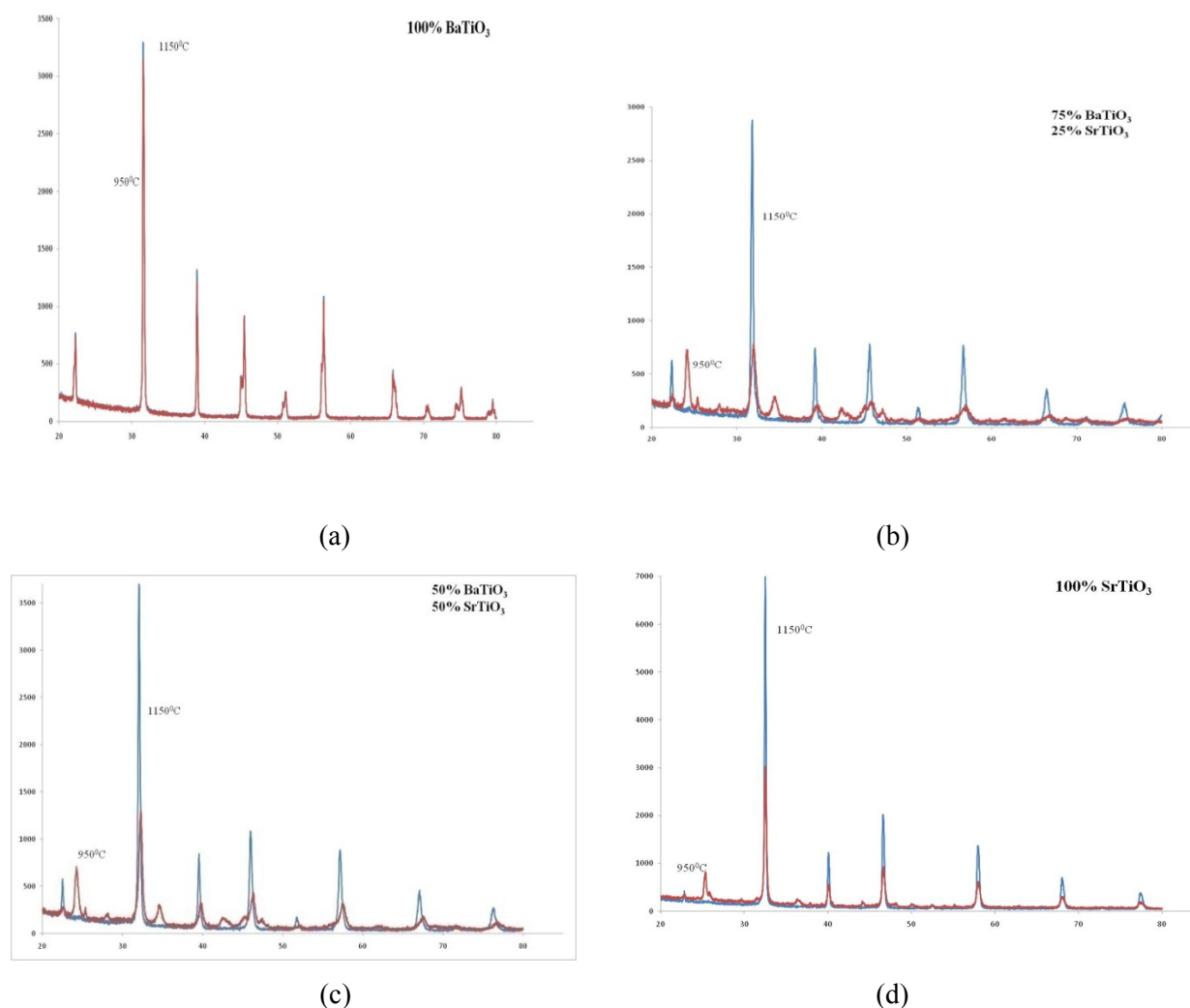


Fig. (1-5) XRD Patterns of  $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$  as increasing percentage of Sr from 0 to 100.

Observed and calculated 'd' values are in agreement with the reported 'd' values. For material  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ , percentage of x (Sr) in the mixture is varied steps as 0, 25, 50, 75 and 100. When  $x=0$ , and 0.25 X-ray diffraction pattern confirms tetragonal crystal structure. As amount of x (Sr) increased in the mixture from the percentage such as 25, 50, 75 the position of most intense peak was shifted from  $31^\circ$  to  $32^\circ$  which also confirms variation of percentage of Sr. Because in pure  $\text{BaTiO}_3$  (tetragonal) most intense peak is generally observed at an angle of  $31.495^\circ$  and for pure  $\text{SrTiO}_3$  it is observed at  $32.4369^\circ$ . All the samples shows position of most intense peak is in between  $31.495^\circ$  and  $32.4369^\circ$ . When  $x=0.5$  mix phase is observed and it is also reported that the perovskite structure is very clean only at  $1400^\circ\text{C}$  for the solid state method. When  $x=0.75, 1.00$  cubic crystal structure was confirmed.

From values of lattice parameter it is observed that, as percentage of x (Sr) increased in mixture of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  from 0 to 100, value of lattice parameters is decreased from 3.9950 to 3.9050 as shown in the table 1.

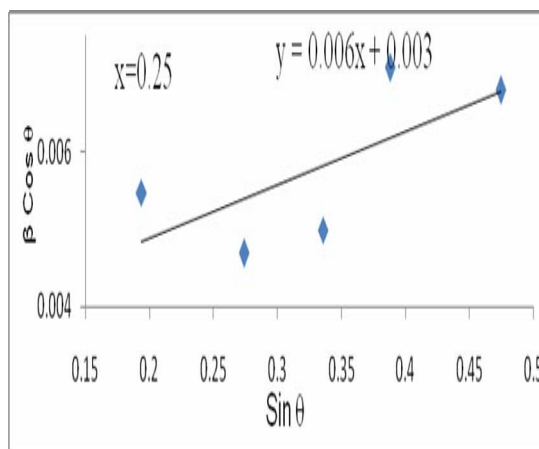
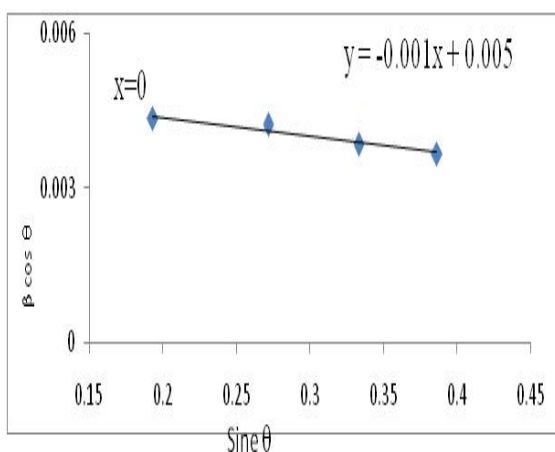
Table 1 Lattice parameter variation of  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$

Sr. No.	Value of x	Name of the sample	Lattice parameter A.U.	Particle size A.U.
1	x=0	$\text{BaTiO}_3$	3.9950	3.1910
2	x=25	$\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$	3.9758	2.5301
3	x=50	$\text{Ba}_{0.50}\text{Sr}_{0.50}\text{TiO}_3$	3.9458	2.5204
4	x=75	$\text{Ba}_{0.25}\text{Sr}_{0.75}\text{TiO}_3$	3.9159	2.7621
5	x=100	$\text{SrTiO}_3$	3.9050	2.9788

Particle size was calculated by well-known Scherrer's formula.

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

Where, D is the particle size,  $\lambda$  is the wavelength of x-rays used,  $\beta$  is full width at half maxima of peak in radians, and  $\theta$  is Bragg's angle. The value of calculated particle size is listed in the table 1. As explained in [9] in the plot of  $(\beta \cos \theta)$  Vs  $(\sin \theta)$  is drawn for different reflections where  $\beta$  is the full width at half maximum (FWHM) and  $\theta$  is Bragg angle. One expects a horizontal straight line of pure (natural) particle size. Thus by knowing value of  $\beta$  for five intense peaks for each sample, we have plotted  $\beta \cos \theta$  against  $\sin \theta$ . Fig. 6 show plots of  $\beta \cos \theta$  against  $\sin \theta$  for  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ . From those plots, it is clearly observed that as percentage of x (Sr) increases from 0 to 100, the slope of the plot goes on increasing from almost zero to 0.010. This is due to shifting of crystal axis from tetragonal to cubic crystal structure. One expects a horizontal straight line of pure (natural) particle size. A nonzero slope of the straight line indicates the presence of strains caused by inhomogeneous lattice distortions and/or compositional fluctuations. Alternatively a small yet non-zero slope of the straight line 'or' inclined line may indicate the presence of ordered micro-domains which are in the process of development.



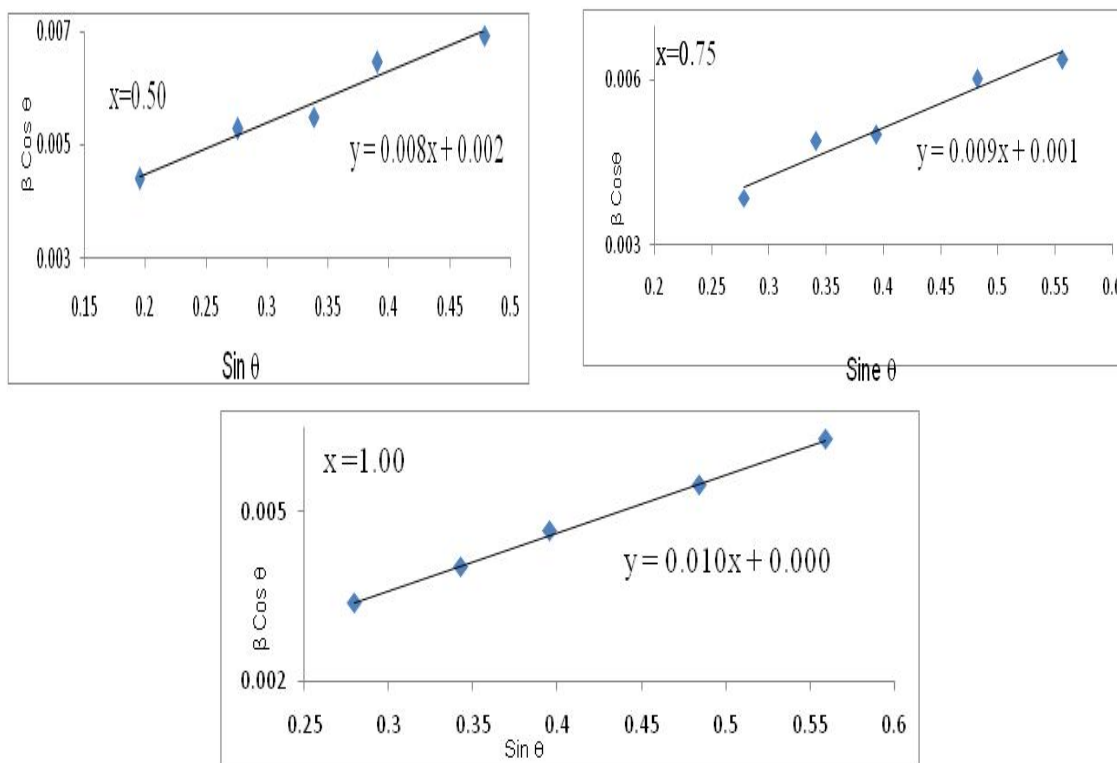


Fig 6: plots of  $\beta\cos\theta$  against  $\sin\theta$  for  $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$  as increasing percentage of Sr from 0 to 1.00.

### Transport Properties

In the measurement of electrical resistivity/ Impedance , two probe method is used. With the help of digital multimeter (APLAB MT 4080 A) Impedance (Z) at varying temperature is recorded. The first two barium rich samples ( $x=0.00$  &  $0.25$ ) are found to be tetragonal. Hence they are compared separately. Fig 7 shows the temperature dependence of impedance of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$ ,  $x=0.00, 0.25$ . Temperature dependence study shows that for pure  $\text{BaTiO}_3$ , impedance value about  $240\text{ k}\Omega$  average; remains constant up to  $280^\circ\text{C}$  and thereafter there is a sharp fall from  $240\text{ k}\Omega$  to about  $165\text{ k}\Omega$ .

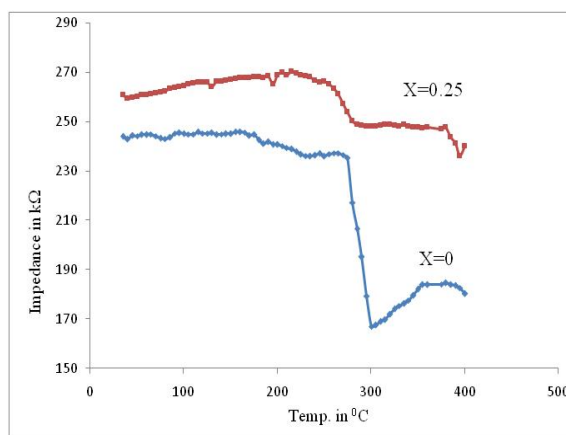


Fig .7 Plot of Temperature against impedance of  $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$  (where  $x=0.00$  and  $0.25$ )

Literature survey reveals that temperature above 110 °C structure of BaTiO<sub>3</sub> changes from tetragonal to cubic phase. At room temperature pure BaTiO<sub>3</sub> is reported as an insulator. Small overshoots at lower temperature may be due to experimental error. Structure change and the partial transition of Ti<sup>4+</sup> to Ti<sup>3+</sup> at higher temperature could be the reason to make sample little conducting,  $Ti^{4+} + e^{-} = Ti^{3+}$  gives electron concentration where, weakly bound electron which is easy to be excited to free electron. Similar kind of trend is observed when x=0.25 except, the impedance is increased little and transition temperature is blurred. Fig. 8 shows the temperature dependence of impedance, (Ba<sub>1-x</sub>Sr<sub>x</sub>)TiO<sub>3</sub> where [x=1.00, 0.75, 0.50]. It is observed that there is systematic decrease in impedance value from 230 kΩ to 70 kΩ when lighter Sr is replaced by heavier Ba. SrTiO<sub>3</sub>, BaTiO<sub>3</sub> contain electro-Active bulk and grain boundary regions, whose transport properties depend on the close control of microstructure–stoichiometric relationships [10]. BaTiO<sub>3</sub> is ferroelectric where as SrTiO<sub>3</sub> is not ferroelectric therefore Ferroelectric behavior of BaTiO<sub>3</sub> brings additional complexity in BaTiO<sub>3</sub>- SrTiO<sub>3</sub> compound, affecting the polarization and charge transport.

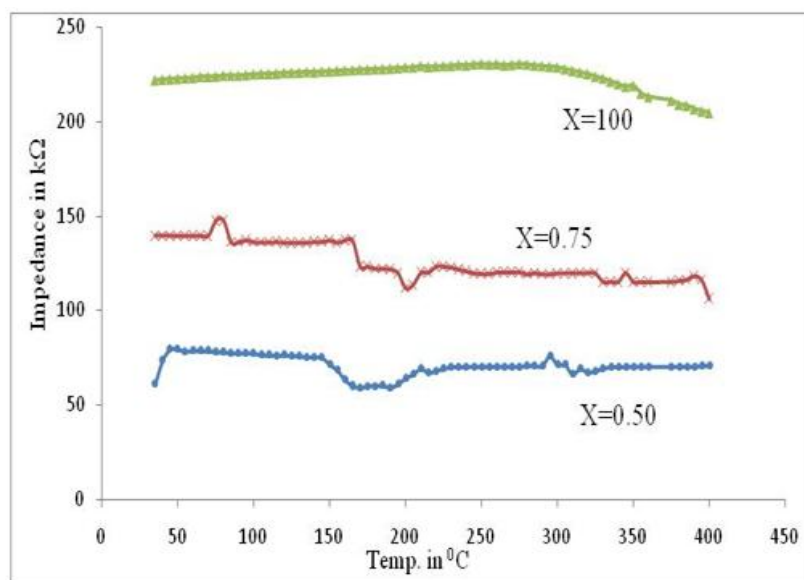


Fig. 8 Plot of Temperature against impedance of Ba<sub>(1-x)</sub>Sr<sub>x</sub>TiO<sub>3</sub> (where x= 0.50, 0.75, 1.00)

### Dielectric Studies

For measuring capacitance (C) a digital L-C-R meter APLAB MT 4080A was used. From the values of capacitance of the sample measured at 10 KHz, the dielectric constant (ε) of the sample was calculated with the formula;

$$\epsilon = C d / A.$$

Where A is the area of the pellet and 'd' be its thickness.

Relative dielectric constant  $k = \epsilon / \epsilon_0$ . The room temperature dielectric constant of (Ba<sub>1-x</sub>Sr<sub>x</sub>)TiO<sub>3</sub>, where x= 0.00, 0.25, 0.50, 0.75, 1.00 measured at 10 KHz are tabulated in Table 2.

Table 2. Dielectric constant

Composition x	Room temperature dielectric constant
0.00	170
0.25	110
0.50	130
0.75	45
1.00	30

The first two barium rich samples ( $x=0.00$  &  $0.25$ ) are found to be tetragonal. Hence they are compared separately. Fig.9 and 10 shows temperature dependence of dielectric constant and loss of pure  $\text{BaTiO}_3$  ( $x=0$ ) and  $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$  ( $x=0.25$ ). Pure  $\text{BaTiO}_3$  leads to a better crystalline structure with higher permittivity values and sharp transition temperature. The material with  $x=0.25$ , the permittivity has low values and transition temperature is blurred. The maximum value of permittivity for  $x=0.00$  is 260 at  $320^\circ\text{C}$  and for  $x=0.25$  it is about 120 and is appeared to be almost independent of temperature up to  $400^\circ\text{C}$ .

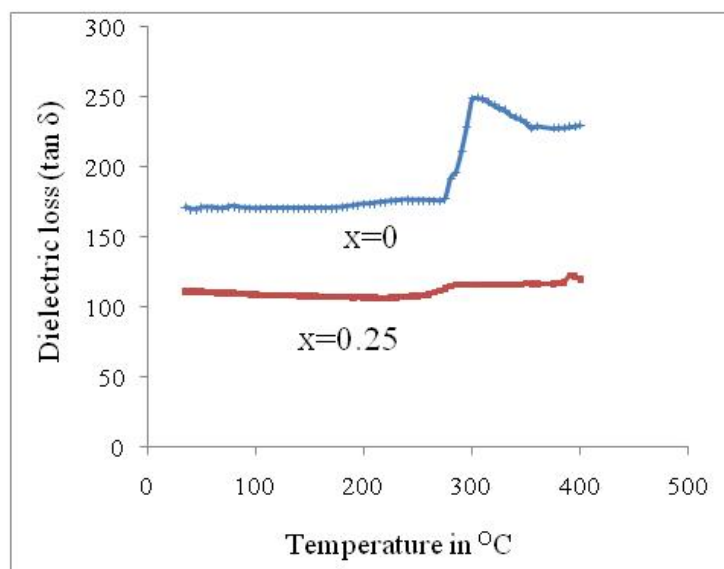


Fig. 9 Plot of Temperature against dielectric constant of  $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$  (where  $x=0.00$  and  $0.25$ ).

Fig.11 and 12 shows temperature dependence of dielectric constant and loss of pure  $\text{SrTiO}_3$  ( $x=1.00$ ),  $\text{Ba}_{0.25}\text{Sr}_{0.75}\text{TiO}_3$  ( $x=0.75$ ), and  $\text{Ba}_{0.50}\text{Sr}_{0.50}\text{TiO}_3$  ( $x=0.50$ ). The XRD patterns of pure  $\text{SrTiO}_3$  ( $x=1.00$ ) and  $\text{Ba}_{0.25}\text{Sr}_{0.75}\text{TiO}_3$  ( $x=0.75$ ) is found to be cubic, whereas  $\text{Ba}_{0.50}\text{Sr}_{0.50}\text{TiO}_3$  ( $x=0.50$ ) shows existence of impurities, including  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{TiO}_2$  [11] and difficult to be completely eliminated from the sample when reacted in 1:1 molar ratio.



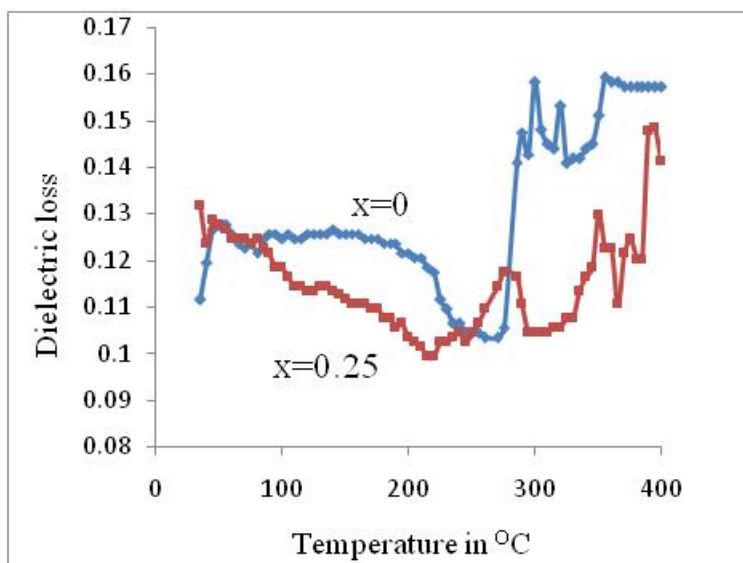


Fig 10 Plot of Temperature against dielectric loss of  $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$  (where  $x= 0.00$  and  $0.25$ )

Lower sintering temperature ( $1150^\circ\text{C}$ ) may be one of the reasons for not having clean perovskite structure. The dielectric constant of pure  $\text{SrTiO}_3$  has the lowest value as compared to dielectric constant for mixed crystal. Pure  $\text{SrTiO}_3$  showed an almost flat dielectric relaxation. The increment in dielectric constant with the increment of Ba may be due to the fact that soft mode frequency decreases with the increase of Ba in  $\text{SrTiO}_3$ [9] and also may be due to increase in the unit cell size thereby increasing polarization to some extent. Fig.10 shows temperature dependence of dielectric loss ( $\tan \delta$ ) of pure  $\text{SrTiO}_3$  ( $x=1.00$ ),  $\text{Ba}_{0.25}\text{Sr}_{0.75}\text{TiO}_3$  ( $x=0.75$ ) and,  $\text{Ba}_{0.50}\text{Sr}_{0.50}\text{TiO}_3$  ( $x=0.50$ ). The heavier  $\text{Ba}^{2+}$  ion substituting for lighter  $\text{Sr}^{2+}$  results in the increase in  $\tan \delta$  on an average up to about  $300^\circ\text{C}$ .

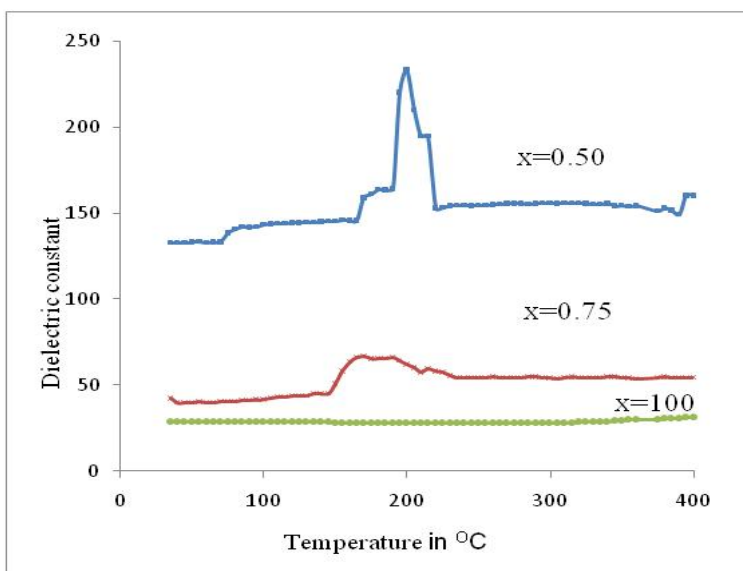


Fig. 11 Plot of Temperature against dielectric constant of  $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$  (where  $x= 0.5, 0.75$  and  $1.00$ )



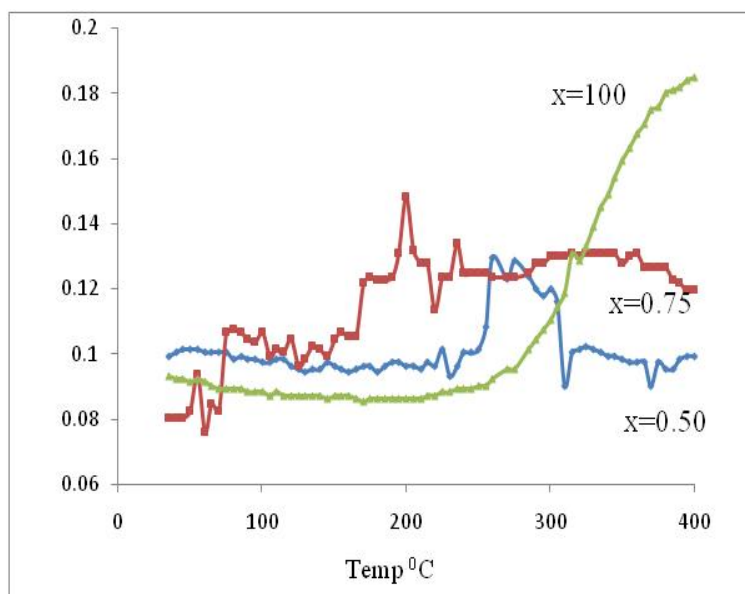


Fig .12 Plot of Temperature against dielectric loss of  $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$  (where  $x = 0.5, 0.75$  and  $1.00$ )

## Conclusion

All the samples were prepared by high temperature solid state reaction. The structural information such as, type of the unit cell, size of the unit cell, particle size is obtained using XRD. Material with  $x=0.00$  &  $0.25$  stabilize in tetragonal phase. When  $x=0.5$  mix phase is observed due to lower sintering temperature and it is also reported that the perovskite structure is very clean only at  $1400^\circ\text{C}$  for the solid state method. When  $x=0.75, 1.00$  cubic crystal structure was confirmed.

Temperature dependence of impedance shows that for pure  $\text{BaTiO}_3$ , impedance value is about  $240 \text{ k}\Omega$  average; remains constant up to  $280^\circ\text{C}$  and thereafter there is a sharp fall from  $240 \text{ k}\Omega$  to about  $165 \text{ k}\Omega$ . From temperature dependence of impedance of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$  ( $x = 1.00, 0.75, 0.50$ ). It is observed that there is systematic decrease in impedance value from  $230 \text{ k}\Omega$  to  $70 \text{ k}\Omega$  when lighter Sr is replaced by heavier Ba.  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$  contain electro-Active bulk and grain boundary regions, whose transport properties depend on the close control of microstructure–stoichiometric relationships, Grain boundaries, play an important role in the electrical properties of a variety of ceramic materials and components.

Pure  $\text{BaTiO}_3$  leads to a better crystalline structure with higher permittivity values and sharp transition temperature. At temperature about  $300^\circ\text{C}$   $\text{BaTiO}_3$  shows diffuse phase transition. The material with  $x=0.25$ , the permittivity has low values and transition temperature is blurred. The maximum value of permittivity for  $x=0.00$  is  $260$  at  $320^\circ\text{C}$  and for  $x=0.25$  it is about  $120$  and is appeared to be almost independent of temperature up to  $400^\circ\text{C}$ . The substitution of an  $\text{Sr}^{2+}$  ion at  $\text{Ba}^{2+}$  site, decreases the unit cell size and hence the polarization is reduced<sup>20</sup>. However, the reduction in ionic mass of the  $\text{A}^{2+}$  site lowers the anharmonicity in the potential energy of the mean separation between ions which is responsible for the loss factor. The lighter  $\text{Sr}^{2+}$  ion substituting for the heavier  $\text{Ba}^{2+}$  results in the decrease



in  $\tan \delta$  [12]. The dielectric constant of pure  $\text{SrTiO}_3$  has the lowest value as compared to dielectric constant for mixed crystal. Pure  $\text{SrTiO}_3$  showed an almost flat dielectric relaxation. The increment in dielectric constant with the increment of Ba may be due to the fact that soft mode frequency decreases with the increase of Ba in  $\text{SrTiO}_3$  and also may be due to increase in the unit cell size thereby increasing polarization to some extent.

Crystal structure of  $\text{BaTiO}_3$  is very similar to  $\text{SrTiO}_3$ . In contrast to  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  is not ferroelectric. Ferroelectric behavior of  $\text{BaTiO}_3$  brings additional complexity in  $\text{BaTiO}_3$ - $\text{SrTiO}_3$  compound, affecting the polarization and charge transport.

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