

# Structural and Dielectric Studies on 0.8Ba0.2 (Bi<sub>0.5(1-x)</sub>Sm<sub>0.5x</sub>K<sub>0.5</sub>)TiO<sub>3</sub> lead free ceramic system

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**Abstract:** Sm substituted 0.8BaTiO<sub>3</sub>-0.2Bi<sub>0.5</sub>K<sub>0.5</sub>TiO<sub>3</sub> lead free ceramic materials with composition 0.8Ba0.2 (Bi<sub>0.5(1-x)</sub>Sm<sub>0.5x</sub>K<sub>0.5</sub>)TiO<sub>3</sub> (x=0.01,0.03,0.05) were prepared by conventional solid state reaction method and followed by high energy ball milling process. The X-ray diffraction studies confirm the tetragonal structural of the material at the room temperature. With increase of Sm substitution, density is decreasing. Microstructure studies were done with the help of scanning electron microscope. Temperature and frequency dependant dielectric studies indicate that dielectric constant decreasing with the substitution of Sm. Sm substitution effects the Curie temperature and it is decreasing with increase of Sm substitution. Relaxor behaviour is observed in all the Sm substituted samples. Degree of diffuseness is calculated from the modified Curie-Weiss law and it was found to be increase with the substitution of Sm.

**Keywords:** lead free ceramics; BaTiO<sub>3</sub>; Bi<sub>0.5</sub>K<sub>0.5</sub>TiO<sub>3</sub>; dielectric.

## 1. INTRODUCTION

BaTiO<sub>3</sub> (BT), a well known and well studied lead free ceramic material. It has been used as multilayer ceramic capacitors (MLCC), piezoelectric sensors, thermistors etc [1-7]. The low ferroelectric to paraelectric transition temperature (Curie temperature) limits the usage of BT at high temperatures. The Curie temperature can be modified by doping with other elements or by mixing BT with other perovskite lead free ceramics. Among the perovskite materials, BiKTiO<sub>3</sub> (BKT), BiNaTiO<sub>3</sub> and KNbO<sub>3</sub> are well known perovskite lead free ceramic materials. T.Takenaka et al [8]. has studied the BKT- BT solid solution and found that curie temperature of BT increases with addition of BKT. Their study limited to preparation of different combinations of BT-BKT solid solution. Ramesh et al. studied the dielectric and impedance properties of Ce, Zr and Nd substituted 0.8BaTiO<sub>3</sub> -0.2 Bi<sub>0.5</sub>K<sub>0.5</sub>TiO<sub>3</sub> (here after abbreviated as BT-BKT20) lead free ceramic materials [9-12]. In the present paper, we report the structural and dielectric properties of Sm substituted 0.8Ba0.2(Bi<sub>0.5(1-x)</sub>Sm<sub>0.5x</sub>K<sub>0.5</sub>)TiO<sub>3</sub> (x=0.01,0.03,0.05) lead free ceramic material.

## 2. EXPERIMENTAL DETAILS

Ceramic samples of Sm substituted with composition 0.8Ba0.2(Bi<sub>0.5(1-x)</sub>Sm<sub>0.5x</sub>K<sub>0.5</sub>)TiO<sub>3</sub> (x=0.01,0.03,0.05) has been synthesized by conventional solid state route followed by an high energy ball milling process using high purity (>99.9%) BaCO<sub>3</sub> (Merck), Bi<sub>2</sub>O<sub>3</sub> (Loba), K<sub>2</sub>CO<sub>3</sub> (Merck), TiO<sub>2</sub> (Loba) and Sm<sub>2</sub>O<sub>3</sub> (Loba) as starting raw materials. The powders were mixed in required proportions accordingly and ball milled in ethanol medium for 24 hr. Ball milled powders were grounded and calcined at 1000°C for 6 hr. After calcination the powders were grounded for uniformity. The calcined powders were mixed with 5% of Poly vinyl alcohol and uniaxially pressed cylindrical pellets were prepared by applying a pressure of 4000kg/cm<sup>2</sup>. These pellets were sintered at 1200°C for 2hr. After sintering the pellets were polished to a thickness of 1.33 mm and diameter of 12 mm. Sintered pellets were coated with silver paste on both surfaces and heated at 300°C for 1hr to use as electrodes for dielectrical measurements.

Structural identification studies were done on calcined powders by using a Phillips X-ray diffractometer using CuK $\alpha$  radiation ( $\lambda=1.5406$  Å) in the range of 20° to 70° at a scan rate of 2°/minute. Microstructures of the materials were studied by using a Scanning electron microscope JEOL Model JSM - 6390LV. Dielectric studies were carried out on Newton's 4<sup>th</sup> limited (PSM 1735) LCR meter from 20Hz to 1MHz frequency range. Dielectric studies were done in the temperature range of 40°C to 300°C.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Structural studies

Structural characterization of the Sm substituted 0.8Ba0.2(Bi<sub>0.5(1-x)</sub>Sm<sub>0.5x</sub>K<sub>0.5</sub>)TiO<sub>3</sub> (x=0.01,0.03,0.05) lead free ceramics were done by using X-ray diffraction in the 2 $\theta$  range of 20° to 70°. Room temperature powder X-Ray diffractograms of

different amounts of Sm substituted  $0.8\text{Ba}0.2(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  are shown in the figure1. All the samples shows the perovskite structure and no secondary phases were observed. It implies that  $\text{Sm}^{3+}$  has entered into the  $0.8\text{Ba}0.2(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  lattice to form a solid solution. Tetragonal symmetry of the Sm substituted samples were confirmed via the splitting of the reflections (101)/(110), (002)/(200) and (112)/(211) observed at  $31^\circ$ ,  $45^\circ$  and  $56^\circ$  respectively. These are in good agreement with the JCPDS data [13].

Substitution of  $\text{Sm}^{3+}$  causes shifting of the diffraction peaks towards the higher angles. This is due to the substitution of small size  $\text{sm}^{3+}$  cation ( $0.96 \text{ \AA}$ ) in the place of big size  $\text{Bi}^{3+}$  ( $1.03 \text{ \AA}$ ). Substituting with the small size cation expands the lattice and hence decreases of lattice parameters. The values of lattice parameters ( $a(\text{ \AA})$ ,  $c(\text{ \AA})$ ) are shown in the table1. In the present study, no change in the structure was observed. From the values of  $c/a$  ratio, it is clear that increase of Sm substitution decreases the tetragonality. The values of density are shown in the table 1. Observed low values of density (theoretical and experimental) are due to the evaporation of Bismuth and Potassium during the high temperature sintering process [12]. The evaporation of Bi and K affects the electrical properties of the BTBKT-20 material. So substituting a thermally stable material can improve the electric properties. Microstructure images of Sm substituted  $0.8\text{Ba}0.2(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  samples are shown in the figure2.

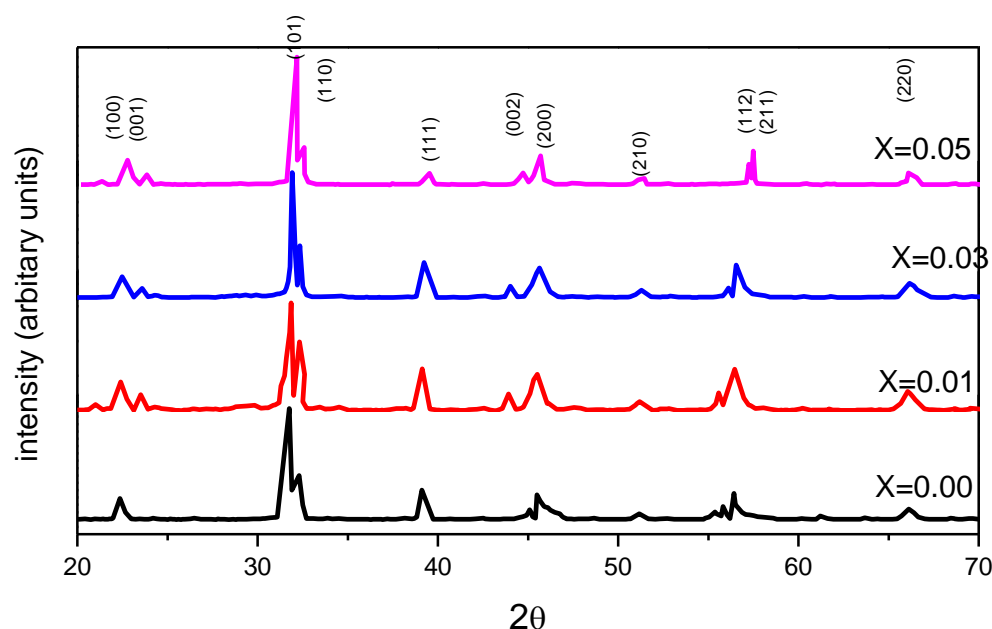


Fig1. X-ray diffractograms of Sm substituted  $0.8\text{Ba}0.2(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  ( $x=0.01, 0.03, 0.05$ ) lead free ceramics.

Table 1. Various parameters as function of Sm substitution in  $0.8\text{Ba}0.2(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  ( $x=0.01, 0.03, 0.05$ ) lead free ceramics.

X	0.01	0.03	0.05
a (Å)	3.986	3.977	3.972
c (Å)	4.088	4.069	4.062
c/a	1.0255	1.0231	1.0226
Theoretical density(Kg/m <sup>3</sup> )	6.848	6.905	6.928
Exp. density(Kg/m <sup>3</sup> )	6.177	6.187	6.145
R.density	90.2	89.6	88.7
$\epsilon_{RT}$ (1KHz)	2462	2444	2411
$\epsilon_{max}$ (1KHz)	2640	2626	2599
tan $\delta$ (at RT for 1KHz)	0.10	0.10	0.11
$\gamma$ (1KHz)	1.14	1.31	1.51

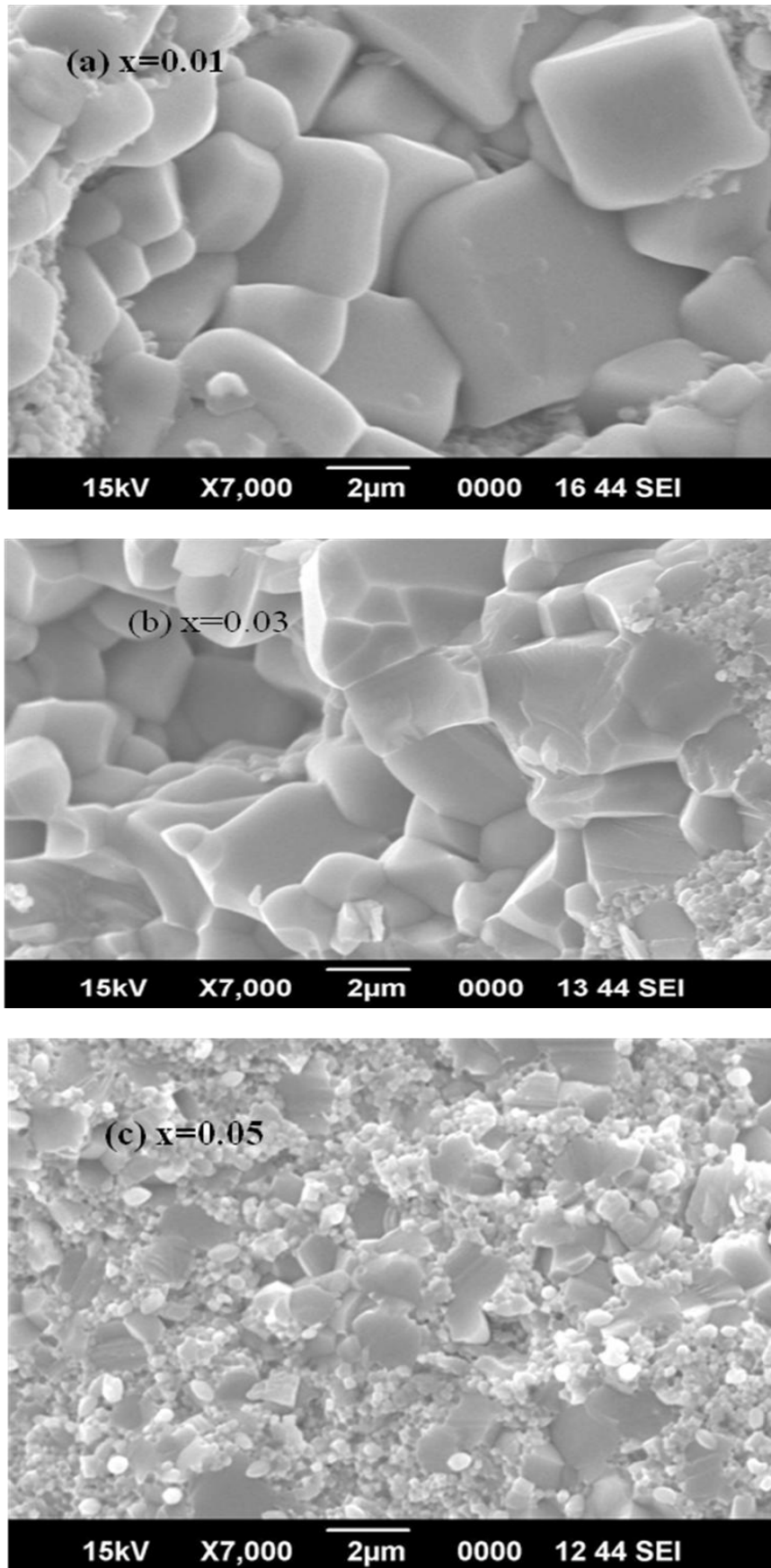


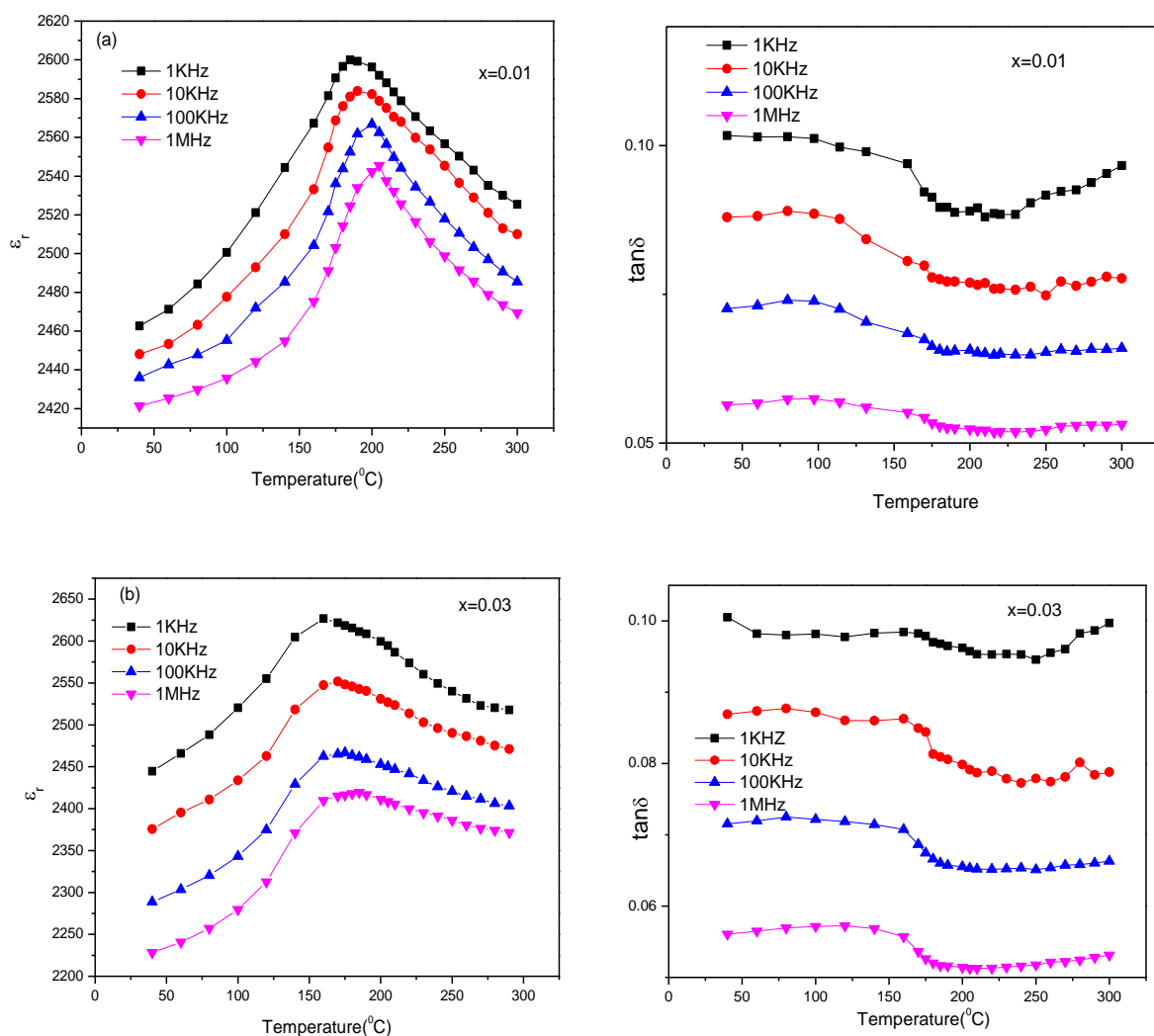
Fig2. Microstructure images of Sm substituted  $0.8\text{Ba}0.2(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  ( $x=0.01, 0.03, 0.05$ ) lead free ceramics.  
(a)  $x=0.01$  (b)  $x=0.03$  (c)  $x=0.05$

### 3.2. Dielectric Studies

Measurement of dielectric studies for Sm substituted  $0.8\text{Ba}0.2(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  ( $x=0.01, 0.03, 0.05$ ) lead free ceramics as a function of temperature at different frequencies are shown figure 3. From figure 3, it is clear that as the frequency increases dielectric constant decreases. Also as the Sm content increases, the room temperature dielectric constant and maximum dielectric constant values were decreasing. Similar kind of behaviour is observed for  $\text{Nd}^{3+}$  substituted BT-BKT 20 [12] lead free ceramics.

Figure 3 shows the dielectric loss measured for all the Sm substituted samples as a function of temperature at different frequencies. Dielectric loss is increasing with increase of Sm content. Dielectric loss is higher at lower frequencies and decreases with increase of frequency. It shows that at higher frequencies dipoles were unable to follow applied AC field and hence decrease in dielectric loss at higher frequencies. Zhi Jing et al.[14] has shown that dielectric constant value also depends on the density of the samples. It means that decrease of dielectric constant can also be understood from the density of the samples. Decrease of density or increasing of porosity (figure 2) with increase of Sm substitution is also be responsible for decrease of dielectric constant.

From the figure 3, it is clear that Curie temperature is decreasing with the increase of Sm substitution. This clearly shows that Sm substitution strongly influences the ferroelectric to paraelectric phase transition temperatures. In the present material  $0.8\text{Ba}0.2(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$ , A-site has three different valence cations with different sizes i.e  $\text{Bi}^{3+}$  ( $1.03\text{\AA}$ ),  $\text{Ba}^{2+}$  ( $1.38\text{\AA}$ ) and  $\text{K}^+$  ( $1.38\text{\AA}$ ). According to the ionic radii values, when  $\text{Sm}^{3+}$  added to the  $0.8\text{Ba}0.2(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$ , it can occupy any of the A-sites. When  $\text{Sm}^{3+}$  occupies other than  $\text{Bi}^{3+}$ , leads to the imbalance of the charge and creates A-site vacancies. This weakens the coupling reaction between A-site cation and  $\text{BO}_6$  octahedron [15], hence Curie temperature decreases.



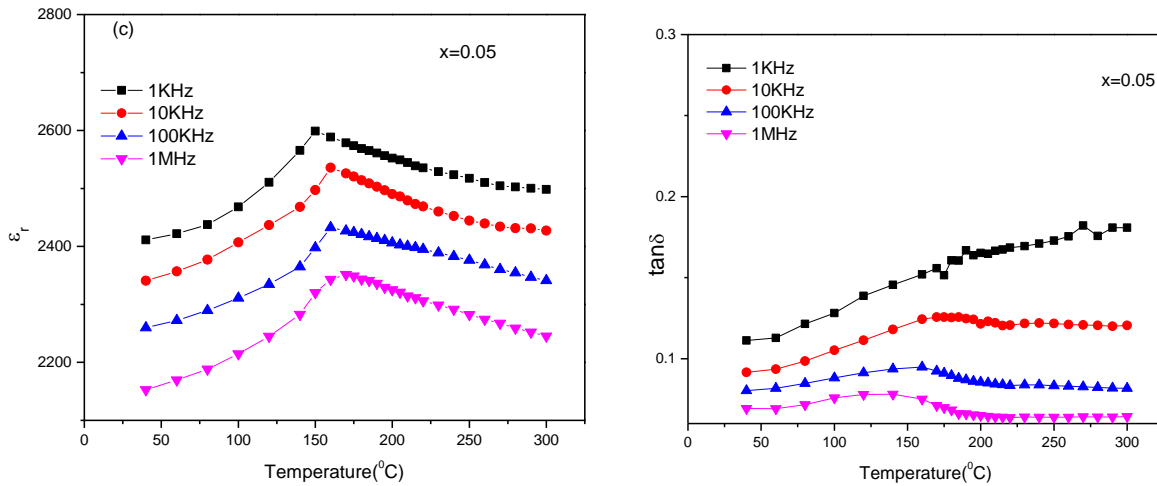


Fig3. Variation of Dielectric constant & dielectric loss as a function of temperature at different Frequencies for  $0.8\text{Ba}_{0.2}(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  ( $x=0.01,0.03,0.05$ ) lead free ceramics. (a)  $x=0.01$  (b)  $x=0.03$  (c)  $x=0.05$

All the Sm substituted samples exhibiting relaxor behaviour. This relaxor behaviour is not just due to the Sm substitution, but even the Sm unsubstituted sample itself shows the relaxor behaviour [9]. But the relaxor behaviour increases with the increase of Sm substitution.

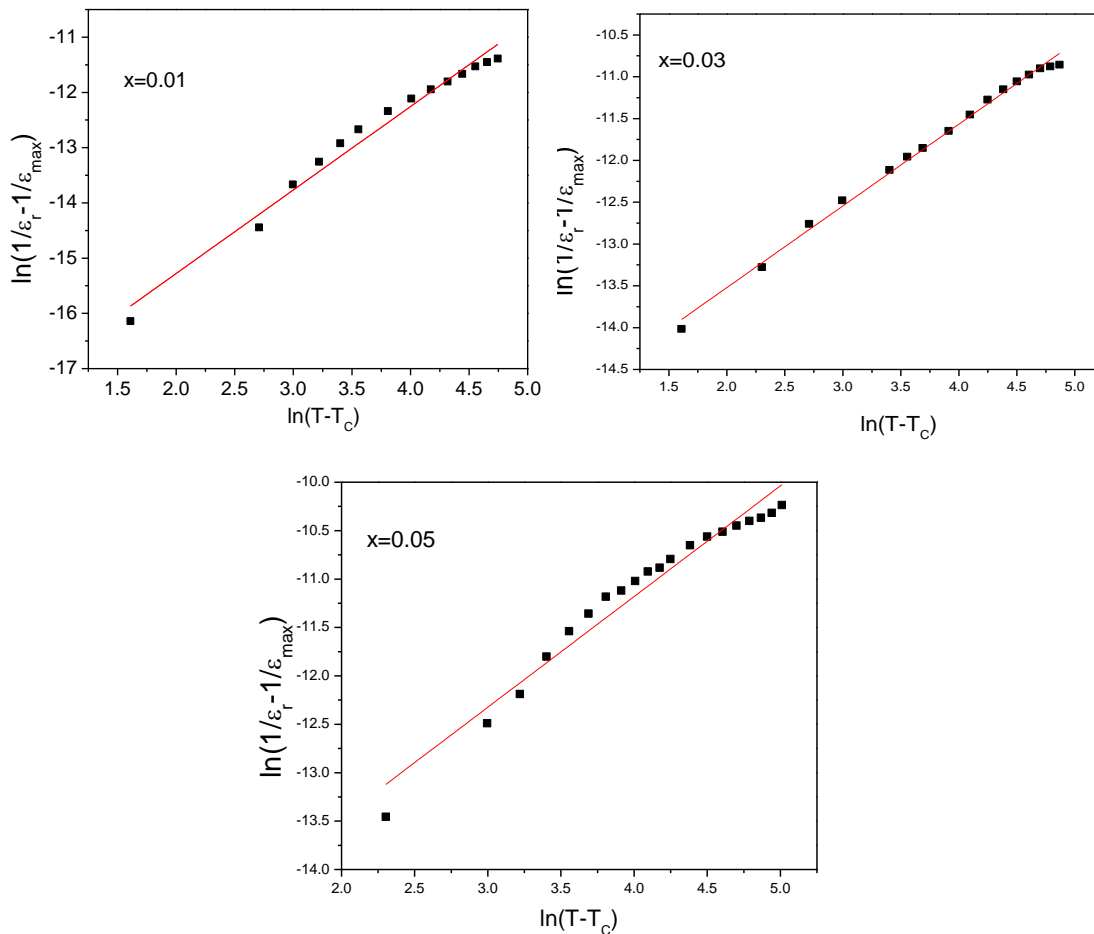


Fig4. Modified Curie-Weiss law for  $0.8\text{Ba}_{0.2}(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  ( $x=0.01,0.03,0.05$ ) lead free ceramics (solid line represents linear fitting).

The observed relaxor behaviour is due to the multiple occupation of different valence cations ( $\text{Ba}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{K}^{+}$ ) at the A-site and different homovalent cations [16,17]. Diffuseness of a phase transition can be calculated from the modified Curie-Weiss law [18].

$$\frac{1}{\epsilon} - \frac{1}{\epsilon_{\max}} = \frac{(T-T_C)^\gamma}{C} \quad (1)$$

Where  $\gamma$  is degree of diffuseness/relaxation and the value of  $\gamma$  lies between 1 & 2. The material is normal ferroelectric and follows ideal Curie-Weiss law if  $\gamma = 1$  and when  $\gamma = 2$ , the material is diffused ferroelectric material. Degree diffuseness is calculated for all the Sm substituted samples and it found to be increasing. Figure 4 shows the Curie-Weiss law fit for  $0.8\text{Ba}_{0.2}(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  lead free ceramics. The values of degree of diffuseness are shown in the table1.

#### 4. CONCLUSIONS

Sm substituted  $0.8\text{Ba}_{0.2}(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  ( $x=0.01,0.03,0.05$ ) lead free ceramics were prepared by conventional solid state reaction method and followed by high energy ball milling method. The formation of single phase tetragonal structure in the all the Sm substituted samples were confirmed by X-ray diffraction studies. Frequency and temperature dependent dielectric studies shows the relaxor behaviour in all the Sm substituted  $0.8\text{Ba}_{0.2}(\text{Bi}_{0.5(1-x)}\text{Sm}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  ( $x=0.01,0.03,0.05$ ) samples. Dielectric constant was decreasing with the substitution of Sm. Curie temperature was also decreasing with the substitution of Sm. Degree of diffuseness was calculated and it was increasing with the substitution of Sm.

#### REFERENCES

- [1] Su-Wei Zhang, Hailong Zhang, Bo-Ping Zhang, Gaolei Zhao, "Dielectric and piezoelectric properties of  $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ti}_{0.88}\text{Zr}_{0.12})\text{O}_3$  ceramics sintered in a protective atmosphere" *J.Eur. Ceram. Soc.*, vol.29, pp. 3235, 2009.
- [2] Cheng.B. L., Wang C., Wang S. Y., Lu H. B., Zhou Y. L., Chen Z. H., "Dielectric properties of  $(\text{Ba}_{0.8}\text{Sr}_{0.2})(\text{Zr}_{x}\text{Ti}_{1-x})\text{O}_3$  thin films grown by pulsed-laser deposition, *J. Eur. Ceram. Soc.*, vol.25, pp. 2295, 2005.
- [3] Moura.F, Simoes.A.Z, Stojanovic.B.D, Zaghete.M.A, Longo.E, Varela.J.A, "Dielectric and ferroelectric characteristics of barium zirconate titanate ceramics prepared from mixed oxide method" *J. Alloys Comp.*, vol.462, pp.129-134,2008.
- [4] Sandeep Mahajan, Thakur.O.P, Chandra Prakash, Sreenivas.K., "Effect of Zr on dielectric, ferroelectric and impedance properties of  $\text{BaTiO}_3$  ceramic" *Bull. Mater. Sci.*, vol.34, pp.1483-1489, 2011.
- [5] Zhi Yu, Chen Ang, Ruyan Guo, Bhalla.A.S, "Dielectric properties and high tunability of  $\text{Ba}(\text{Ti}_{0.7}\text{Zr}_{0.3})\text{O}_3\text{Ba}(\text{Ti}_{0.7}\text{Zr}_{0.3})\text{O}_3$  ceramics under dc electric field", *Appl. Phys.lett.*, vol.81, pp.1285-1287,2002.
- [6] Zhi Yu, Chen Ang, Ruyan Guo, Bhalla.A.S, "Dielectric properties of  $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  solid solutions" *Mater. Lett.*, vol.61, pp.326-329, 2007.
- [7] Sateesh.P, Omprakash.J, Kumar.G.S, Prasad.G, "Studies of phase transition and impedance behavior of  $\text{Ba}(\text{Zr}, \text{Ti})\text{O}_3$  ceramics" *J. Adv. Dielec.*, vol.5, pp. 1550002, 2015.
- [8] Yuji Hiruma, Hajime Nagata, Tadashi Takenaka, "Dielectric,ferroelectric and piezoelectric properties of barium titanate and bismuth potassium titanate solid solution ceramics" *J. Cera. Soc. Japan*, vol. 112 (5), pp.S1125-S1128, 2004.
- [9] Ramesh.M.N.V, Ramesh.K.V, "Dielectric and impedance spectroscopic studies of  $0.8\text{BaTiO}_3-0.2\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$  lead free ceramics" *Int. J. Mod. Phy. B*, vol.29, pp. 1550119-134, 2015.
- [10] Ramesh.M.N.V, Ramesh.K.V, "Effect of Cerium substitution on structural and impedance properties of  $0.8\text{Ba}_{0.2}(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$  lead free ceramics" *Mod.Phy letters B* vol.30(6), pp.1650056-65, 2016.
- [11] Ramesh.M.N.V, Ramesh.K.V, "Structural, dielectric and AC conductivity studies on  $0.8\text{Ba}_{0.2}(\text{Bi}_{0.5}\text{K}_{0.5})\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$  lead free ceramic system" *Mate.Sci.Poland* vol.34(3), pp. 669-675, 2016.
- [12] Ramesh.M.N.V, Ramesh.K.V, "Dielectric and AC conductivity studies of Nd substituted  $0.8\text{BaTiO}_3-0.2(\text{Bi}_{0.5(1-x)}\text{Nd}_{0.5x}\text{K}_{0.5})\text{TiO}_3$  leadfree ceramics" *AIP Conf. Proc.* vol.1731, pp.110043, 2016.
- [13] Tetragonal  $\text{BaTiO}_3$  JCPDS no. 05-0626.
- [14] Zhi Jing, Zhi Y, Chen Ang "Crystalline structure and dielectric properties of  $\text{Ba}(\text{Ti}_{1-y}\text{Ce}_y)\text{O}_3$ " *J.Mat.Science* vol.38, pp.1057-1061, 2003.
- [15] Zupei Yang, Yuting Hou, Bing Liu and Lingling Wei "Structure and electrical properties of  $\text{Nd}_2\text{O}_3$ -doped  $0.82\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.18\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$  ceramics" *Ceram.Intl* 35, pp. 1423-1427, 2009.
- [16] Wanli Zhao, Ruzhong Zuo, "Morphotropic phase boundary and electrical properties of lead-free  $(\text{K}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-\text{Bi}(\text{Ni}_{0.5}\text{Ti}_{0.5})\text{O}_3$  relaxor ferroelectric ceramics" *Cera. Intl.*, 39,pp. 9121-9124,2013.
- [17] Yang, Jianfeng, Hou, Yudong, Wang, Chao, Zhu, Mankang, Yan, Hui, "Relaxor behavior  $(\text{K}_{0.5}\text{Bi}_{0.5})\text{TiO}_3(\text{K}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  ceramics derived from molten salt synthesized single-crystalline nanowires" *J. Appl. Phys.*, 91, pp.023118,2007.
- [18] K. Uchino and S. Nomura, "Critical Exponents of the Dielectric Constants in Dif-fused-Phase-Transition Crystals," *Ferroelectrics Letters*, 44, pp. 55-61,1982.