# Impedance and AC Conductivity Studies of $Sm^{3+}$ Substituted $0.8Ba0.2(Bi_{0.5}K_{0.5})TiO_3$ Lead Free Ceramics

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**Abstract.** Samarium substituted $0.8Ba0.2(Bi_{0.5}K_{0.5})TiO_3$ (here after abbreviated as BTBKT-20) lead free ceramics with composition $0.8Ba0.2(Bi_{0.5(1-x)}Sm_{0.5x}K_{0.5})TiO_3$ (where x=0.01,0.03,0.05) lead free ceramics have been prepared by solid state reaction and followed by high energy ball milling process. The present paper focuses the impedance and ac conductivity studies of Sm substituted BTBKT-20 lead free ceramics. Impedance spectroscopic studies revealthat temperature dependent relaxation process. Single depressed semi circle was observed in Cole-Cole plots, indicates non-Debye kind of relaxation process. Maximum grain resistance was observed for x=0.03 Sm substituted BTBKT-20 sample. Frequency and temperature dependent AC conductivity was calculated and it found to obey the universal Jonscher's power law and the values of activation energies suggest that conduction is ionic in nature.

**Keywords:** lead free ceramics, impedance, ac conductivity, $BaTiO_3$, Ball milling

## INTRODUCTION

Lead based ferroelectric electric materials are known for their excellent ferroelectric and piezoelectric properties. Due to hazardous nature of lead and other environmental concerns, there must be alternatives for the lead free ferroelectric materials with excellent properties. Among the lead free ferroelectrics, $BaTiO_3$ is well studied and can be the alternative for lead based perovskite materials. $BaTiO_3$ ferroelectric material have been used as multilayer ceramic capacitors (MLCC), pyroelectric sensors, actuators, thermisters etc., because of their excellent ferroelectric and piezoelectric properties.

Low Curie temperature of $BaTiO_3$ limits the usage at the higher temperature applications. Tadashi Takenaka et al.[1] has shown that addition Of $Bi_{0.5}$ $K_{0.5}TiO_3$ increases the Curie temperature of $BaTiO_3$ and in our previous studies [2], we have the shown the relaxor behavior of BTBKT-20 lead free ceramics. Evaporation of Bismuth and Potassium at the high temperature sintering process affect the electrical properties of the material. Suitable and stable elements at high temperatures can improve the electrical properties of the material. It was shown that Nd improves the electrical properties of the material [3]. The present study focuses on the electrical properties of Sm substituted BTBKT-20 by using impedance spectroscopy.

## EXPERIMENTAL DETAILS

Ceramic samples of Sm substituted with composition $0.8BaTiO_3$ - $0.2(Bi_{0.5(1-x)}Sm_{0.5x}K_{0.5})TiO_3$ where x=0.01,0.03,0.05 has been synthesized by conventional solid state route followed by high energy ball milling process for 10 hrs using high purity (>99.9%) $BaCO_3$ (Merck), $Bi_2O_3$ (Loba), $K_2CO_3$ (Merck), $TiO_2$ (Loba) and $Sm_2O_3$ (Loba) as starting raw materials. Ball milled powders were grounded and calcined at $1000^0C$ for 6 hr. The calcined powders were mixed with 5% of PVA and uniaxially pressed cylindrical pellets were prepared by applying pressure of 4000kg/cm$^2$. These pellets were sintered at 1200$^0$C for 2hr. Sintered pellets were coated with silver paste on both sides and heated at 300$^o$C for 1hr to use as electrodes for impedance spectroscopy measurements. Impedance spectroscopy studies were carried out on Newton's 4$^{th}$ limited (PSM 1735) LCR meter from 1Hz to 1MHz frequency and temperature range of 350$^0$C to 460$^0$C.

## RESULTS AND DISCUSSIONS

Impedance spectroscopy methods are very useful to study the temperature dependent electric properties of materials such as relaxation times, contribution of grain and grain boundary effects, electrode interface effects to ceramics. Grain and grain boundary contribution can be separated by using impedance data and can be understood with reference to an equivalent circuit, generally consisting series of parallel RC elements.

Figure 1 shows the real part of impedance with frequency at different temperatures for x= 0.01, x=0.03 and x=0.05 Sm substituted BTBKT-20 lead free ceramics. It clearly show $Z^1$ is high at low frequency side for lower temperatures. As temperature and frequency increases, $Z^1$ values were decreasing and all curves merge at high frequency region at all temperatures. This can be explained as release of space charges with rise of temperature and this is responsible for decrease of $Z^1$ values/increase of conductivity with temperature [4].

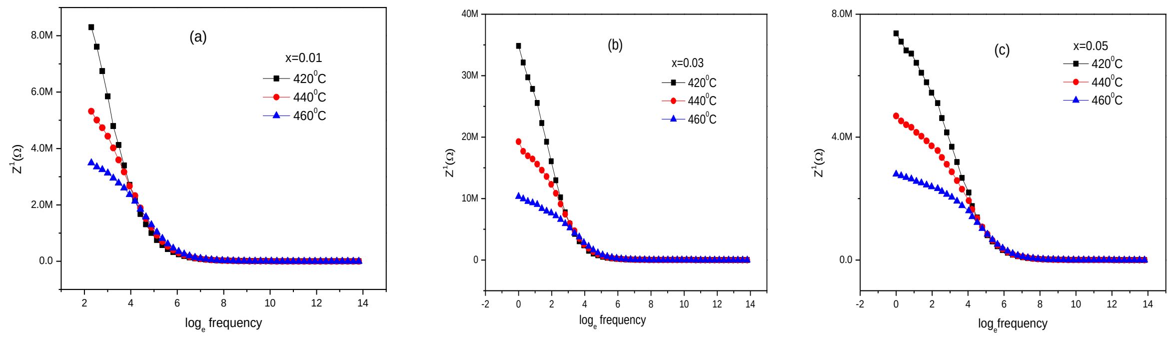


**FIGURE 1.** Variation of real part of impedance $Z^1$ with frequency at different temperatures for Sm substituted $0.8BaTiO_3$ - $0.2(Bi_{0.5(1-x)}Sm_{0.5x}K_{0.5})TiO_3$ lead free ceramics. (a) x=0.01 (b) x=0.03 (c) x=0.05

Figure 2 shows the variation of imaginary part of impedance with frequency at different temperatures. Peak in $Z^{11}$ is observed from 420$^0$C onwards and no peak in observed below this temperature in the measured frequency range. It indicates that no relaxation has taken place below 420$^0$C. This may be due to the presence of defects, complex defects in the material, which can affect the relaxation process [5]. So in the present paper impedance studies were carried from 420$^0$C to 460$^0$C. Relaxation times $(\tau_Z)$ are calculated from the position of peaks at each temperature and shown in the table 1.

Figure 3 shows the Cole-Cole plots at different temperatures for the Sm substituted BTBKT-20 lead free ceramic materials. At all temperatures only single depressed semi-circle below the X-axis was observed. Intercept of semi-circle on $Z^1$ axis gives the value of bulk resistance $(R_g)$. Bulk capacitance $(C_g)$ was calculated from the relation $\tau_Z = R_g C_g$ and is found to decrease with increase in temperature. Values of bulk resistance/grain resistance and grain capacitance are given in table 1. Equivalent circuit is shown in the figure 3(a). Presence of depressed semi-circle in Cole-Cole plots indicates the multiple relaxation times and the relaxation process involved is non-Debye type of relaxation process [6]. It is clear from the table 1 that, grain resistance increased upto x=0.03 and then decreased for x=0.05. This may be due to the occupation of $Sm^{3+}$ (0.96 nm) at the other cations in the A-site. The present material contains three different cations, $Bi^{3+}$(0.96 nm), $K^+$ (1.33nm) and $Ba^{2+}$ (1.34 nm). Occupation of $Sm^{3+}$ at other than $Bi^{3+}$, can create vacancies in the compound and this may be the reason for decrease of grain resistance observed.

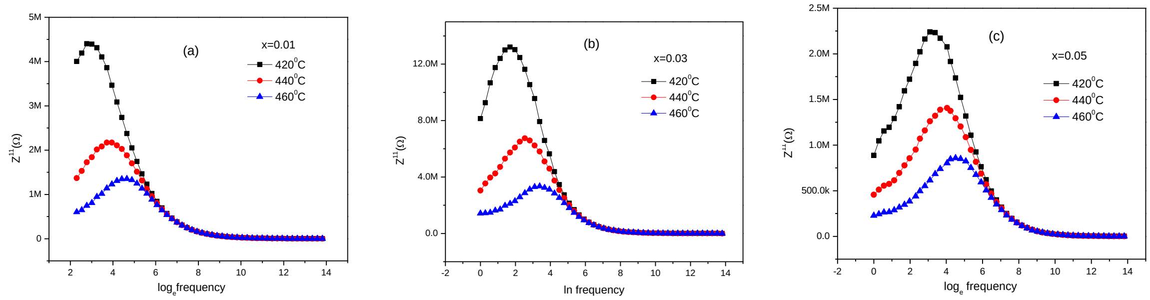


**FIGURE 2.** Variation of imaginary part of impedance with frequency at different temperatures for Sm substituted $0.8BaTiO_3 - 0.2(Bi_{0.5(1-x)}Sm_{0.5x}K_{0.5})TiO_3$ lead free ceramics. (a) x=0.01 (b) x=0.03 (c) x=0.05

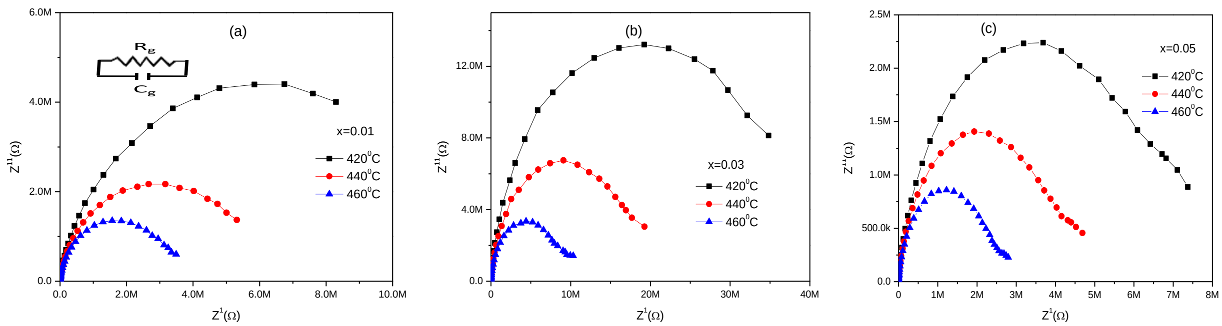


**FIGURE 3.** Cole- Cole plots at different temperatures for Sm substituted $0.8BaTiO_3 - 0.2(Bi_{0.5(1-x)}Sm_{0.5x}K_{0.5})TiO_3$ lead free ceramics. (a) x= 0.01 (inset shows the equivalent circuit) (b) x=0.03 (c) x=0.05

**TABLE 1.** Values of grain resistance (Rg), Grain capacitance (Cg) and Relaxation times $(\tau_Z)$ for Sm substituted $0.8BaTiO_3 - 0.2(Bi_{0.5(1-x)}Sm_{0.5x}K_{0.5})TiO_3$ lead free ceramics where x=0.01, x=0.03, x=0.05

| | **Grain resistance Rg (M-ohms)** | | | **Grain capacitance Cg (nF)** | | | **Relaxation time** $(\tau_Z)$ (m-sec) | | |
|---|---|---|---|---|---|---|---|---|---|
| | **420$^0$C** | **440$^0$C** | **460$^0$C** | **420$^0$C** | **440$^0$C** | **460$^0$C** | **420$^0$C** | **440$^0$C** | **460$^0$C** |
| X=0.01 | 13.4 | 5.20 | 3.12 | 0.74 | 0.59 | 0..48 | 9.95 | 3.07 | 1.52 |
| X=0.03 | 19.2 | 9.1 | 4.4 | 0.19 | 0.39 | 0.78 | 0.37 | 0.36 | 0.34 |
| X=0.05 | 3.6 | 1.93 | 1.22 | 1.98 | 1.59 | 1.43 | 7.16 | 3.07 | 1.75 |

A.C conductivity was calculated as a function of frequency at different temperatures for all the Sm substituted BTBKT-20 lead free ceramics using the following relation.

$$\sigma_{A.C} = \mathcal{E}' \mathcal{E}_0\, \omega\, tan\delta$$

Where $\mathcal{E}'$ is real part of dielectric constant, $\mathcal{E}_0$ is permittivity of the free space, ω is angular frequency and tanδ is dielectric loss tangent. Frequency dependent A.C conductivity was found to obey universal Jonscher's power law[7]

$$\sigma_{A.C} = \sigma_0 + A\omega^s$$

Where $\sigma_0$ is the frequency independent conductivity (D.C conductivity), A is a constant, ω is the frequency of AC field and s is the frequency dependent factor in the range $0 < s < 1$. AC conductivity as a function of frequency at different temperatures is shown in the figure 4.

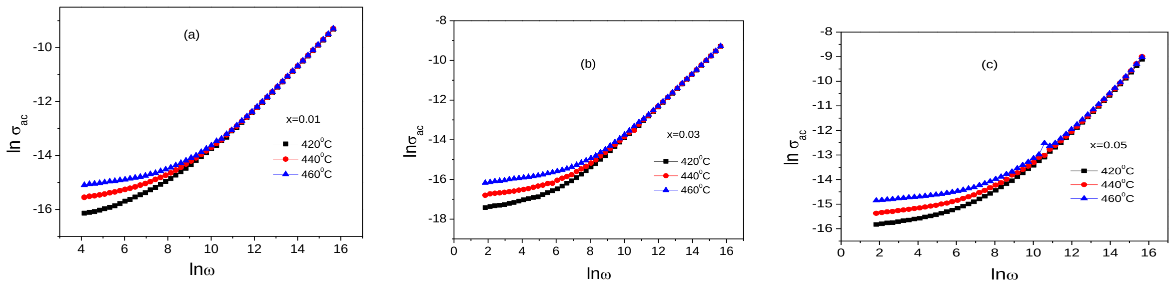


**FIGURE 4.** AC Conductivity at different temperatures for Sm substituted $0.8BaTiO_3$ - $0.2(Bi_{0.5(1-x)}Sm_{0.5x}K_{0.5})TiO_3$ lead free ceramics. (a) x= 0.01 (b) x=0.03 (c) x=0.05

It is clear from the figure 4 that, at lower frequencies A.C conductivity increases with temperature for all the Sm substituted samples. All the curves merge at higher frequency region for all temperatures indicating less defects/less defect mobility. Increase of conductivity with temperature at high frequencies indicates the release of space charges. Conductivity decreased up to x=0.03 and the increased for x=0.05. This may be due to the creation of vacancies in the material. These vacancies are due to the occupation of $Sm^{3+}$ in the place of $K^+$ and $Ba^{2+}$.

Intercept of A.C conductivity curve onto the Y-axis gives frequency independent conductivity i.e. D.C/bulk conductivity. Activation energy ($E_a$) was calculated using the Arrhenius relation at 1 KHz

$$\sigma_{A.C} = \sigma_0 \exp\left(\frac{E_a}{KT}\right)$$

Where 'K'is Boltzmann constant. Activation energies are calculated from linear least square fit of Arrhenius relation. The values of activation energies are 0.31eV, 0.356eV and 0.4eV respectively for the x=0.01, x=0.03,x=0.05 Sm substituted $0.8BaTiO_3$ - $0.2(Bi_{0.5(1-x)}Sm_{0.5x}K_{0.5})TiO_3$ lead free ceramics. The values of activation energy suggest that conduction is ionic in nature.

## CONCLUSIONS

Frequency and temperature dependent electrical properties of Sm substited 0.8Ba - $0.2(Bi_{0.5(1-x)}Sm_{0.5x}K_{0.5})TiO_3$ Where x=0.01,0.03,0.05 lead free ceramics studied with the help of impedance spectroscopy technique. Impedance spectroscopic studies reveal that temperature dependent relaxation process in the present mterial. Electrical properties are improved with Sm substitution. Single depressed semi circle was observed in Cole-Cole plots, indicates non-Debye kind of relaxation process. Maximum grain resistance was observed for x=0.03 Sm substituted BTBKT-20 sample. This is attributed as substitution of stable $Sm^{3+}$ in the place of $Bi^{3+}$. Frequency and temperature dependent AC conductivity was calculated and it found to obey the universal Jonscher's power law and the values of activation energies suggest that conduction is ionic in nature.

## REFERENCES


1. Yuji Hiruma, Hajime Nagata and Tadashi Takenaka J. Cera. Soc. Japan **112 (5)** S1125- S1128 (2004).
2. M. N. V. Ramesh and K. V. Ramesh, Int. J. Mod. Phy. B, **29** 1550119- 1550132 (2015).
3. M. N. V. Ramesh and K.V. Ramesh, "Impedance And Modulus Spectroscopic Studies Of Zr Substituted $0.8BaTiO_3$-$0.2(Bi_{0.5(1-x)}Nd_{0.5x}K_{0.5})TiO_3$ Ceramics" , *DAE solid state physics symposium 2015* AIP. Conf. proc. **1731** 110043 (2016).
4. Sheela devi and A.K.Jha Bull. Mat.Sci. **33** 683-689 (2010).
5. K.Ch.Varadaraju, B.Tilak, K.Sambasiva Rao Appl. Phys. A **106** 533-543 (2012).
6. K.S.Cole and R.S. Cole J. Chem. Phys. **9** 34 (1941).
7. A.K.Jonscher, *Dielectric relaxation in solids*(Chelsea dielectric press, London 1983).