DE GRUYTER OPEN

Structural, dielectric and AC conductivity studies on $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$ lead free ceramic system

M.N.V. Ramesh[1], K.V. Ramesh[2,*]

[1]Department of Physics, GIT, GITAM University, Visakhapatnam, A.P, India.

[2]Department of Electronics and Physics, GIS, GITAM University, Visakhapatnam, A.P, India

Zr substituted $0.8BaTiO_3 0.2Bi_{0.5}K_{0.5}TiO_3$ lead free ceramic materials with a composition $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$ ($0.01 \leqslant x \leqslant 0.06$) were prepared by conventional solid state reaction method followed by high energy ball milling. The X-ray diffraction studies confirmed the tetragonal structure of the material at room temperature. Density was decreasing with the substitution of Zr. Microstructure studies were done by using scanning electron microscope. Temperature and frequency dependent dielectric studies were carried out and showed that the dielectric constant, dielectric loss and Curie temperature were decreasing with the substitution of Zr. Relaxor behavior was observed in all the Zr substituted samples. Degree of diffuseness was calculated from the modified Curie-Weiss law and it was found to increase with the substitution of Zr. Frequency and temperature dependent AC conductivity was calculated and it was found to obey Jonscher's power law. Substitution of Zr decreased the conductivity of the material. Activation energy was calculated and it was decreasing with an increase in Zr substitution.

Keywords: *lead free ceramics; BaTiO_3; Bi_{0.5}K_{0.5}TiO_3; dielectric; AC conductivity*

1. Introduction

Effect of Zr substitution in $BaTiO_3$ has been extensively studied by many authors using different methods for different applications at different experimental conditions [1–11]. Zr substituted $BaTiO_3$ ferroelectric materials have been used as multilayer ceramic capacitors (MLCC), pyroelectric sensors, piezoelectric actuators, etc. Substitution of chemically stable Zr^{4+} in the place of chemically instable Ti^{4+} to $BaTiO_3$ has the following advantages (i) preventing the escape of oxygen atoms from the lattice during high temperature sintering process, (ii) reducing the hopping between Ti^{4+} and Ti^{3+} thereby reducing conductivity of the material, (iii) reducing the grain size and (iv) controlling the leakage current [2, 5, 9]. Substitution of Zr reduces the Curie temperature of $BaTiO_3$ from 120 °C to below the room temperature [8]. Takenaka et al. [12] has shown that Curie temperature of $BaTiO_3$ can be raised by mixing with $Bi_{0.5}K_{0.5}TiO_3$. They showed that this particular composition, i.e. $0.8BaTiO_3$-$0.2Bi_{0.5}K_{0.5}TiO_3$ (hereafter abbreviated as BT-BKT20) has the highest density and Curie temperature of around 200 °C. Ramesh et al. [13] reported results of dielectric and impedance studies of BT-BKT20 with a Curie temperature of 185 °C at 1 KHz. As very few literature items were found on the effect of Zr substitution in BT-BKT20 lead free ceramics, an attempt was made to study the effect of Zr substitution on structural and dielectric properties of BT-BKT20 lead free ceramic materials.

2. Experimental

Ceramic samples of Zr substituted with a composition $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$ ($0.01 \leqslant x \leqslant 0.06$) have been synthesized by conventional solid state route followed by a high energy ball milling process using high purity (>99.9 %) $BaCO_3$ (Merck), Bi_2O_3 (Loba), K_2CO_3 (Merck), TiO_2 (Loba) and ZrO_2 (Loba) as starting

*E-mail: kv_ramesh5@yahoo.co.in

raw materials. The powders were mixed in required proportions accordingly and ball milled in ethanol medium for 24 h. The ball milled powders were ground and calcined at 960 °C for 8 h. After the calcination the powders were ground to achieve uniformity. The calcined powders were mixed with 5 % of polyvinyl alcohol and uniaxially pressed into cylindrical pellets by applying a pressure of 4000 kg/cm^2. The pellets were sintered at 1300 °C for 3 h. After sintering, the pellets were polished to a thickness of 1.33 mm and diameter of 12 mm. The sintered pellets were coated with a silver paste on both surfaces and heated at 300 °C for 1 h to use as electrodes for dielectric measurements.

Structural identification studies were done on calcined powders by using a Phillips X-ray diffractometer with CuKα radiation ($\lambda = 1.5406$ Å) in the range of 20° to 70° at a scan rate of 2°/min. Microstructure of the materials was studied by using a scanning electron microscope JEOL Model JSM-6390LV. Dielectric studies were carried out on Newton's 4th limited (PSM 1735) LCR meter in a frequency range of 20 Hz to 1 MHz. Dielectric studies were done in the temperature range of 40 °C to 300 °C. AC conductivity studies were done in the frequency range of 20 Hz to 1 MHz and in the temperature range of 375 °C to 450 °C.

3. Results and discussions

3.1. Structural studies

Structural characterization of the Zr substituted 0.8Ba0.2(Bi$_{0.5}$K$_{0.5}$)Ti$_{1-x}$Zr$_x$O$_3$ lead free ceramics was done by using X-ray diffraction in the 2θ range of 20° to 70°. Room temperature powder X-ray diffractograms of BT-BKT20 substituted with different amounts of Zr are shown in the Fig. 1. All the samples show the perovskite structure and no secondary phases are observed within the detection limit of X-ray diffraction. It implies that Zr^{4+} has entered into the BT-BKT20 lattice to form a solid solution. Tetragonal symmetry of the Zr substituted samples was confirmed by the splitting of the reflections (1 0 1)/(1 1 0), (0 0 2)/(2 0 0) and (1 1 2)/(2 1 1) observed at 31°, 45° and 56°, respectively, and these were in good agreement with the JCPDS data [13, 14].
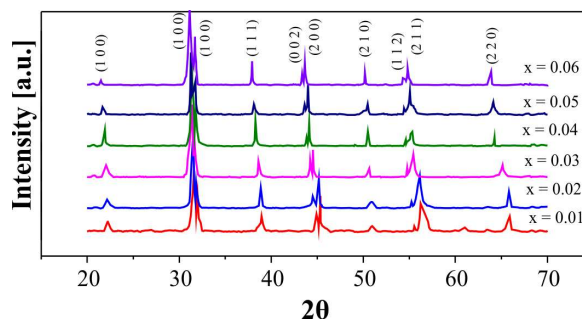

Fig. 1. X-ray diffractograms of Zr substituted 0.8Ba0.2(Bi$_{0.5}$K$_{0.5}$)Ti$_{1-x}$Zr$_x$O$_3$ lead free ceramics.

Substitution of Zr causes shifting of the reflection/diffraction peaks towards the lower angles. This is due to the substitution of large size Zr^{4+} cation (0.072 nm) in the place of comparatively small size cation Ti^{4+} (0.0601 nm). Substituting with the bigger size cation expands the lattice and results in an increase of lattice parameters. The values of lattice parameters (a [Å], c [Å]) are shown in Table 1. In the present composition range, no change in the structure was observed. As the Zr substitution was increasing, the tetragonality (c/a ratio) and density were decreasing. The low values of density (theoretical and experimental) are due to the evaporation of bismuth and potassium during the high temperature sintering process [12]. Microstructure images of Zr substituted samples are shown in Fig. 2.

3.2. Dielectric studies

Measurement results of dielectric properties of Zr substituted 0.8Ba0.2(Bi$_{0.5}$K$_{0.5}$)Ti$_{1-x}$Zr$_x$O$_3$ (x = 0.01 to 0.06) lead free ceramics as a function of temperature at different frequencies are shown Fig. 3. From Fig. 3, it is seen that at a particular temperature, dielectric constant decreases as the frequency increases for all the compositions. Also as the Zr content increases, the room temperature dielectric constant and maximum dielectric constant values are also decreasing. It is well known that as the Zr content in BaTiO$_3$ increases the dielectric constant values decrease [1, 2, 5, 7, 9].

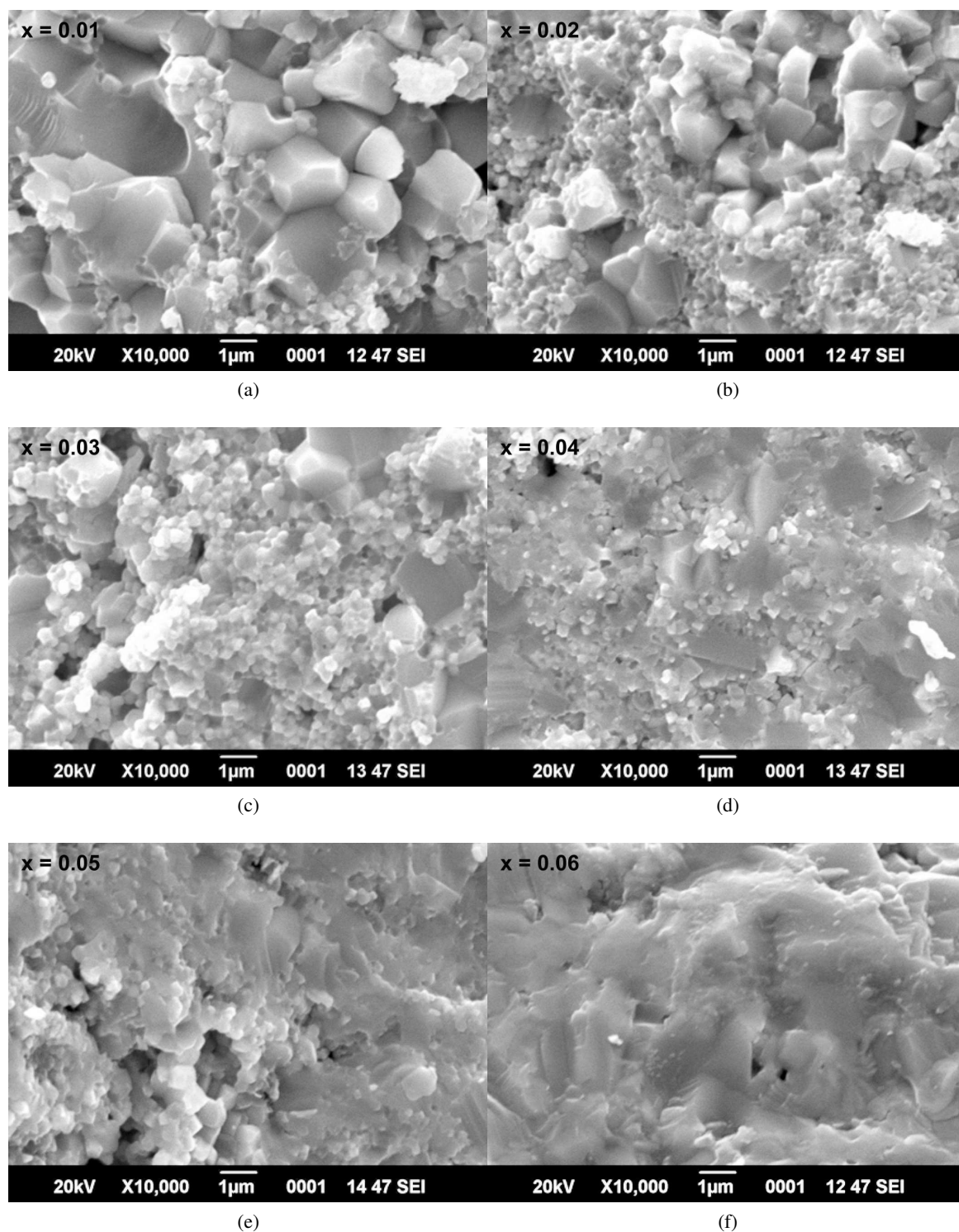Fig. 3 depicts the dielectric loss measured for all the Zr substituted samples as a function

Fig. 2. Microstructure images of Zr substituted 0.8Ba0.2(Bi$_{0.5}$K$_{0.5}$)Ti$_{1-x}$Zr$_x$O$_3$ (x = 0.01 to 0.06) lead free ceramics.

Table 1. Various parameters as a function of Zr substitution in $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$ (x = 0.01 to 0.06) lead free ceramics.

x	0.01	0.02	0.03	0.04	0.05	0.06
a [Å]	3.995	4.003	4.012	4.022	4.032	4.045
c [Å]	4.096	4.103	4.111	4.118	4.126	4.133
c/a	1.025	1.0249	1.0246	1.0238	1.0233	1.0217
Theoretical density[kg/m^3] [11, 15]	5860	5840	5810	5790	5760	5720
Exp. density[kg/m^3]	5284	5269	5253	5234	5230	5222
ε_{RT} [1 kHz]	1650	1550	1451	1408	1361	1315
ε_{max} [1 kHz]	2256	2065	2078	1605	1518	1466
tanδ (at RT for 1 kHz)	0.32	0.29	0.25	0.2	0.17	0.11
γ[1 kHz]	1.41	1.42	1.60	1.71	1.82	1.78
E_{AC} [eV]	0.28	0.34	0.37	0.23	0.18	0.14

of temperature at different frequencies. Dielectric loss is decreasing with an increase of Zr content. Dielectric loss is higher at lower frequencies and decreases with an increase of frequency. It shows that at higher frequencies dipoles were unable to follow the applied AC field and hence, a decrease in dielectric loss at higher frequencies occurred [6–8, 11]. Zhi et al. [16] reported that dielectric constant value also depends on the density of the samples. The decrease in density or increase in porosity (Fig. 2) with the increase in Zr substitution is responsible for the decrease of dielectric constant and loss.

From Fig. 3, it is also seen that ferroelectric to paraelectric phase transition temperature (Curie temperature) is decreasing with the increase in Zr content. This is due to the substitution of large size Zr^{4+} cation (0.072 nm) in place of small size Ti^{4+} cation (0.0605 nm) as this substitution depresses the oriented displacement of B-site ions in the oxygen octahedra. Therefore, the interaction between B-site ions and oxygen ions in the oxygen octahedra would become weaker, resulting in the decrease of phase transition temperature [1, 2, 8, 9, 11].

All the Zr substituted samples exhibit the diffused and dispersive ferroelectric to paraelectric phase transition, indicating relaxor behavior. The relaxor behavior is not just due to the Zr substitution, but even the Zr unsubstituted sample itself shows the relaxor behavior [13]. But the relaxor behavior increases with the increase of Zr substitution. In the case of Zr substituted $BaTiO_3$, the relaxor behavior is observed only at the higher values of Zr substitution (>0.3 mole) [17]. In the present study on the composition $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$, the relaxor behavior is observed for all Zr doped samples (x = 0.01 to 0.06). This is due to the multiple occupation of different valence cations (Ba^{2+}, Bi^{3+}, K^+) at the A-site and different homovalent cations (Ti^{4+}, Zr^{4+}) at the B-site [13, 18, 19]. Diffuseness of the phase transition can be calculated from the modified Curie-Weiss law [20]:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{max}} = \frac{(T - T_C)^\gamma}{C} \qquad (1)$$

where γ is degree of diffuseness/relaxation and the value of γ lies between 1 and 2. When $\gamma = 1$, the material is normal ferroelectric and follows an ideal Curie-Weiss law and when $\gamma = 2$, the material is diffused ferroelectric material. Degree of diffuseness has been calculated for all the Zr substituted samples and it was found to be increasing. Fig. 4 shows the Curie-Weiss law fit for the x = 0.01 and x = 0.06. The values of degree of diffuseness are shown in the Table 1.

3.3. AC conductivity studies

Effect of Zr substitution on conductivity can be understood by studying AC conductivity. So, the frequency dependent electrical conductivity was calculated at different temperatures for all
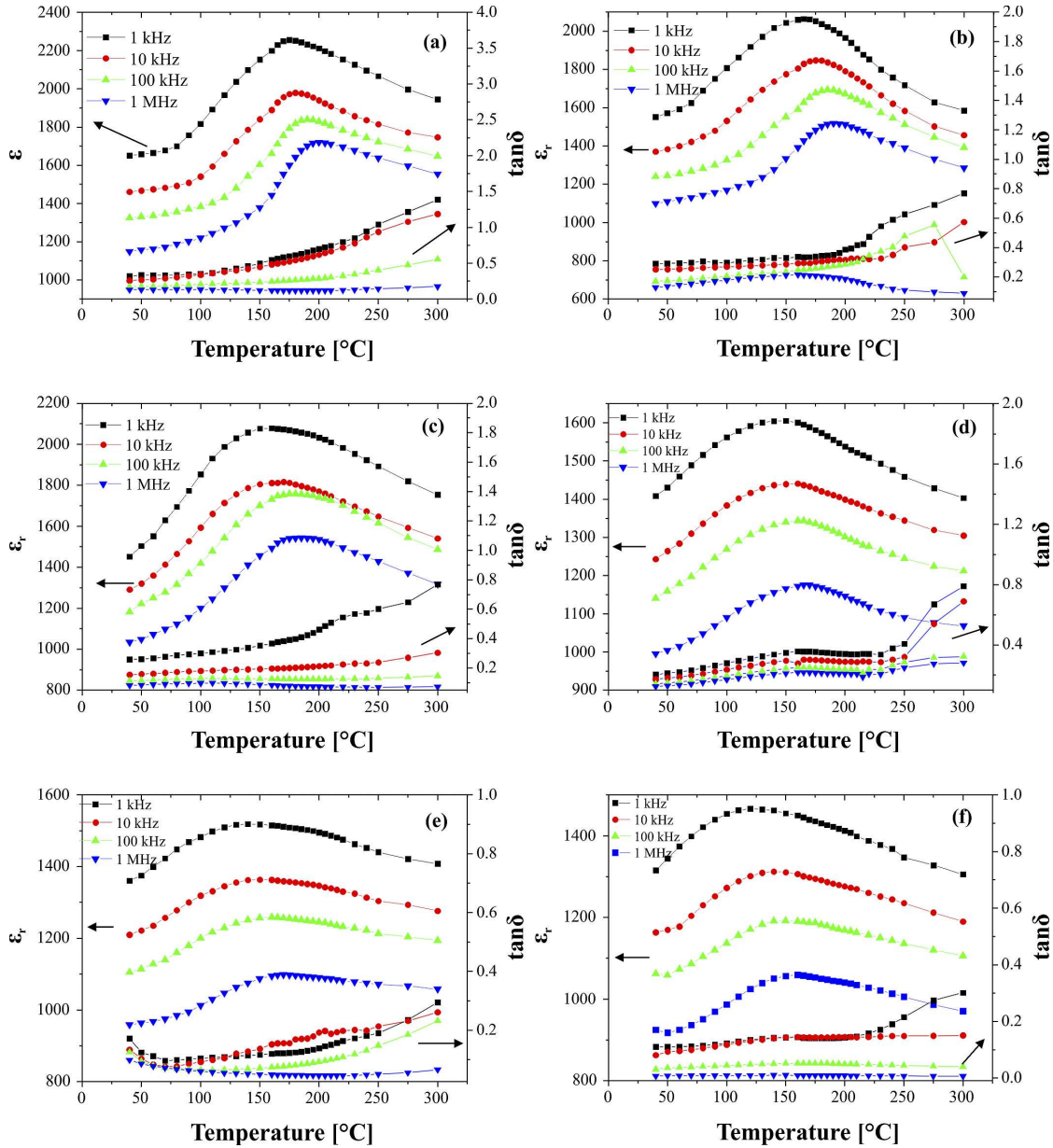
Fig. 3. Variation of dielectric constant and dielectric loss as a function of temperature at different frequencies for 0.8Ba0.2(Bi$_{0.5}$K$_{0.5}$)Ti$_{1-x}$Zr$_x$O$_3$ (x = 0.01 to 0.06) lead free ceramics: (a) x = 0.01; (b) x = 0.02; (c) x = 0.03; (d) x = 0.04; (e) x = 0.05; (f) x = 0.06.

the Zr substituted 0.8Ba0.2(Bi$_{0.5}$K$_{0.5}$)Ti$_{1-x}$Zr$_x$O$_3$ lead free ceramics by using the relation:

$$\sigma_{A.C} = \varepsilon' \varepsilon_0 \omega \tan \delta \qquad (2)$$

where ε' is the real part of dielectric constant, ε_0 is permittivity of free space, ω is angular frequency and tanδ is dielectric loss tangent [13]. AC conductivity was calculated at temperatures 375 °C,

400 °C, 425 °C and 450 °C. It is observed that at the above mentioned temperatures, frequency dependent conductivity was found to obey universal Jonscher's power law [21]:

$$\sigma_{A.C} = \sigma_0 + A\omega^s \qquad (3)$$

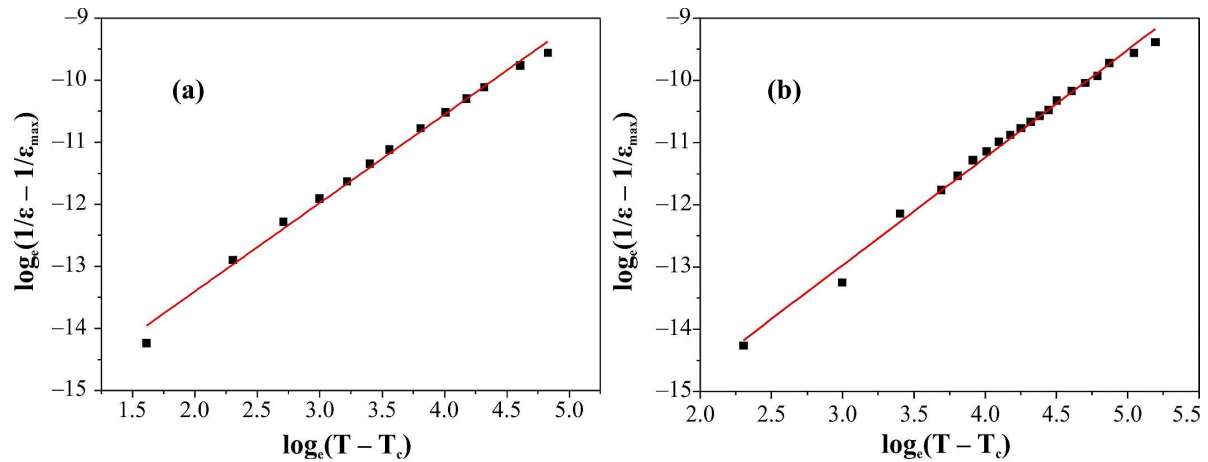where σ_0 is the frequency independent conductivity (DC conductivity), A is a constant,

Fig. 4. Modified Curie-Weiss law for $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$ (x = 0.01 and 0.06) lead free ceramics (solid line represents linear fitting): (a) x = 0.01; (b) x = 0.06.

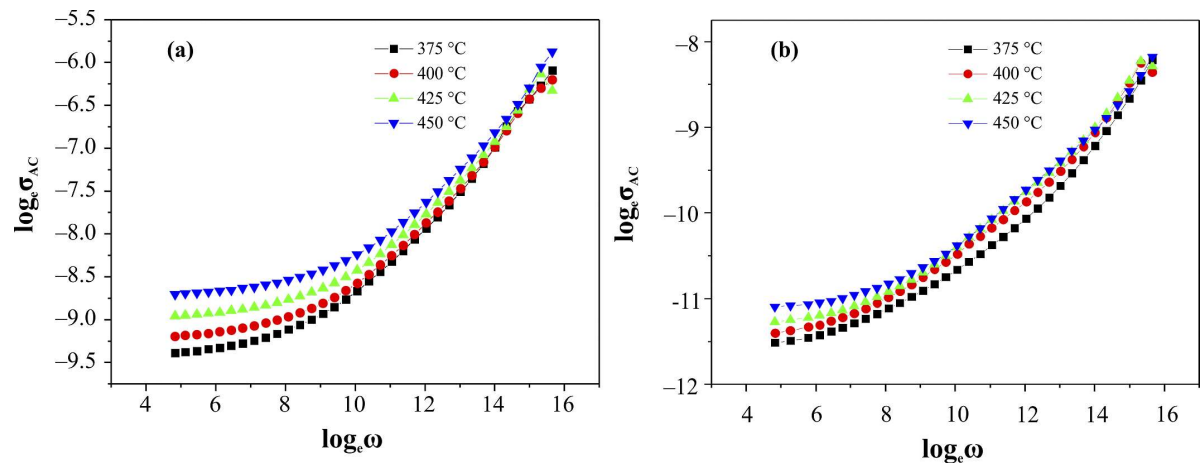Fig. 5. Frequency dependent AC conductivity for $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$ (x = 0.01 and 0.06) lead free ceramics at different temperatures: (a) x = 0.01; (b) x = 0.06.

ω is the frequency of AC field and s is the frequency dependent factor in the range of $0 < s < 1$. Fig. 5 shows the frequency dependent AC conductivity at different temperatures for $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$ lead free ceramics with x = 0.01 and x = 0.06.

It is clear from Fig. 5 that conductivity increases as the frequency and temperature increase. Dispersion in conductivity was observed at lower frequencies for all the Zr substituted samples and all the curves merged at higher frequency region for all temperatures indicating less defect mobility. The increase of conductivity

with temperature at high frequencies indicates possible release of space charges, due to which reduction in the barrier height of the material occurs. Plateau region is observed in the low frequency region (frequency independent conductivity, i.e. DC/bulk conductivity) and this plateau region of frequency is increasing with an increase of temperature. This is observed for all the Zr substituted samples. From Fig. 6, it is clear that as the Zr substitution is increasing AC conductivity is decreasing. This is due to the substitution of chemically more stable Zr which reduces the electronic hopping between Ti^{4+} and Ti^{3+}, thereby, increasing the resistivity of the material. Activation energy

(E_{AC}) was calculated by using Arrhenius relation and it was found to be decreasing from 0.28 eV for x = 0.01 to 0.14 eV for x = 0.06 at 1 kHz. The values are shown in the Table 1.
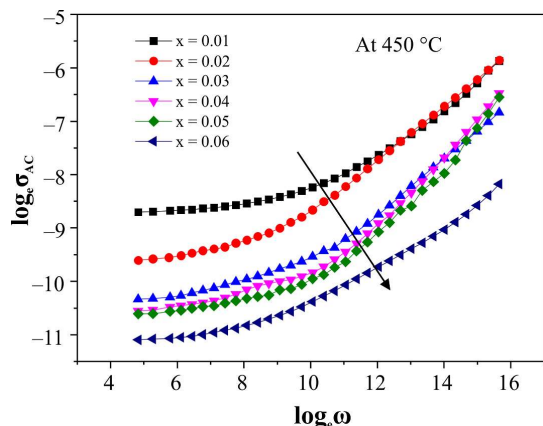

Fig. 6. Frequency dependent AC conductivity for $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$ at 450 °C (x = 0.01 to 0.06).

4. Conclusions

Zr substituted $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$ (x = 0.01 to 0.06) lead free ceramics were prepared by conventional solid state reaction method followed by high energy ball milling method. The formation of single phase tetragonal structure in all the Zr substituted samples was confirmed by X-ray diffraction studies. Frequency and temperature dependent dielectric studies showed the relaxor behavior in all the Zr substituted $0.8Ba0.2(Bi_{0.5}K_{0.5})Ti_{1-x}Zr_xO_3$ samples. Dielectric constant and dielectric loss were decreasing with the substitution of Zr. Curie temperature was also decreasing with the substitution of Zr. Degree of diffuseness was calculated and it was increasing with the substitution of Zr. Frequency and temperature dependent AC conductivity obeyed power law. Decrease in AC conductivity with Zr substitution can be attributed to reduction in the electron hopping between Ti^{3+} and Ti^{4+}.

References

[1] SAWANGWAN N., BARREL J., MACKENZIE K., TUNKASIRI T., *Appl. Phys A-Mater.*, 90 (2008), 723.
[2] JAMES A.R., CHANDRA P., PRASAD G., *J. Phys. D Appl. Phys.*, 39 (2006), 1635.
[3] SU-WEI Z., HAILONG Z., BO-PING Z., GAOLEI Z., *J. Eur. Ceram. Soc.*, 29 (2009), 3235.
[4] CHENG B.L., WANG C., WANG S.Y., LU H.B., ZHOU Y.L., CHEN Z.H., *J. Eur. Ceram. Soc.*, 25 (2005), 2295.
[5] MOURA F., SIMOES A.Z., STOJANVOIC B.D., ZAGHETE M.A., LONGO E., VARELA J.A., *J. Alloy. Compd.*, 462 (2008), 129.
[6] SANDEEP M., THAKUR O.P., CHANDRA P., SREENIVAS K., *B. Mater. Sci.*, 34 (2011), 1483.
[7] YU Z., ANG C., GUO R., BHALLA A.S., *Appl. Phys. Lett.*, 81 (2002), 1285.
[8] YU Z., ANG C., GUO R., BHALLA A.S., *Mater. Lett.*, 61 (2007), 326.
[9] TANG X.G, CHEW K.H., CHAN H.L.W., *Acta Mater.*, 52 (2004), 5177.
[10] YUJI U., KOSUKE T., TAKASHI K., AKIHIDE K., HIROKI M., *Jpn. J. Appl. Phys.*, 51 (2012), 09LE01.
[11] SATEESH P., OMPRAKASH J., KUMAR G.S., PRASAD G., *J. Adv. Dielec.*, 5 (2015), 1550002.
[12] HIRUMA Y., HAJIME N., TAKENAKA T., *J. Ceram. Soc. Jpn.*, 112 (5) (2004), S1125.
[13] RAMESH M.N.V., RAMESH K.V., *Int. J. Mod. Phys. B.*, 29 (2015), 1550119.
[14] *Tetragonal BaTiO3 JCPDS Card No. 05-0626.*
[15] ASHCOFT N.W., DAVID MERMIN N., *Solid State Physic*, Brooks Cole, California, 1976.
[16] ZHI J., ZHI Y., CHEN A., *J. Mater. Sci.*, 38 (2003), 1057.
[17] DOBAL P.S., DIXIT A., KATIYAR R.S., YU Z., GUO R., BHALLA A.S., *J. Raman Spectrosc.*, 32 (2001), 69.
[18] WANLI Z., RUZHONG Z., *Ceram. Int.*, 39 (2013), 9121.
[19] YANG J., HOU Y., WANG C., ZHU M., YAN H., *Appl. Phys. Lett.*, 91 (2007), 023118.
[20] UCHINO K., NOMURA S., *Ferroelectrics Lett.*, 44 (1982), 55.
[21] JONSCHER A.K., *Dielectric Relaxation in Solids*, Chelsea Dielectric Press, London, 1983.