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Physics

AN EXPERIMENTAL STUDY ON PHASE TRANSITION BEHAVIOR OF $(Ba_{1-x}Mg_x)TiO_3$ (x= 0.04 & 0.08) CERAMICS

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Abstract

$(Ba_{1-x}Mg_x)TiO_3$ (x = 0.04 and 0.08) (BMT) powders are synthesized using a dry route involving solid state thermo-chemical reaction in a mixture of $BaCO_3$, MgO and TiO_2. The powders were calcined at temperature 1000°C and are compacted to pellets using hydraulic press. The samples are then sintered at temperature 1325°C to achieve above 96% of theoretical density. The structure of samples as obtained by XRD is tetragonal. It is observed that BMT samples revels dielectric anamoly around 90°C and 86°C for BMT04 and BMT08 respectively, which are the transition temperature from ferroelectric to paraelectric phase during heating mode at frequency 100 KHz. The peak values of dielectric data in cooling mode are higher than heating mode, which gives the thermal hysteresis of 2°C and 1°C for these samples respectively. In BMT04, the decrease in thermal hysteresis with concentration of Mg^{2+} indicates the phase transition towards diffuse phase or relaxor. The peak temperature of dielectric data are constant with frequency, which confirms that samples may be regular phase transition. The real part of dielectric data decrease with increase of frequency. The curie temperature obtained from Curie-Wiess behavior for BMT are lower than the transition temperature, confirming the transition is first order type. Decrease of activation energy studied on the basis of resistance of BMT samples also confirms the phase transition behavior changing from FE tetragonal towards PE cubic phase transition with increase of Mg^{2+} contents.

Keywords: *Phase transitions, thermal hysteresis, resistivity, dielectric property*

Introduction

Recent developments in microelectronics technologies have created a great demand of low and high dielectric constant materials. As we know that internet is the fastest growing industry of the 21st century, the low and high dielectric constant materials are one of the keys components of the internet devices that perform transmission, communication and storage functions (Hippel 1954). Currently, there has been keen interest in the field of ceramic materials due to their excellent mechanical and physical properties. Electronic ceramics are very useful in device fabrication. The electronic ceramics, such as, Barium titanate ($BaTiO_3$), Lead titanate ($PbTiO_3$), Lead zirconate ($PbZrO_3$) with ABO_3 perovskite structure show ferroelectric and anti-ferroelectric behaviors which are being used in many applications in electronics and optics (Lines 1997). The large number of applications of these materials is the consequences of ferroelectric and anti-ferroelectric properties such as dielectric, piezoelectric, pyroelectric and electro-optic properties. Such properties can be improved and modified by chemical substitutions at A or B site of ABO_3 structure. Barium titanate, perovskite structure, is a common ferroelectric material with a high dielectric constant, widely utilized to manufacture electronic components such as multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers, and a variety of electro-optic devices (Morell and Niepce 1991). Because of people's demands, dielectric (essentially non-conducting) characteristics of ceramics materials are increasing rapidly. At the same time people are attempting to reduce the size of all communication devices as small and as light as possible. Due to this trend, high dielectric constant materials such as barium titanate nowadays become more and more important in the fabrication of devices (Tarrev 1975). More over due to tough strength as well as high dielectric constant ceramic materials are becoming much

attractive towards research field. Barium titanate is an oxide of barium and titanium with the chemical formula $BaTiO_3$. Barium titanate is a common ferroelectric material which adopts the perovskite structure type ABO_3. It is a ferroelectric material, with a photorefractive effect and piezoelectric properties. It has five phases as a solid, listing from high temperature to low temperature: hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral crystal structure (Wei and Yao 2007). All of the structures exhibit the ferroelectric effect except cubic. In this work, we have studied the phase transition behavior of $(Ba_{1-x}Mg_x)\ TiO_3$ (for x = 0.04 and 0.08) ceramics obtained by dry-route method.

Materials and Methods

We have synthesized $(Ba_{1-x}Mg_x)\ TiO_3$ (x = 0.04 and 0.08) powders by dry-route method involving solid state thermochemical reaction between TiO_2, $BaCO_3$ and MgO. Powders, which were weighed and then milled for 6hrs in acetone. After drying, the mixture was calcined in an alumina crucible at 1000ºC for 4hrs. The calcined powders were remilled for 4hrs and then dried. The powders added with 5% PVA (poly-vinyl alcohol) were compacted into disc shaped pellets with a diameter of 1.32 cm using a hydraulic press at an optimized load in the range of 70 KN to 80 KN. The green pellets of both pure and Mg doped barium titanate were sintered at 1325ºC for 4hrs. In order to measure the dielectric properties, silver paste was painted on the polished ceramic samples as the electrodes and heated at 500ºC for 30 min. The electrical properties of the ceramics were determined by a HIOKI 3532-50 LCR HITESTER. The dielectric constant (ε_r) was calculated from the capacitance (C) using the equation

$$\varepsilon_r = Cd/\varepsilon_o A$$

where, $\varepsilon_o = 8.854 \times 10^{-12}$ F/m, d= plate separation, A=area of plate ($A=\pi D^2/4$, "D" is diameter of the pellet). The pellets formed are used for the various characteristics. The structure and lattice parameters are determined from X-ray study with the help of TEL-X-OMETER (TEL-580) and D_2 PHASER DIFFRACTORMETER (BRUKER AXIS GERMAN) from National Academy of Science and Technology (NAST), Lalitpur, Nepal.

Results and Discussion

a) Crystal structure

The X-ray diffraction analysis confirmed formation of the desired crystalline structure. For X-ray characterization, sintered pellets are crushed into fine powder using mortar and pestle. We have carried out the XRD experiment to determine the lattice parameters for $(Ba_{1-x}Mg_x)\ TiO_3$ (x = 0.04 and 0.08) using tetragonal phase by embedded into the UNITCELL software. The figure 1 and 2 shows the X-ray diffraction profiles of the BMT04 and BMT08 samples respectively in which the splitting of reflection 200 confirms the tetragonal structure of the samples so the strong perovskite reflections are indexed with respect to a tetragonal structure with indices [1 0 0], [1 1 0], [1 1 1], [2 0 0] and [2 1 0] are shown in figure. XRD patterns were scanned in the 2θ range of 10ºC - 80ºC at room temperature.

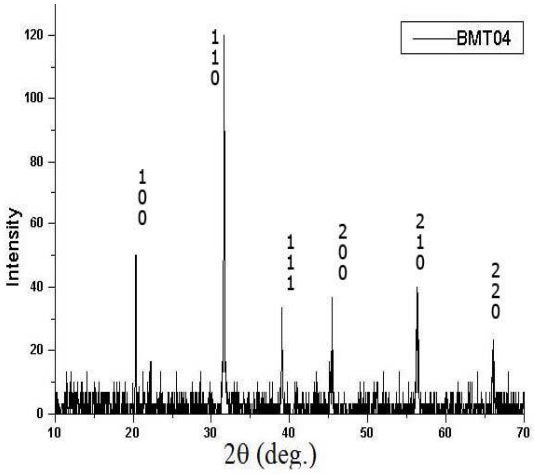

Figure 1. XRD-data of BMT04 sample.

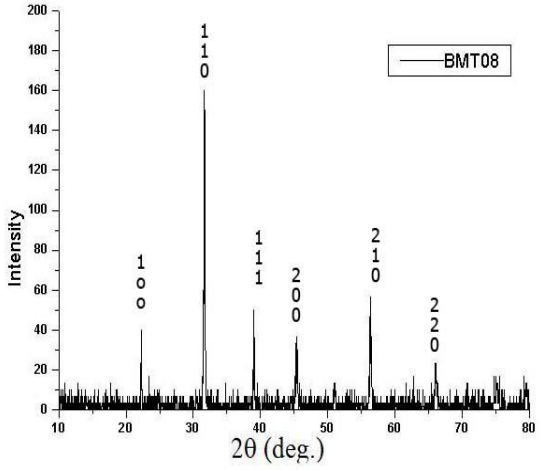

Figure 2. XRD-data of BMT08 sample.

b) Ferroelectric to paraelectric phase transition

The dielectric measurements were carried out at different frequencies. The variation of real part of dielectric constant with temperature during heating

mode for samples BMT04 and BMT08 at 100 KHz are as shown in figure 3 and 4 respectively.

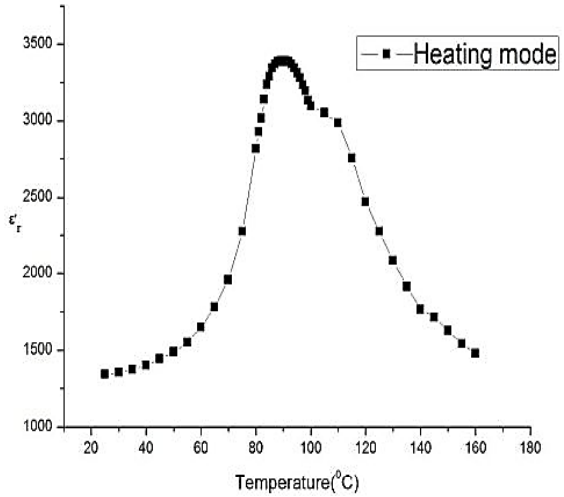

Figure 3. Variation of real part of dielectric constant with temperature at 100 KHz for BMT04 during heating cycle.

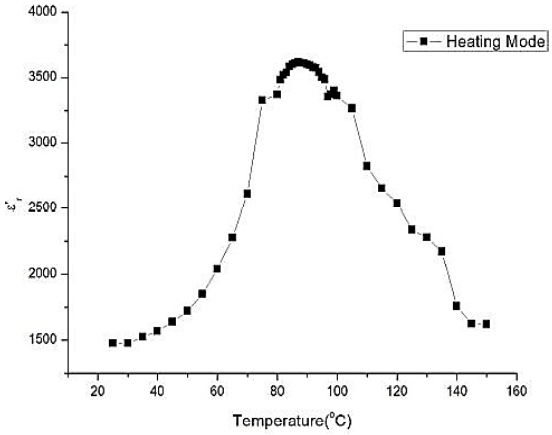

Figure 4. Variation of real part of dielectric constant with temperature at 100 KHz for BMT08 during heating cycle.

For these samples the ferroelectric to paraelectric phase transition are occurs at temperatures 90°C and 86°C respectively. The result obtained is exactly matched with the reported result by Miao *et al*. (2006). The peak values of dielectric constants for heating mode are 3397.689 and 3620.789 for BMT04 and BMT08 samples whereas the corresponding values of dielectric constants at temperature 30°C are 1338.939 and 1524.182 for respective samples. There are several reports which supports our results (Pandey 1989; Tiwari 1995; Yasuda 1996; Shvartsman 2006; Wei and Yao 2007). It is observed that the substitution of Mg^{+2} concentration in BMT lowers the ferroelectric to paraelectric phase transition temperature is almost linearly with compositions as shown in figure 5.

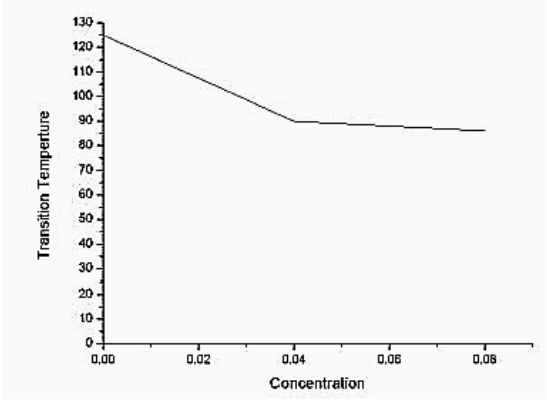

Figure 5. Variation of transition temperature with concentrations.

c) Thermal hysteresis

The hysteresis is obtained from the difference between the transition temperatures during heating and cooling modes i.e. gives the value of thermal hysteresis. Figures 6 and 7 illustrates the variation of real part of dielectric constants for both heating and cooling modes at frequency 100 KHz for samples BMT04 and BMT08 respectively.

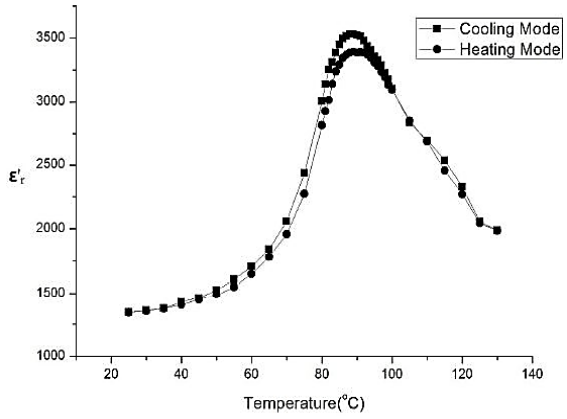

Figure 6. Variation of real part of dielectric constant with temperature for both heating and cooling cycle at 100KHz for BMT04.

The value of thermal hysteresis observed in BMT04 is 2°C but for BMT08 is 1°C. The decreasing value of thermal hysteresis indicate that ferroelectric to paraelectric phase transition in BMT04 is tending towards is diffused or relaxor phase transition.

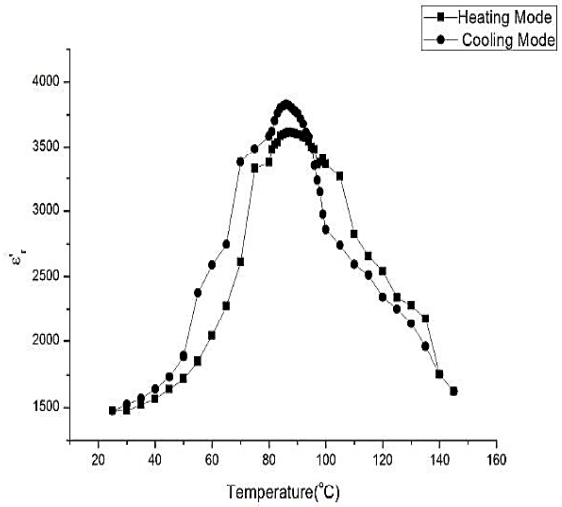

Figure 7. Variation of real part of dielectric constant with temperature for both heating and cooling cycle at 100KHz for BMT08.

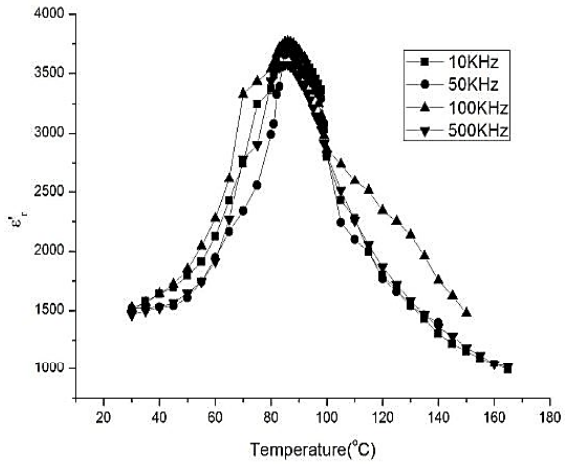

Figure 9. Variation of real part of dielectric constant with temperature at with temperature at different frequencies for BMT08.

d) Frequency dependence of dielectric data

The variation of real parts of the dielectric constant with temperature for different frequencies 1KHz, 10KHz, 100KHz, 500KHz and 1MHz for the samples BMT04 and BMT08 as shown in figure 8 and 9. As can be seen, the parameter has dependence in frequency.

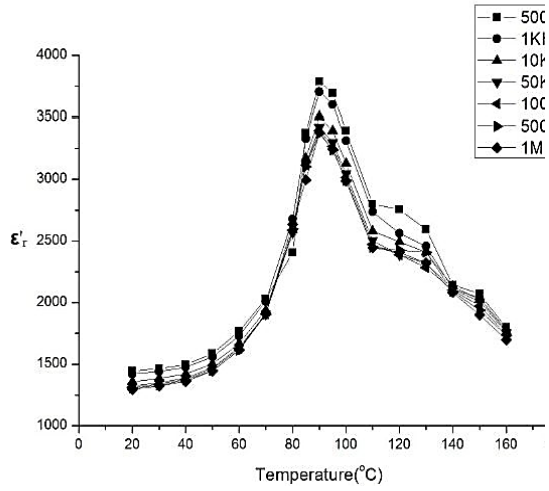

Figure 8. Variation of real part of dielectric constant with temperature at with temperature at different frequencies for BMT04.

We have also carried out the dielectric measurement of the samples with respect to frequencies at various temperature i.e. 25°C, 50°C, 75°C, 100°C, 125°C and 150°C.

Figure 10 shows the variation of real part of dielectric constant as a function of natural log of frequency at different temperatures for BMT04. It is evident from this figures that the dielectric data decreases with the increase of frequency. It is also noted that the dielectric data decreases with temperature up to transition temperature then starts to increase.

In the frequency dependence measurements the dielectric data decreases up to frequency 1 MHz and then it starts increasing due to anomalous dispersion effect in the sample.

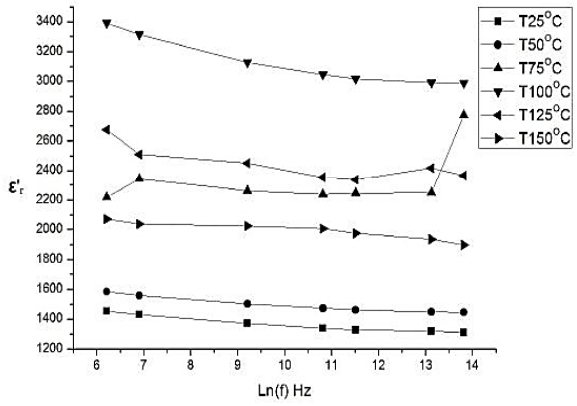

Figure 10. Variation of real part of dielectric constant as a function of logarithm of ln(f) function for different temperatures for BMT04 sample.

e) Curie - Weiss Law

The dielectric constant of BMT samples exhibits Curie-Weiss behavior with temperature at very

close to transition temperature followed by the relation;

$$\varepsilon'_r = C/(T-T_0)$$

where C is Curie constant and T_o is Curie temperature. The validity of Curie-Weiss law for BMT samples are demonstrated in Figure 11, which shows the variation of dielectric stiffness ($1/\varepsilon_r$) with temperature.

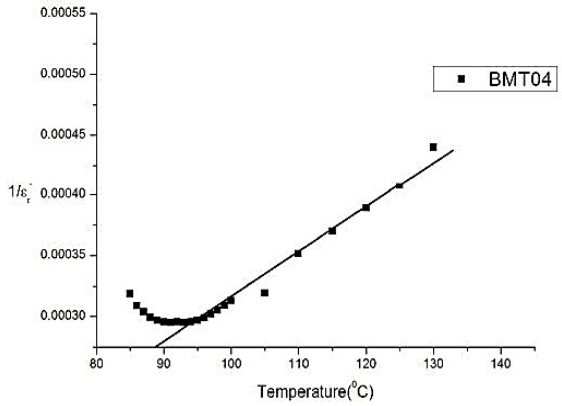

Figure 11. The variation of dielectric stiffness ($1/\varepsilon_r$) with temperature for BMT04 at 100 KHz.

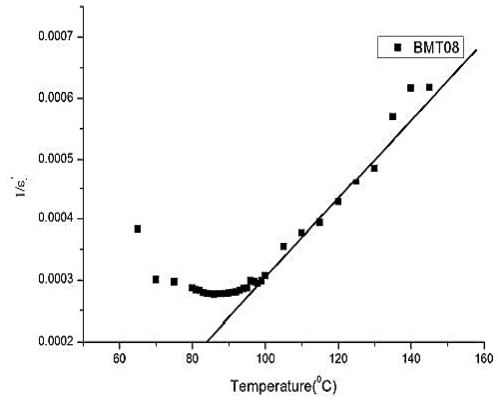

Figure 12. The variation of dielectric stiffness ($1/\varepsilon_r$) with temperature for BMT08 at 100 KHz.

From this figure, we have calculated the Curie constant using the slope of the fitted straight line. The observed values of Curie constant for BMT04, and BMT08 are; 1.85×10^5 and 1.66×10^5 whereas the reported value of Curie constant for BMT00 or $BaTiO_3$ is 1.592×10^5(Pandey 1989). The Curie temperatures observed from the above plots for BMT04 and BMT08 are 88°C, and 84°C respectively, are the intercept values of X- axis in the dielectric stiffness versus temperature plots. The Curie temperature of our sample is less than that of transition temperature in the ferroelectric to Paraelectric phase which is the characteristic of the first order phase transition. From these figures, it is also evident that the deviation from Curie-Wiess law is marked in BMT08 confirming the phase transition tending towards diffuse type phase transition or relaxor.

f) Resistance measurement

We have also carried out the resistance measurement as a function of temperature with the help of the HIOKI3532-50 LCR HITESTER. Figures (13, 14) show the variation of resistances with temperature during heating mode of frequency 100 KHz for BMT04 and BMT08.

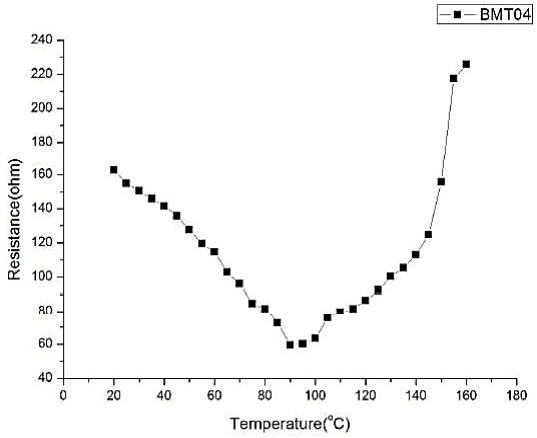

Figure 13. The variation of resistance with temperature for BMT04 at frequency 100KHz.

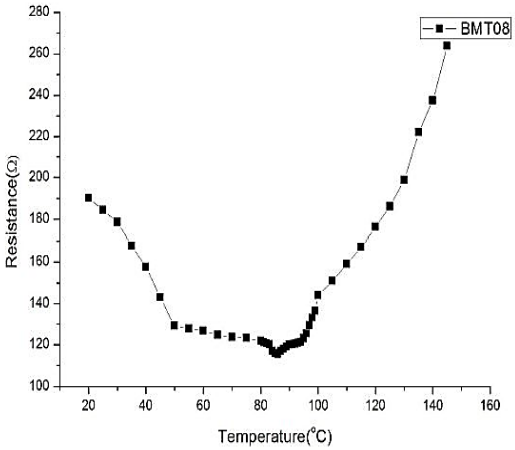

Figure 14. The variation of resistance with temperature for BMT08 at frequency 100KHz.

It is evident from this figure that resistances decrease with increase of temperature up to about transition temperature as observed in dielectric

data. Above transition temperature, the resistance is increased. The decrease of resistance with increase of temperature up to transition temperature represents NTCR (negative temperature coefficient of resistance) effect. Whereas the increase of resistance with temperature starting from transition temperature represents PTCR (positive temperature coefficient of resistance) effect. The values of activation energy and resistivity different samples are given in table 1.

Table 1. The values of activation energy and resistivity.

SN	Sample	$\emptyset$ (eV)	$\rho_o(\Omega m)$
1	BMTO4	0.6735	$8.99X10^9$
2	BMTO8	0.1736	$1.84X10^8$

Conclusion

By liquid displacement method with glycerin the experimental densities of samples BMT04 and BMT08 are 6.730 gm/cc and 6.540 gm/cc respectively. Whereas the theoretical densities are 6.792 gm/cc and 6.754 gm/cc for BMT04 and BMT08 respectively. The structure of BMT04 and BMT08 samples is tetragonal. The peak value of dielectric data are found to be at temperature 88°C and 83°C for BMT04 and BMT08 respectively, which are the transition temperatures at frequency 100 KHz. At transition temperature there is a change of phase from ferroelectric to paraelectric phase on heating. It is also observed that substitution of Mg^{2+} in BMT lowers the transition temperature linearly. It is also noted that the peak value of dielectric constant is higher during cooling mode than that of heating mode.

The peak value of temperatures at heating and cooling mode are different, which gives the thermal hysteresis of 2°C and 1°C for BMT04 and BMT08 respectively. It is also noted that the dielectric data decreases with temperature up to transition temperature then starts to increase. In the frequency dependence measurements the dielectric data decreases up to frequency 1 MHz and then it starts increasing due to anomalous dispersion effect in the sample. The Curie temperature obtained from Curie Weiss behavior for BMT04 and BMT08 are 88°C and 84°C respectively. The observed values of Curie constant for BMT04 and BMT08 are; 1.85×10^5 and 1.66×10^5. The value of slope or gamma is 1.055, 1.522 for samples BMT04 and BMT08 respectively. This confirms that the phase transition in BMT04 is regular type, whereas sample BMT08 tending towards diffused type or relaxor type. The activation energy for BMT04 and BMT08 are 0.6735eV and 0.1736eV respectively.

Acknowledgements

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