

# Temperature Sensitive Conductivity Studies of NBT-Based Lead-Free Ternary System

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## Abstract.

The frequency and temperature dependence electrical conduction characteristics of a lead-free 0.78NBT-0.2ST-0.02BT ternary system were investigated by impedance spectroscopy. Variation of real part of conductivity with frequency reveals a frequency independent and a dispersive region obeying Jonscher power law. The relatively higher values of S-parameter in the mid temperature range envisage the presence of localized relaxation or hopping of the charge carriers. The activation energies calculated from the temperature dependent hopping frequency and dc conductivity, portray the increase of unsuccessful hops of the charge carriers with increase in temperature according to the Jump relaxation model. Interestingly the conductivity values could be curbed by introduction of BT in to NBT-ST. The collapsing of the scaled conductivity spectrum in to a single master curve depicts the temperature independent conduction relaxation mechanism.

**Keywords:** Conductivity, Ternary system, activation energy, relaxation mechanism

## 1. INTRODUCTION

Relaxor ferroelectrics (RFEs), particularly  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (commonly abbreviated as NBT) has been the center of interest in the electronic industries to cater the urgent surge for creating a lead free environment. Extensive research has brought in the use of these ceramics as sensors, actuators, ultrasonic transducers, multilayer capacitors, non-volatile memories etc., owing to their adequate electromechanical properties along with peculiar phase transition and relaxor behaviour [1]. However, NBT comes with some detrimental properties like large coercive field and high conductivity which makes the poling process difficult. During high temperature sintering, possibly the volatilization of  $\text{Bi}^{2+}$  ions along with partial reduction of  $\text{Ti}^{4+}$  ions to  $\text{Ti}^{3+}$  incorporates oxygen vacancies, which may be responsible for its large conductivity [2, 3]. In this context, solid solutions of NBT with other perovskites like  $\text{BaTiO}_3$  (BT),  $\text{SrTiO}_3$  (ST),  $\text{K}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$  (KBT),  $\text{KNO}_3$  (KN),  $\text{K}_{0.5}\text{Na}_{0.5}\text{NO}_3$  (KNN) [4-8] are considered among which the rarely investigated species NBT-ST emerges as a potential candidate for lead free alternative to widely used PZT in piezoelectric applications. Substitution of  $\text{Sr}^{2+}$



ions found to be suitable to improve the relaxor properties in NBT. Further, introduction of BT into NBT-ST enhances its piezoelectric properties forming a noteworthy ternary system. Recently, studies on piezoelectric and dielectric properties of NBT-ST-BT has been carried out by Praharaj et al. [9, 10]. Nevertheless, a special attention on conductivity study of the samples is highly desirable to facilitate the ease of poling process. From such a viewpoint, an attempt has been made to probe into the conductivity of 0.78NBT-0.2ST-0.02BT (NBT-ST-2BT) ternary solid solution and improve its electrical properties. Impedance spectroscopy has been used as an effective tool to explore the conductivity relaxation of the sample.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials and Method

Dense ceramic samples of 0.78Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>-0.2SrTiO<sub>3</sub>-0.02BaTiO<sub>3</sub> with 100% perovskite phase were prepared from Na<sub>2</sub>CO<sub>3</sub> (99.8%, Acros Organics, New Jersey, USA), Bi<sub>2</sub>O<sub>3</sub> (99.9%, Kojundo Chemical Lab Co., Saitama, Japan), SrCO<sub>3</sub> (99.9%, Aldrich), BaCO<sub>3</sub> (99.98%, Sigma-Aldrich, St. Louis, USA) and TiO<sub>2</sub> (99.9%, Sigma-Aldrich, St. Louis, USA) by high temperature solid state reaction method. The details of sample preparation has been given elsewhere [9].

### 2.2. Characterization Techniques

The impedance measurements were carried out in a PSM1735 Impedance Analyser (N4L-NumetriQ) at a frequency range of 10<sup>-3</sup> – 10<sup>3</sup> kHz and by using a programmable furnace in the temperature range of 50 – 650 °C. Prior to this, the sintered pellets were sectioned and polished to a 0.25 µm finish. Both the surfaces of the samples were electroded with silver paste and then annealed at 500 °C for 2 hrs.

## 3. RESULTS AND DISCUSSION

Fig. 1(a) and its inset representing the  $Z'$  ( $f$ ) spectra of NBT-ST-2BT in the temperature range 50-650 °C follow a sigmoidal pattern. As indicated in the figure, the  $Z'$  values decrease with the increase in temperature in the low frequency regime and forms a plateau like region from 400 °C onwards. A decreasing trend in the magnitude of  $Z'$  with temperature clearly indicates the increase of conductivity which may be possibly attributed to the formation of oxygen vacancies with rising temperature to maintain the charge neutrality. This is followed by high frequency tail or saturation region which may be due to the lowering of barrier height at high frequencies and release of space charge increasing the ac conductivity of the system.  $Z''(f)$  spectra shown in Fig. 1(b) and its inset in the same temperature range also shows a marked dependence on temperature. The plot at all temperatures consists of a low frequency peak ( $\geq 400$  °C) and a high frequency tail. It also displays a decrease in the  $Z''_{\max}$  values along with an asymmetric broadening of the peaks and a shift in the inflation frequency (frequency corresponding to  $Z''_{\max}$ ) to higher frequency side with the rise in temperature. Such facts suggest temperature sensitive relaxation processes and active conduction mechanism [3]. Hence to probe into the electrical properties of the system under investigation, a meticulous survey of the conductivity performance is the sole aim of this piece of work. Fig. 2 illustrates the frequency dependence of real part of conductivity from 50 °C to 650 °C. Interestingly, the values of conductivity obtained are much less than that reported earlier for NBT-ST samples [11] which may be attributed to the introduction of Ba<sup>2+</sup> ions at the A-site of the perovskite compound.

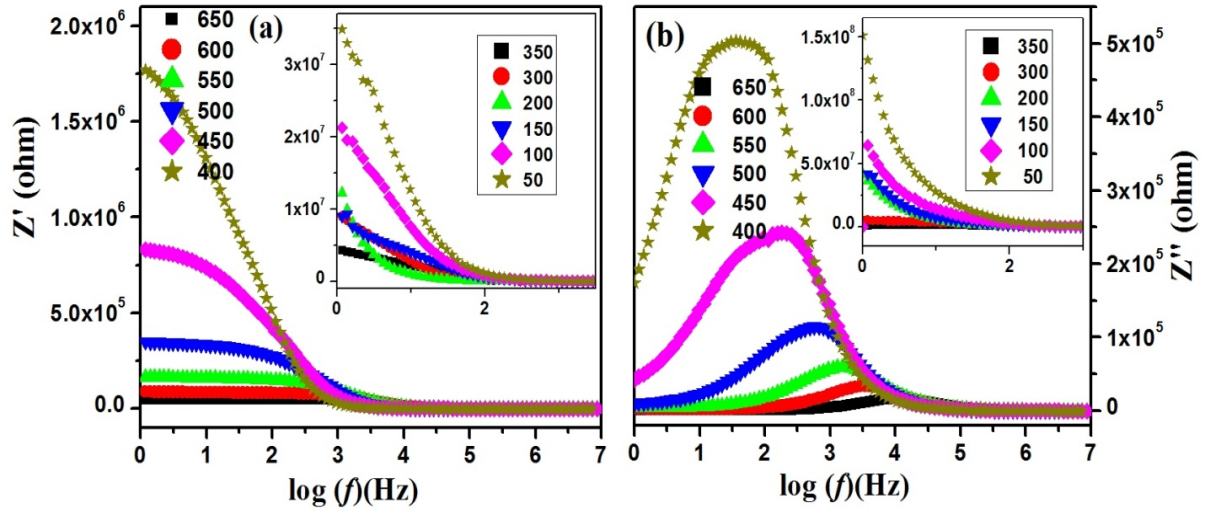


**Figure 1.** Frequency dependent  $Z'$  and  $Z''$  of NBT-ST-2BT at different temperatures

At all temperatures, the plot consists of a nearly frequency independent region corresponding to dc conductivity ( $\sigma_{dc}$ ) segregated from a frequency dispersive region. It can be noted that the frequency at which dispersion gains prominence shifts towards the higher frequency side as the temperature increases. The onset of conductivity relaxation is indicated by a crossover from frequency independent region to frequency dispersive region and is analyzed by using Jonscher power law [12]:

$$\sigma(\omega) = \sigma_{dc} + A\omega^S \quad (1)$$

where  $\sigma_{dc}$  is the dc conductivity,  $S$ -parameter represents the degree of interactions between the mobile charge carriers with the surrounding lattice lying between 0 and 1; both  $A$  and  $S$  are weakly temperature dependent. Values of the  $S$ -parameter at all temperatures lie around 0.9 which depicts the interactive nature of the charge carriers. A closer introspection of the  $S$ -parameter (Fig. 3(c)) reveals that in the mid temperature range the values are relatively more than the high and low temperature zone.

This suggests localized relaxation associated with the charge carriers (polar nano regions as NBT-ST-2BT is a RFE [9]) rather than long range barrier hopping in the mid temperature range [3]. The non-existence of polar nano regions in the high temperature regime which are almost frozen at low temperatures give rise to long ranged conduction relaxation. The frequency response of the electrical conductivity may be explained by the jump relaxation model [13]. According to this model, at lower frequencies of the ac field, there is a high probability of the charge carriers hopping to their neighboring sites and staying there since the neighborhood has enough time to be relaxed with respect to the new position of the charge carriers. The conductivity in the low frequency region is related to the successful hopping mechanism and gives rise to the dc conductivity. However, beyond the low frequency region, the number of unsuccessful hops increases due to higher frequencies of the ac field. Such a transformation arises at a frequency called the hopping frequency ( $f_H$ ). In the present sample,  $f_H$  is calculated using the formula [14]:

$$f_H = (\sigma_{dc} / A)^{1/S} \quad (2)$$

The  $f_H$  is found to be temperature dependent and obeys the Arrhenius law (Fig. 3(a)):

$$f_H = f_0 e^{-(E_a / kT)} \quad (3)$$

where  $E_a$  is the activation energy for the successful hopping.

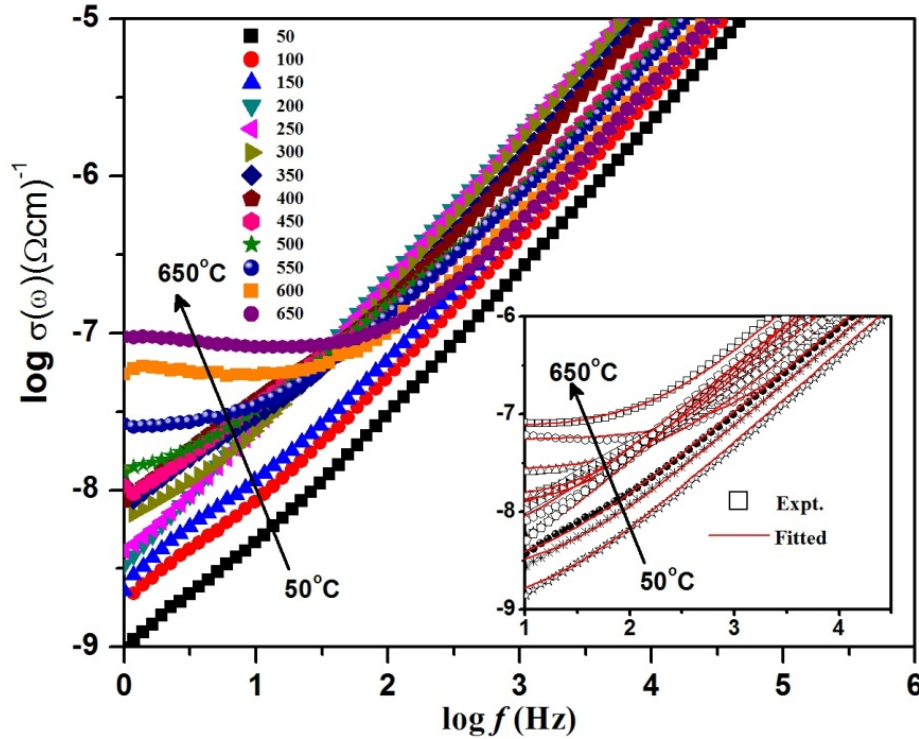


**Figure 2.** Frequency dependent ac conductivity of NBT-ST-2BT at different temperatures

The plot separates into two distinct regions of different activation energies bridged by a flat region. The flat region may associate with the temperature range over which the nucleation of PNRs takes place. Values of  $E_a$  obtained enunciate the fact that the number of success hops is more at low temperatures. At higher temperatures, the flipping frequencies of the charge carriers increase leading to more unsuccessful hops. To further support this fact,  $\log \sigma_{dc}$  vs  $1000/T$  [Fig 3(b)] obeying Arrhenius law:

$$\sigma_{dc} = \sigma_0 e^{(E_{dc}/kT)} \quad (4)$$

where  $E_{dc}$  is the activation energy for dc conduction. The higher value of  $E_{dc}$  in the high temperature interval gives an impression that the frequency dispersion increases as the temperature increases. Further it is also found that values of  $E_a$  and  $E_{dc}$  are close to each other. To have a better insight into the common underlying physics of the conductivity mechanism, scaling studies have been conducted and at different temperatures, the real part of conductivity following [15]:

$$\sigma(\omega) / \sigma_{dc} = F(f/f_0) \quad (5)$$

where  $f_0$  is the scaling frequency,  $F$  is the scaling function independent of temperature. Fig. 3(d) demonstrates the scaled conductivity spectra which collapsed into one master curve at temperatures which clearly depicts nearly temperature insensitive conduction mechanism though a little dispersion is found on the higher frequency side.

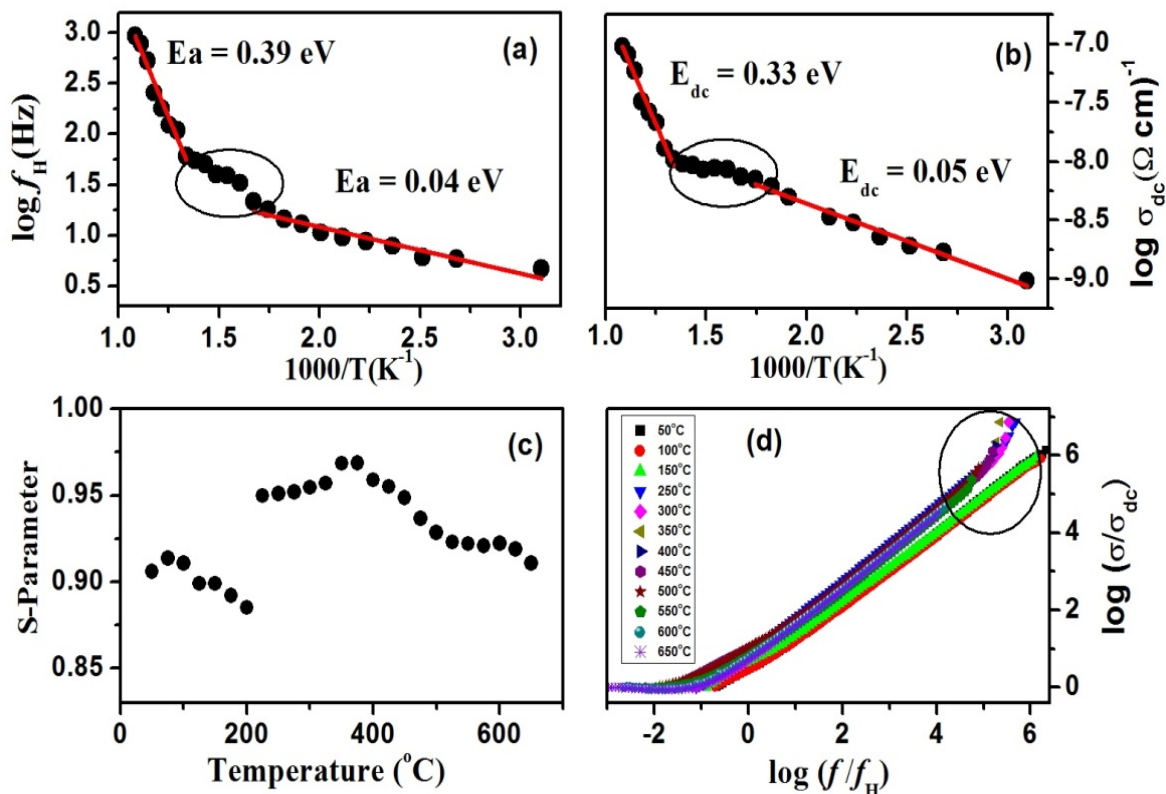


**Figure 3.** (a)  $\log f_H$  vs.  $1000/T$ , (b)  $\log \sigma_{dc}$  vs.  $1000/T$ , (c) S-parameter vs. Temperature and (d) conductivity scaling curves of NBT-ST-2BT at different temperatures.

#### 4. Conclusion

NBT-ST-2BT ceramics prepared by conventional solid state reaction technique show an increase in the conductivity with temperature as evidenced from the  $Z'(f)$  and  $Z''(f)$  spectra. The variation of real part conductivity with frequency which consisted of a nearly frequency independent region and a frequency dispersive region followed the universal power law. The higher values of S-parameter in the mid temperature range symbolize conductivity due to localized hopping or short ranged ordered orderings. The temperature dependence of hopping frequency and dc conductivity obey Arrhenius law and activation energies calculated from both the fittings segregated into two distinct regions with a flat and temperature insensitive region in between them. Finally, the scaling studies on conductivity reveal almost temperature insensitive conduction mechanism due to the collapsing of the all the curves into a single master curve. It is observed that the conductivity can be pinned down by the introduction of BT in to NBT-ST system furnishing an easier poling process of the sample.

#### Reference

- [1] J. Rodel, W. Jo, K.T.P. Seifert, E. Anon, T. Granzow, and D. Damjanovic, 2009, *Journal of American Ceramic Society*, Vol. 92, pp.1153.
- [2] T.R. Shrout and S.J. Zhang, 2007, *Journal of Electroceramics*, Vol. 17, pp. 111.
- [3] R. Kumari, N. Ahlawat, A. Agarwal, S. Sanghi, M. Sindhu, and N. Ahlawat, 2016, *Journal of Alloys and Compounds*, Vol. 676, pp. 452.
- [4] S.S. Sundaria, B. Kumar, and R. Dhanasekaran, 2013, *Ceramic International*, Vol. 391, pp. 555.

- [5] D. Rout, K.S. Moon, S.J.L. Kang and I.W. Kim, 2010, *Journal of Applied Physics*, Vol.108, pp. 084102.
- [6] Babu G A, Raja R S, Bhaumik I, Ganesamoorthy S, Ramasamy P and Gupta P K 2015 *Material Research Bulletin*, Vol. 53, pp. 136.
- [7] Jiang X, Wang B, Luo L, Li W, Zhou J and Chen H 2014 *Solid State Chemistry*, Vol.213, pp. 72.
- [8] P. Laoratanakul, R. Yimniun, and S. Wongsanenmai, 2011, *Current Applied Physics*, Vol. 11, pp.161.
- [9] S. Praharaj, D. Rout, V. Subramanian and S.-J. L. Kang, 2016, *Ceramic International*, Vol. 42, pp. 12663.
- [10] S. Praharaj, D. Rout, S.-J. L. Kang and I.W. Kim, 2016, *Materials Letter*, Vol. 184, pp. 197.
- [11] A.R. Malathi, G.S. Kumar and G. Prasad, 2015, *Ferroelectrics*, Vol. 481, Vol. 21.
- [12] A.K. Jonscher, 1977, *Nature, London*, Vol. 264, pp. 673.
- [13] K. Funke, 1992, *Progress Solid State Chemistry*, Vol. 29, pp.11.
- [14] B. Roling, A. Happe, K. Funke, and M.D. Ingram, 1997, *Physics Review Letter*, Vol. 78, pp. 2160.
- [15] P. Singh, O. Prakash, and D. Kumar, 2011, *Physics Review B*, Vol. 84, pp. 174306.