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Research Article

Electrical conduction in $NaNbO_3$-$BaTiO_3$ Ceramics: Impedance Spectroscopy Analysis

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Abstract

Lead-free ceramic system (1-x)$NaNbO_3$-x$BaTiO_3$ for x = 0, 0.25, 0.50, 0.75 and 1.0 were prepared by conventional ceramic technique. The ac conductivity data were found to obey the power law and showed negative temperature coefficient of resistance behaviour. The ac conductivity data were used to evaluate the activation energy of the compounds. The correlated barrier hopping model was found to successfully explain the mechanism of charge transport in this system.

Keywords: *Ceramic, Lead free, AC conductivity, Conduction mechanism, Hopping model*

1. Introduction

Perovskite ABO_3-type materials exhibiting high dielectric permittivity are of current interest due to their practical applications in various electronic/microelectronic devices. Most of the materials used for these applications are in general, lead bearing compounds *e.g.* $PbTiO_3$, $PbZr_{1-x}Ti_xO_3$, $PbMg_{1/3}Nb_{2/3}O_3$, $PbFe_{1/2}Nb_{1/2}O_3$, *etc.* With an aim of getting alternatives to the lead-based materials, several investigations have been carried to study the electrical properties of $Ba(Fe_{1/2}Nb_{1/2})O_3$ (D. Bochenek *et al*, 2009; S. Eitssayeam *et al*, 2006; U. Intatha *et al*, 2007; S. Ke *et al*, 2008; S. Bhagat and K. Prasad, 2010), $Ba(Bi_{1/2}Nb_{1/2})O_3$ (K. Prasad *et al*, 2009; K. Prasad *et al*, 2010a) $Ba(Al_{1/2}Nb_{1/2})O_3$ (K. Prasad *et al*, 2010b), $Ba(Fe_{1/2}Ta_{1/2})O_3$ (W.-H. Jung *et al*, 2010), $Ba(Bi_{1/2}Ta_{1/2})O_3$ (A. Mishra *et al*, 2012), $Ba_{0.06}(Na_{1/2}Bi_{1/2})_{0.94}TiO_3$-$Ba(Fe_{1/2}Ta_{1/2})O_3$ (S.K. Roy *et al*, 2017), $Ba(Sb_{1/2}Nb_{1/2})O_3$ (K. Prasad *et al*, 2011a), $BaY_{0.5}Nb_{0.5}O_3$ (K. Prasad *et al*, 2010c), $Ba(In_{1/2}Nb_{1/2})O_3$ (K. Prasad *et al*, 2011b), $Ba(Sm_{1/2}Nb_{1/2})O_3$–$BaTiO_3$ (K. Amar Nath and K. Prasad, 2012), $Ba(Y_{1/2}Nb_{1/2})O_3$-$BaTiO_3$ (K. Prasad *et al*, 2014), $Ba(Fe_{1/2}Nb_{1/2})O_3$–$BaTiO_3$ (S. Bhagat *et al*, 2014), $Ba(Bi_{1/2}Ta_{1/2})O_3$-$BaTiO_3$ (J. Kumar *et al*, 2014), *etc*. for these applications. In recent years, a number of pure and/or modified forms of sodium-based solid solutions have been investigated for their possible applications in electronic devices (C.K. Suman *et al*, 2005; S.K. Roy *et al*, 2016; K. Kumari *et al*, 2016; A. Singh *et al*, 2015; S.K. Roy *et al*, 2013; Lily *et al*, 2013; U.K. Mahto *et al*, 2016). One such ceramic system in this series is perovskite $NaNbO_3$-$BaTiO_3$. These materials are mechanically tough and lead-free. Only few reports are available on the electrical and electromechanical properties of $NaNbO_3$-$BaTiO_3$ system (J.T. Zeng *et al*, 2006; R. Zuo *et al*, 2016; S. Xie *et al*, 2009; W.Q. Cao *et al*, 2016). However, the information about the electrical properties of this system is still not complete and consistent. The study of electrical conductivity in the ferroelectric compounds are very important since the associated physical properties like pyroelectricity, piezoelectricity and strategy for poling are dependent on the nature and magnitude of conductivity in these materials.

Therefore, to have knowledge about the performance of this ceramic system, it becomes important to know the carrier transport mechanism and hence the system deserved further investigation. An extensive literature survey suggested that no attempt, to the best of our knowledge, has so far been made to understand the conduction mechanism in the system using impedance spectroscopy technique. The complex impedance spectroscopy technique is being recognized as a non-destructive powerful technique to study the electrical properties of solids (C.K. Suman *et al*, 2005), where the electrical properties are often represented in terms of some complex parameters like complex impedance ($Z^*(\omega) = Z' - jZ'' = R_s - j/\omega C_s$), complex permittivity ($\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$), complex electric modulus ($M^*(\omega) = M' + jM''$) and complex admittance ($Y^*(\omega) = Y' + jY'' = 1/R_p + j\omega C_p$). They are interrelated as: $M^* = 1/\varepsilon^* = j\omega C_o Z^* = j\omega C_o(1/Y^*)$ and the loss tangent,

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$\tan\delta = \varepsilon''/\varepsilon' = Z'/Z'' = M''/M'$, where R_s, C_s are the series resistance and capacitance; R_p, C_p are the parallel resistance and capacitance. Keeping in view the growing interest in sodium-based solid solutions, the present work reports the impedance and ac conductivity studies on (1-*x*)$NaNbO_3$-*x*ABO_3; $0 \le x \le 1$ (abbreviated hereafter as NN-*x*BT) ceramics. An attempt has also been made to explain the conduction mechanism in the system using complex impedance spectroscopy technique.

2. Experimental details

Polycrystalline ceramics having the nominal chemical formula (1-*x*)$NaNbO_3$-*x*$BaTiO_3$ for *x* = 0, 0.25, 0.50, 0.75 and 1.0 were prepared using a standard solid-state reaction method. The raw materials used were AR-grade (purity +99.9%) Na_2CO_3, $BaCO_3$, Nb_2O_5 and TiO_2 in a suitable stoichiometry. Formation of all the compounds was checked by X-ray diffraction technique. Measurements of electrical impedance (Z), phase angle (θ), loss tangent (tanδ) and capacitance (C) were carried out on a symmetrical cell of type Ag|ceramic|Ag, where Ag is a conductive paint coated on either side of the pellets as a function of frequency (20 Hz - 1 MHz) at different temperatures (25°C - 300°C) using a computer-controlled Impedance analyzer (E4990A-120, Keysight Technologies, USA). The samples were preheated to 100°C to evaporate the moisture, if any, and then cooled to room temperature and then experiments were carried out. Ac conductivity data were obtained using the relations: $\sigma_{ac} = \omega\varepsilon_o\varepsilon''$; where ε'' is the imaginary part of the dielectric constant.

3. Results and discussion

The logarithmic frequency dependence of real (Z') and imaginary (Z") parts of impedance of NN-*x*BT, at different temperatures are plotted in Figures 1 and 2, respectively. It is observed that the values of Z' decreases monotonically with increasing frequency for all temperatures. Also, the values of Z' decrease with the rise of temperature. This indicates the negative temperature coefficient of resistance (NTCR) character of NN-*x*BT ceramics. It is observed that the value of Z' decreases upon increasing $BaTiO_3$ content. Further, at lower temperatures, the values of Z" decrease monotonically suggesting the absence of any relaxation. This suggests that the relaxation species are immobile defects and the orientation effect might be associated. As the temperature increases, the peak in Z"-*f* plots starts appearing (Figure 2), which shifts towards higher frequency side with the increment in temperature showing the resistance of the bulk material is decreasing and supports NTCR character of NN-*x*BT. Upon further rise in temperature Z"-*f* plots exhibited double peaks, which clearly indicated the introduction of grain boundary effect. Besides the magnitude of Z" peaks decreases while the width of the peak increases with increasing temperature and the peaks are slightly asymmetric in nature for all the compounds, which suggests that there is a spread of relaxation times *i.e.* the existence of a temperature dependent electrical relaxation in the materials (K. Prasad *et al*, 2007).

Figure 3 shows the variation of ac conductivity (σ_{ac}) of NN-*x*BT as a function of frequency at different temperatures between 25°C and 300°C. The nature of variation of σ_{ac} with frequency exhibits dispersion throughout the chosen range of frequency. Also, the values of σ_{ac} increase with rise in frequency as well as temperature. Such increment in conductivity is due to the movement of thermal ions (generally comes from hopping motion of ions) from one preferable site to the other. The plots get flattened (low frequency plateau) upon further rise in temperature. The high-frequency conductivity dispersion may be attributed to ac conductivity whereas the frequency independent plateau region of the conductivity pattern corresponds to the dc conductivity (σ_{dc}) of the material. The switch from frequency-independent to the frequency-dependent region shows the onset of the conductivity relaxation phenomenon which shifts to higher frequency side with the increase in temperature, indicates the translation from long range hopping to the short range ion-motion. Such dependence is associated with displacement of carriers which move within the sample by discrete hops of length *R* between randomly distributed localized sites. Furthermore, the ac conductivity, in most of the materials due to localized states can be expressed as: $\sigma_{ac} = \sigma(0) + \sigma(\omega)$; where $\sigma(0)$ and $\sigma(\omega)$ are respectively the frequency independent and dependent part of conductivity. Also, $\sigma(\omega)$ found to obey universal behaviour in the frequency sensitive region: $\sigma(\omega) = A\omega^s$ with $0 \le s \le 1$, ω is angular frequency of applied ac field and A [= $\pi N^2e^2/6k_BT$ (2α)] is a constant, e is the electronic charge, T-temperature, α-polarizability of a pair of sites, and N-the number of sites per unit volume among which hopping takes place. Such variation is associated with displacement of carriers which move within the sample by discrete hops of length *R* between randomly distributed localized sites. The term $A\omega^s$ can often be explained on the basis of two distinct mechanisms for carrier conduction: (i) quantum mechanical tunneling (QMT) through the barrier separating the localized sites; and (ii) correlated barrier hopping (CBH) over the same barrier. The values of the index s were obtained from the slopes of the plots in the low frequency region, which always comes out to be less than 1 and are decreasing with the rise in temperature. This observation is consistent with correlated barrier hopping model (S. Bhagat and K. Prasad, 2010). Therefore, the electrical conduction in the system may be considered due to the short range translational type hopping of charge carriers. Besides, the value of s approaching to zero at higher temperatures indicates that the dc conductivity dominates at higher temperatures in the low frequency region following the Jonscher's power law.

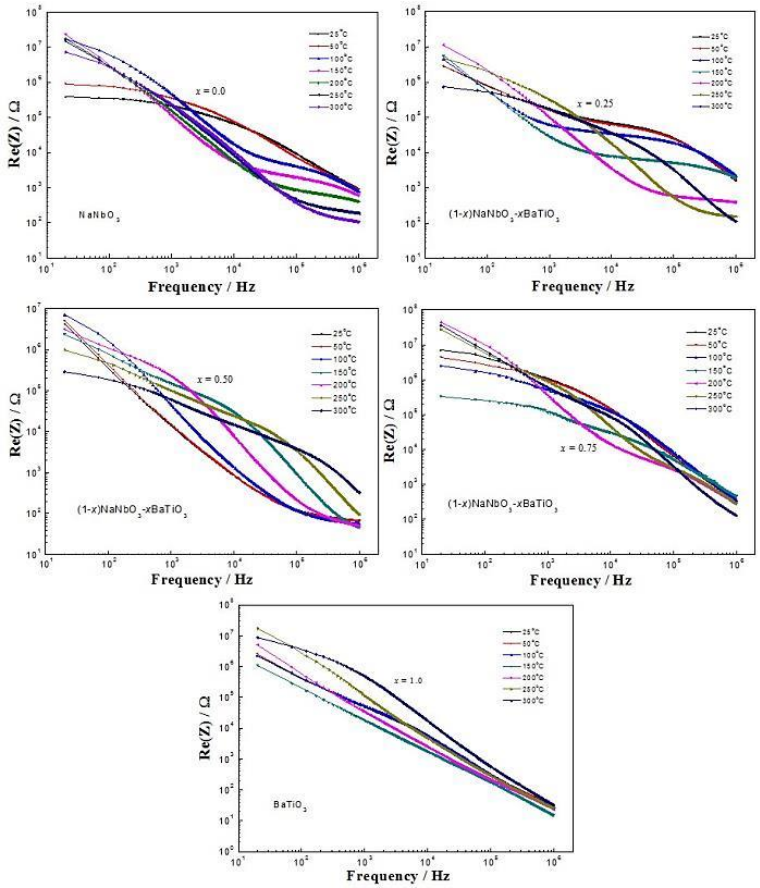

Fig. 1 Frequency dependence of real part of impedance of $NaNbO_3$-$BaTiO_3$ ceramics at different temperatures

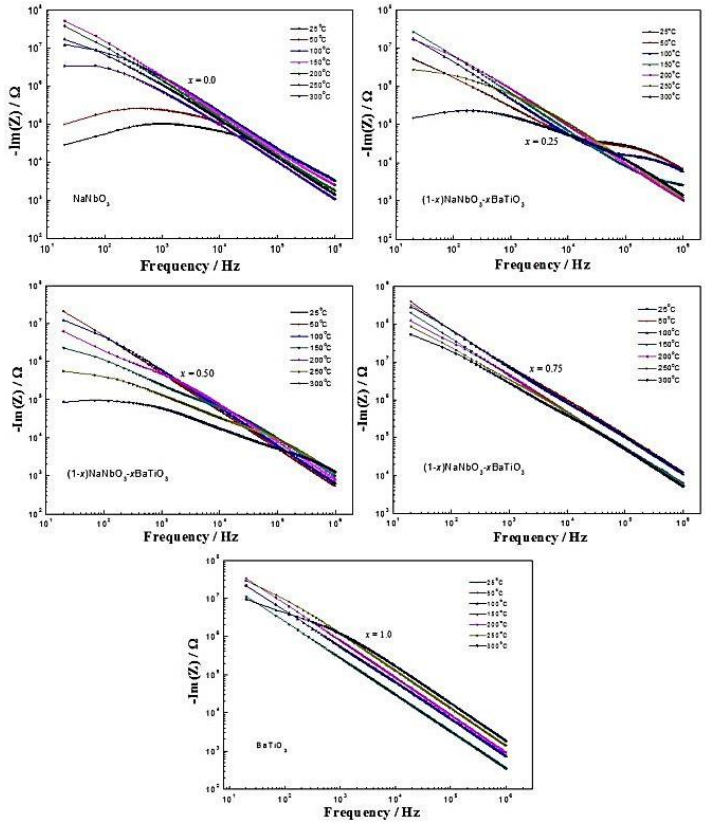

Fig. 2 Frequency dependence of imaginary part of impedance of $NaNbO_3$-$BaTiO_3$ ceramics at different temperatures

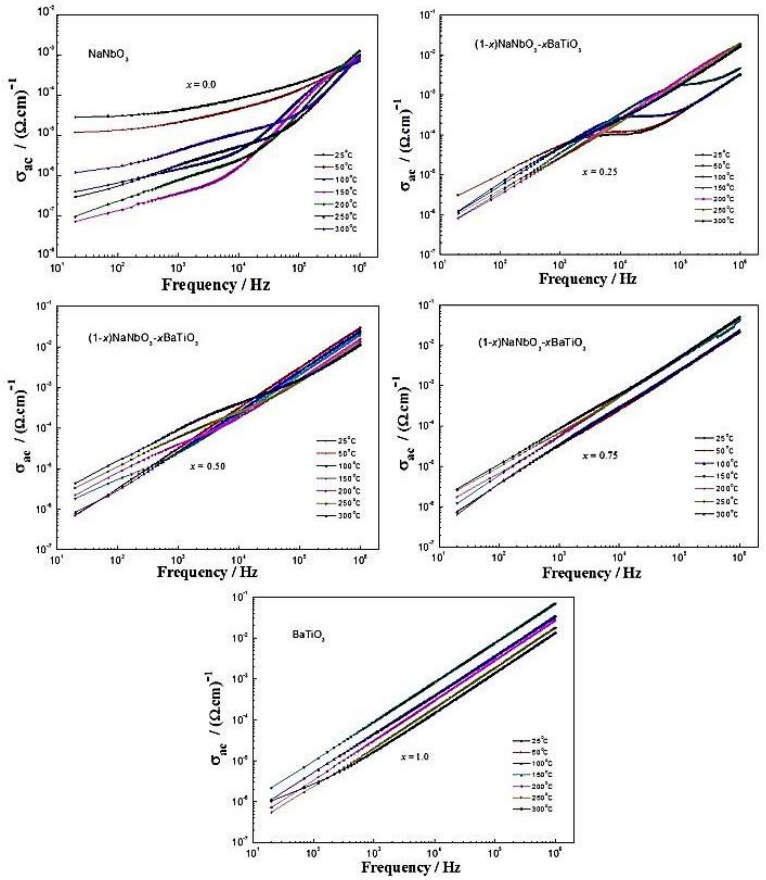

Fig. 3 Frequency dependence of ac conductivity of $NaNbO_3$-$BaTiO_3$ ceramics at different temperatures

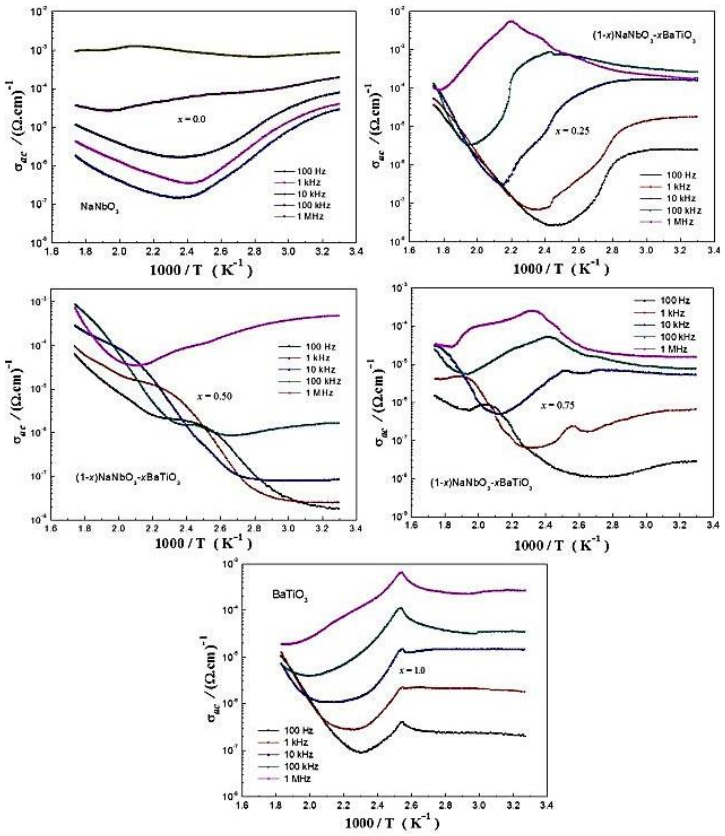

Fig. 4 Variation of ac conductivity with inverse of temperature at different frequencies for $NaNbO_3$-$BaTiO_3$ ceramics

It can be seen that the slope of the curves change with changing temperature, which clearly indicates that the conduction process is dependent on both temperature as well as on frequency. Further, a decrease in the values of σ_{ac} is observed with the rise in temperature for all the compounds, thereby indicating the negative temperature coefficient of resistance (NTCR) character of the samples like that of semiconductors. This may happen due to the accumulation of charge species at the barriers (grain boundaries) which get thermally activated, that plays a dominant role at elevated temperature showing NTCR characteristics. With the rise in temperature, these charge species have sufficient energy to jump over the barrier, responsible for increasing the conductivity and hence the grain boundary resistance decreases beyond these temperatures.

Hopping conduction mechanism is generally consistent with the existence of a high density of states in the materials having band gap like that of semiconductor. Due to localization of charge carriers, formation of polarons takes place and the hopping conduction may occur between the nearest neighboring sites. Figure 4 shows the variation of ac conductivity versus $10^3/T$. The activation energy for conduction was obtained using the Arrhenius relationship: $\sigma_{ac} = \sigma_o \exp(-E_a / k_B T)$; where E_a is the activation energy of conduction and T is the absolute temperature. The nature of variation shows the negative temperature coefficient of resistance (NTCR) behaviour of NN-xBT. A linear least squares fitting of the conductivity data to this equation gives the value of the activation energy, E_a. It can be seen that the value of σ_{ac}, in general, deccreases with the increment in x and is minimum for x = 0.75. The minimum and maximum values of E_a are observed in case of x = 0.75 and 1.0, respectively. The low values of E_a might be due to the transport of charge carriers through hopping between localized states in a disordered manner (K. Prasad *et al*, 2006). Further, the increase in conductivity with temperature may be considered on the basis that within the bulk, the oxygen vacancies due to the loss of oxygen are usually created during sintering and the charge compensation follows the reaction: $O_o \rightarrow \frac{1}{2}O_2 \uparrow + V_o^{\bullet\bullet} + 2e^-$, which may leave behind free electrons making them n-type (K. Prasad *et al*, 2005).

Conclusions

Polycrystalline (1-x)$NaNbO_3$-$x$$BaTiO_3$; ($0 \le x \le 1$) were prepared using a high-temperature solid-state reaction technique The ac conductivity is found to obey the universal power law and showed the NTCR character. The correlated barrier hopping model is found to successfully explain the mechanism of charge transport in the system. Further, the frequency dependent ac conductivity at different temperatures indicated that the conduction process is thermally activated process.

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