Raman Spectroscopy and Low Temperature Dielectric Properties of (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ Ceramics

Srinivas Pattipaka$^1$ and D. Pamu$^1$

$^1$Department of Physics, Indian Institute of Technology Guwahati, Guwahati-781039, India

Email: pamu@iitg.ernet.in

Abstract. In the present study, lead-free Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) ceramics were prepared by solid state reaction route and the structural, microstructural and dielectric properties have been reported. The Rietveld refinement method and Raman spectroscopy were used to analyze the structural properties of BNT ceramics. The Rietveld refinement analysis of all the sintered samples revealed the rhombohedral crystal symmetry with R3c space group. The sintered (1100 °C) BNT ceramics exhibited homogeneous grain distribution with an average grain size of 1.40 µm. The dielectric properties of BNT ceramics were investigated over the frequency range of 1 MHz-100 MHz in the temperature range of 133K–653K. The obtained values of dielectric constant ($\varepsilon_r$), dielectric loss (tanδ) and Curie temperature ($T_C$) of the ceramics are 525, 0.067 and 603 K respectively, as measured at 1 MHz. The temperature dependent AC-conductivity ($\sigma_{ac}$) of the BNT ceramics was analyzed using Arrhenius law and the activation energies ($E_A$) were estimated in different regimes. The obtained $E_A$ values are in the range of 12.37 – 23.99 meV in the temperature regime 1 (R1: 133K – 278K), whereas in regime 2 (R2: 320K – 603K) in the range 51.5 – 126.2 meV. The frequency (1 MHz – 100 MHz) dependent $\sigma_{ac}$ measured at different temperatures was analyzed using Jonscher’s power law and super linear power law (SLPL). The obtained results indicate the BNT ceramics have potential applications in high frequency tunable devices.

1. Introduction

Lead zirconate titanate (Pb(Zr,Ti)O$_3$, PZT) is a well-known piezoelectric material and has been widely used in many applications, such as transducers, filters, actuators and sensors owing to their excellent piezoelectric properties [1]. Nevertheless, lead is toxic and harmful for human health and environment [2]. Therefore, it is necessary to replace the PZT with lead-free piezoelectric materials. The lead-free piezoelectric materials with perovskite structure, such as (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ (BNT) [3], BaTiO$_3$ (BT) [4] and (K$_{0.5}$Na$_{0.5}$)NbO$_3$ (KNN) [5] have
been widely studied because of their excellent piezoelectric properties. Amongst all lead-free piezoelectrics, BNT based ceramics have been considered as a good candidate because of its large remnant polarization ($P_r = 38 \mu\text{C/cm}^2$), coercive field ($E_c = 73\ \text{kV/cm}$) at room temperature and high Curie temperature ($T_c = 320\ ^\circ\text{C}$) [3]. A high dielectric constant and low dielectric loss are the key parameters to develop the high performance piezoelectric devices. The BNT ceramics were synthesized by various methods and the studies were mainly focused on ferroelectric, piezoelectric and dielectric properties [6, 7]. However, there are no reports available on the dielectric and AC-conductivity analysis of BNT ceramics measured in the frequency range of 1MHz – 100 MHz and in the low temperature range of 133K – 653K. The significance of studying the AC-conductivity of ferroelectric ceramics in the low temperature regime lies in unveiling the dielectric relaxations and hopping nature of charge carriers. These studies are useful for considering the applicability of BNT ceramics in high frequency tunable devices. This has motivated us to pursue the systematic analysis of structural, microstructural and dielectric properties of BNT ceramics in the broad frequency and temperature range.

2. Experimental Details

Lead-free Bi$_{1/2}$Na$_{1/2}$TiO$_3$ ceramics were prepared by using conventional solid state reaction method. Highly pure Bi$_2$O$_3$ (Alfa-Aesar, 99.975%), Na$_2$CO$_3$ (Sigma Aldrich, 99.99%), TiO$_2$ (Sigma-Aldrich, 99.99%) were chosen as starting materials and weighed according to the desired stoichiometry. These powders were mixed for 5 hr using a planetary ball mill (M/s Fritsch GmbH, Germany, Pulverisette 6) using deionised water as a grinding media. All the mixtures were dried at 120 ºC and calcined at 800 ºC for 3 hr. These calcined powders were again ground for 10 hr to reduce the initial particle size. Organic binder poly vinyl alcohol was added to the finely ground powder and finally pressed into pellets of 10 mm diameter and 1 – 2 mm thickness. The prepared samples were sintered in the range of 1050 – 1150 ºC for a constant duration of 3 hr. The density of sintered pellets was measured using Archimedes’s principle. The samples sintered at 1100 ºC displayed the maximum density. Hence, these samples are chosen for further studies. For dielectric measurements, both sides of the samples were coated with silver paste to be used as electrodes and the pellets were heated at 150 ºC for 10 minutes.

The structural properties of the BNT ceramics have been characterized by using x-ray diffractometer (M/s Rigaku, TTRAX III 18 KW) with Cu-K$_\alpha$ radiation ($\lambda = 1.5406\ \text{Å}$). Raman spectra of the BNT ceramics was collected using (M/s Horiba Jobin Yvon, LABRAM HR) Raman spectrometer employing a He-Ne source (514 nm as the excitation wavelength). Microstructure and surface morphology of the ceramics were analyzed with Field emission scanning electron microscope (FESEM) (M/s Zeiss, Sigma). The temperature and frequency dependence of dielectric properties were measured over a frequency (1 MHz to 100 MHz) and temperature range (133K to 653K) by using RF impedance material Analyzer (M/s Agilent Technologies, E4991A and M/s Novocontrol, BDS 2200).

3. Results and Discussion

The Rietveld refined XRD pattern of the sintered BNT ceramics is shown in Figure 1. The XRD analysis revealed the formation of a single phase with rhombohedral crystal symmetry at room temperature.
Figure 1. Reitveld refined XRD pattern of the BNT samples sintered at (a) 1050 °C, (b) 1100 °C and (c) 1150 °C for 3 hr.

The lattice parameters, atomic positions and occupancy of the Bi, Na, Ti, and O atoms were refined by using Fullprof software, considering R3c space group. The obtained lattice parameters and unit cell volumes are listed in Table 1. The lattice volume and density increases with sintering temperature up to 1100 °C and decreases beyond that. The density of the prepared samples was found to be in the range of 90-95 % of the theoretical density. The density and lattice volume decreases as the sintering temperature increases to 1150 °C. The grain boundary movements increase with sintering temperature. As a result, some closed pores remain inside the grains. Hence, the density of the ceramics sintered at 1150 °C is lower than 1100 °C.

Table 1. Rietveld refined parameters of BNT ceramics at different sintering temperatures.

| Sintering Temperature (°C) | $\chi^2$ | a = b (Å) | c (Å) | Volume (Å$^3$) |
|--------------------------|----------|-----------|------|---------------|
| 1050                     | 3.57     | 5.4980    | 13.4370 | 351.7562     |
| 1100                     | 2.33     | 5.5010    | 13.4486 | 352.4488     |
| 1150                     | 5.17     | 5.4988    | 13.4099 | 351.1523     |

Raman spectroscopy is the most useful technique to study the structural deformation of perovskite systems. Figure 2 shows the Raman spectra of BNT ceramics (sintered at (a) 1050, (b) 1100 and (c) 1150 °C for 3 hr) measured over the range of 50 – 1000 cm$^{-1}$. The Raman spectrum is fitted with Origin software by using Gaussian function. There are nine vibrational modes observed at 83, 131, 227, 291, 371, 530, 599, 772 and 862 cm$^{-1}$, which are shown in Figure 2. The obtained results are in good agreement with the earlier reports [8, 9].
Figure 2.  Raman spectra of BNT samples sintered at (a) 1050 °C, (b) 1100 °C and (c) 1150 °C.

The BNT ceramics possess rhombohedral crystal symmetry with R3c space group. According to the group theory, R3c space group consist of 13 Raman active optical modes ($\Gamma_{\text{Raman}} = 4A_1 + 9E$), where $A_1$ and $E$ modes are Raman and IR active. These Raman active optical modes are due to disorder in the A-site of BNT system associated to BiO$_6$ and NaO$_6$ clusters [10]. The scattering of light with respect to incoming polarization is responsible for splitting of optical modes into transverse (TO) and longitudinal (LO) components. The Raman active $A_1$ (TO$_1$) modes at 83 cm$^{-1}$ and 131 cm$^{-1}$ are related to the BiO$_6$ and NaO$_6$ clusters, respectively. The Raman active $E$ (TO$_2$) modes at 227, 291 and 371 cm$^{-1}$ are associated to the octahedral TiO$_6$ clusters and were observed in many perovskites [11]. The Raman-active LO$_2$ modes are responsible for low intensity peaks and are related to short range electrostatic forces associated with the lattice iconicity [9, 12]. The TO$_3$ mode located around 530 cm$^{-1}$ and 599 cm$^{-1}$ corresponds to the (O-Ti-O) stretching symmetric vibrations of the TiO$_6$ clusters. The LO$_3$ modes observed at 772 and 862 cm$^{-1}$ are due to the presence of sites within the rhombohedral lattice containing distorted octahedral TiO$_6$ clusters [9]. These results indicate that intensity of all Raman modes increased with sintering temperature due to enhancement in disorder of A-site in BNT ceramics. However, no significant change was observed in the Raman shift as well as full width at half maximum (FWHM) in the spectra for sintered samples.

Figure 3. FESEM micrographs of the BNT samples sintered at (a) 1050 °C, (b) 1100 °C and (c) 1150 °C.

Figure 3 shows the FESEM micrograph of the BNT ceramics, sintered at 1050, 1100 and 1150 °C for 3 hr. The average grain size has been calculated using linear intercept method and is found to increase from 1.09 to 1.98 μm with rise in sintering temperature. The sample sintered at 1100 °C, exhibits rectangular shape grains with average grain size of 1.40 μm. This sample showed well defined grain boundaries and less porosity, which indicates that the sintered (1100 °C) BNT ceramics having a high dense microstructure.
Figure 4 shows the temperature variation of dielectric constant ($\varepsilon_r$) and dielectric loss (tan$\delta$) of BNT ceramics, sintered at 1100 °C for 3 hr, measured at different frequencies from 1 MHz to 100 MHz. The $\varepsilon_r$ increases with temperature from 133K to 300K, which is almost independent of frequency but has a frequency dependency at high temperature. The BNT ceramics undergo structural transitions from ferroelectric rhombohedral to antiferroelectric tetragonal structure around 473K, which is also known as depolarization temperature ($T_d$), and there is another transition from antiferroelectric tetragonal to paraelectric cubic structure around 603 K, which is the Curie temperature ($T_C$). The $T_C$ of the BNT ceramics was estimated based on the temperature at which the maxima of dielectric constant is reached (~603K), which is in good agreement with our earlier report [9]. However, a weak anomaly in $\varepsilon_r$ ($T_d \sim 473$k) is obtained at 1 MHz and further disappears with increasing frequency due to the stabilization of non-polar phase in the BNT samples [13]. The obtained $\varepsilon_r$ and tan$\delta$ are 277, 525 and 0.040, 0.067 at 133K and 298K (1MHz), respectively. Above $T_C$, $\varepsilon_r$ is found to decrease due to the increasing randomness of dipoles with temperature and it tends to weaken the dielectric properties in cubic phase. The decrease in $\varepsilon_r$ with increasing frequency measured over a temperature range (133K – 653K) is due to the reduction in the polarization. The dielectric loss also exhibited similar behaviour at low temperature and rises at the high temperatures with increase in the frequency and is attributed to the enhancement in ionic conductivity in the BNT system. The tan$\delta$ also exhibited clear anomalies at phase transition temperatures.

The frequency dependence of AC-conductivity of BNT ceramics can be explained on the basis of Jonscher’s power law at different temperatures,

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s$$

Where, $\omega = 2\pi f$ is the angular frequency, $\sigma_{dc}$ is the dc conductivity, ‘A’ is the temperature dependent pre-exponential factor and ‘s’ is the frequency exponent [14]. However, the term $\sigma_{dc}$ disappeared at high frequencies, and it follows the super linear power law (SLPL) or nearly constant loss (NCL) ($\sigma \propto \omega^s$), ($s\geq1$) [15]. If $s<1$, it corresponds to the translational short-range hopping motion, which is a characteristic of low or intermediate frequencies and is associated with the grain boundary conductivities. On the other end, $s\geq1$ correspond to the re-orientational or localized hopping mechanism, and it represents the grain conductivity at higher frequencies [16]. The AC-conductivity response is more complex and there are no
clear theoretical details so far. Lunkenheimer et al. [15] analyzed the AC-conductivity of different disordered materials at high frequencies (> 1MHz) using SLPL and NCL. Shanming et al. [17] observed the NCL and SLPL behaviour either at low temperatures/low frequencies or high temperature/high frequencies.

**Figure 5.** (a) The frequency dependence of electrical conductivity $\log(\sigma_{ac})$ fitted by using Jonscher's power law and (b) Temperature dependence of the exponent ‘$s$’ and ‘$A$’ of BNT ceramics at different temperatures.

Figure 5 (a) shows the frequency dependence of electrical conductivity $\sigma_{ac}(\omega)$ of BNT ceramics measured at different temperatures (133K - 603K) and analyzed using Jonscher’s power law. The symbols indicate the experimental data, and the solid line represents the fitting of the experimental data by using equation (1). The fitting parameters such as ‘$A$’ and ‘$s$’ were extracted for all the measured temperatures and are shown in Figure 5 (b). From the plots, two regimes were clearly identified, which gives us two different slopes. The exponent ‘$s$’ is almost constant (~1.30) below 273K, which shows a weak dependence on temperature. Above the 273K, ‘$s$’ varies linearly/super-linearly with temperature, which is a characteristic of the SLPL [17]. The obtained results ($s>1$) indicate that hopping motion is localized or re-orientational via small polarons. The small polaron hopping mechanism in BNT ceramics is thermally activated beyond the low temperature (>298K). In the low frequency and low temperature region, the conductivity is mainly due to the successful hoping between different sites but this hoping reduces with a rise in the frequency. Also, as the frequency increases, the ratio of successful to unsuccessful hoping changes with frequency. Therefore, the dispersion is observed at high frequencies. On the other hand, the coefficient ‘$A$’ exhibited the maximum value at 273K where the ‘$s$’ shows the minimum and it further decreases with increasing temperature. This might be due to the large extent of interaction among the charge carriers and polarization.
Figure 6. The variation of $\ln(\sigma_{ac})$ with reciprocal temperature of BNT ceramics in different regimes (R1, R2).

The activation energy ($E_A$) of the BNT ceramics have been calculated by using Arrhenius relation [18].

$$\sigma_{ac} = \sigma_0 \exp \left( -\frac{E_A}{k_B T} \right)$$  \hspace{1cm} (2)

Where, $\sigma_0$ is the pre-exponential factor, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. The $E_A$ values were estimated from the slope of $\ln(\sigma_{ac})$ versus $1000/T$ plot, where the linear variation observed in regime R1 and R2, and are shown in Figure 6. The $E_A$ values were found to decrease from 23.99 meV to 12.37 meV with increasing the frequency from 1 MHz to 100 MHz in R1, whereas the $E_A$ values were found to be enhanced from 51.5 meV to 126.20 meV in R2. The different activation energies at distinctive temperature regions are due to a difference in the conductivity and domain mechanism [19]. The lower $E_A$ values in R1 are attributed to the carrier transport mechanism associated with the hopping between localized states. The higher values of $E_A$ in the R2 are due to the formation of small polarons and oxygen vacancies [19]. The small polarons are created by the interaction between the charge carriers and lattice, and this deformation will increase with the temperature. The oxygen as well as A-site vacancy would be created in the sample at higher sintering temperatures, which could be the reason for increment in the conductivity. The higher conductivity observed near the phase transition temperature is due to the change in domain structure, which can cause the release of charge carriers and enhance the conductivity within the sample.

4. Conclusion
Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) ceramics have been prepared by conventional solid state reaction method. The structural properties of BNT ceramics were explained using Rietveld refinement method and Raman spectroscopy. BNT ceramics sintered at 1100 °C, exhibited the uniform grain size with less porosity. The dielectric properties of BNT ceramics were examined over the temperature range 133K – 653K and broadband frequency range of 1 MHz – 100 MHz. The temperature dependent dielectric properties of the BNT sample revealed the $T_c$ around 330 °C and $\varepsilon_r = 525$ and $\tan\delta = 0.067$ at 1 MHz. The frequency
dependence of AC-conductivity measured at distinctive temperatures follows the SLPL and hopping motion is localized or reoriented via small polarons. The temperature dependent AC-conductivity of the BNT ceramics was analyzed using Arrhenius law and activation energies ($E_A$) were estimated in different regimes. The obtained high dielectric constant, low dielectric loss and nearly constant loss over a wide range of frequency makes this material suitable for high performance piezoelectric and microwave tunable device applications.

Acknowledgments
The authors acknowledge the financial support from DAE BRNS [37(1)/14/33/2015/BRNS] India.

References
[1] G. H. Haertling 1999 J. Am. Ceram. Soc. 82 797
[2] L. E. Cross 2004 Nature 432 24
[3] G. A. Smolenskii, V. A. Isupov, A. I. Agranovskaya and N. N. Krainik 1961 Sov. Phys. Solid State 2 2651
[4] Q. Xu, S. T. Chen, W. Chen, S. J. Wu, J. Lee, J. Zhou, H. J. Sun and Y. M. Li 2004 J. Alloys Compd. 381 221
[5] L. Egerton and D. M. Dillon 1959 J. Am. Ceram. Soc. 42 438
[6] Y. Hiruma, H. Nagata and T. Takenaka 2009 J. Appl. Phys. 105 084112
[7] M. Cernea, E. Andronescu, R. Radu, F. Fochi and C. Galassi 2010 J. Alloys Compd. 490 690
[8] H. Lidjici, B. Lagoun, M. Berrahal, M. Rguitti, M. A. Hentatti and H. Khemakhem 2015 J. Alloys Compd. 618 643
[9] Srinivas Pattipaka, Mahesh Peddigari and Pamu Dobbidi 2017 Ceram. Int. 43 S151–S157
[10] J. Petzelt, S. Kamba, J. Fabry, D. Noujini, V. Porokhonskyy, A. Ashkin, I. Franke, K. Roleder, J. Suchanicz, R. Klein and G. E. Kugel 2004 J. Phys: Condensed Matter 16 2719
[11] M. Zannen, A. Lahmar, M. Dietze, H. Khemakhem, A. Kabadou and M. Es-Soun 2012 Mater. Chem. Phys. 134 829
[12] A. Chaves, R.S. Katiyar and S.P.S. Porto 1974 Physical Review B 10 3522
[13] A. Hussain, A. Zaman, Y. Iqbal and M.H. Kim 2013 J. Alloys Comp. 574 320
[14] A. K. Jonscher 1983 Dielectric Relaxation in Solids Chelsea Dielectric Press London
[15] P. Lunkenheimer and A. Loidl 2003 Phys. Rev. Lett. 91 207601
[16] K. Funke and Prog 1993 Solid State Chem. 22 111
[17] K. Shanning, H. Huang, Y. Shuhui and Z. Limin 2010 J. Appl. Phys. 107 084112
[18] W. S. Kang, S. K. Lee, J. H. Koh 2015 Ceram. Int. 41 6925–32
[19] O. Raymond, R. Font, N. S. Almodovar, J. Portelles and J. M. Siqueiros 2005 J. Appl. Phys. 97 084107