Volume-5, Issue-10, October - 2016 • ISSN No 2277 - 8160 IF : 3.62 | IC Value 70.36

Original Research Paper Physics

Raman Spectroscopy Study of Impure Bismuth Sodium Titanate

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ABSTRACT

Bismuth sodium titanate, Bi0.5Na0.5TiO3 (BNT) is one of the important ferroelectrics among the lead- free piezoelectric materials with large remnant polarization (Pr = 38 μC/cm2), high Curie temperature (Tc = 320°C), and shows diffuse phase transition (DPT) with perovskite structure. In addition to the DPT, two more phase transitions were reported at 230°C and at 500-600°C. It is observed the coexistence of the cubic and the tetragonal phases in the temperature ranges from 500°C to 540°C, and the tetragonal and the rhombohedral phases from 255°C to 400°C. Raman spectroscopic studies were done on lead-free antimony doped BNT in order to understand the effect of antimony in their local structure and symmetry.

KEYWORDS : Perovskite structure, Raman spectroscopic, XRD

Introduction

The ferroelectric perovskite-type ceramic materials having general formula ABO_3 with different cationic distributions at A/B-sites are being investigated due to their important device applications such as in capacitors, piezoelectric ultrasonic transducers, electrostrictive actuators, SAW substrates, etc.. The doping or compositional changes in these ceramics can control the high electromechanical characteristics. Bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is one of the important ferroelectrics among the lead- free piezoelectric materials with large remnant polarization (P_r = 38 μC/cm^2), high Curie temperature (T_c = 320°C), and shows diffuse phase transition (DPT) with perovskite structure. In addition to the DPT, two more phase transitions were reported at 230°C and at 500-600°C. It is observed the coexistence of the cubic and the tetragonal phases in the temperature ranges from 500°C to 540°C, and the tetragonal and the rhombohedral phases from 255°C to 400°C . Several of its crystal structures, including cubic, tetragonal and rhombohedral, have been studiedover different temperature ranges.

Relaxor behaviour of BNT depends on substitution in both A-site and B-site and also it has been observed that the dopants control the phase transitions, electromechanical properties, relaxor behaviour and the piezoelectric coefficients. Many studies have been performed on BNT to understand the effect of dopants on structural and electrical properties of the material. Some studies focus on dielectric properties, while others focus on piezoelectric properties. BNT is a good material for both applications because it can be modified to enhance a specific desirable behaviour. Both A-site and B-site dopants have been studied to determine how they affect the properties of BNT.

Structural and micro structural studies

Fig.1. shows the XRD patterns of Sb (0.0, 0.01, 0.02 and 0.03) doped $Bi_{0.5}Na_{0.5}TiO_3$ ceramics sintered at 950 °C for 4 h. All the compositions exhibit a pure perovskite structure and no second phases are observed, which implies that Sb ceramic has diffused into the $Bi_{0.5}Na_{0.5}TiO_3$ lattices completely.

The estimated lattice parameters are very close to those obtained in earlier reports. Also Fig.2. shows the XRD patterns of the ceramics in the 2θ range of 44–50 degree.

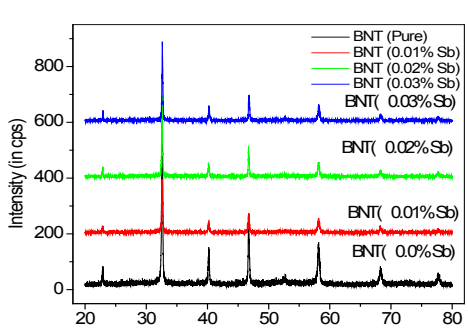

Fig.1. X-ray diffraction patterns of Sb doped BNT ceramics of different compositions.

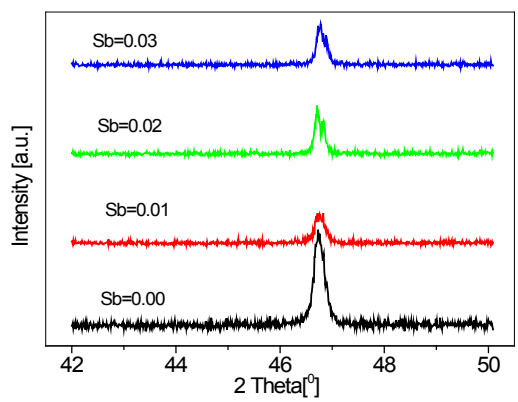

Fig.2. X-ray diffraction patterns of Sb doped BNT ceramics of different compositions in the 2θ range 42-50 degree.

A distinct 002/200 peak splitting appears when doping percentage changes from 0.02 to 0.03, referring to a hexagonal symmetry.To characterize the phase compositions in a more quantitative way, the XRD patterns of the MPB compositions in the 2θ ranges of 46–48 ° were fitted as shown in Fig. 3. The data shows the Lorentzian deconvolution of the 002 and 200 peaks of the tetragonal phase and the 202 peak of the rhombohedral phase. These results suggest that the rhombohedral-hexagonal morphotrophic phase boundary (MPB) appears in ceramic near to doping level at 0.03% Sb content.

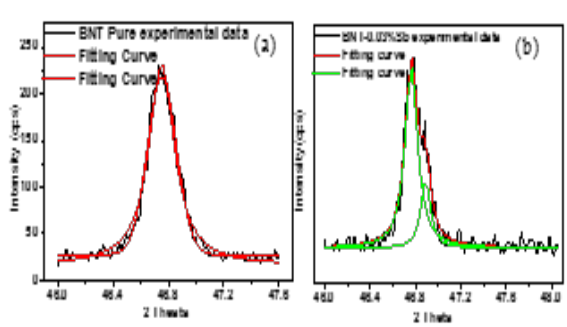

Fig.3. XRD fitting patterns of Sb doped BNT ceramics (a) 0% and (b) 0.03%.

Raman Spectroscopic analysis

Fig.4. represents the Raman spectra of pure BNT and Sb doped BNT with different percentage. There are only five Raman-active modes observed in the range from 100 to 1000 cm^{-1} in agreement with earlier report. BNT ceramics with rhombohedral structure presents 13 Raman-active modes ($\Gamma_{Raman} = 4A_1 + 9E$) due to the disorder in A-site related to distorted octahedral [BiO_6] and [NaO_6] clusters.

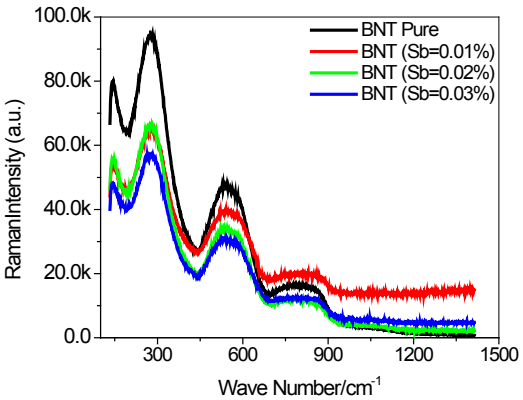

Fig.4. Raman Spectra of Sb doped BNT ceramic with different compositions.

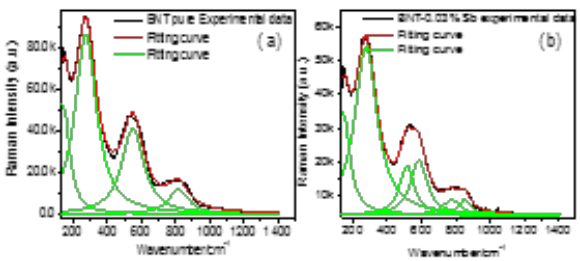

Fig.5. Raman Spectra of BNT Black line is the experimental data and green lines are the fitting curve versus Sb concentration.(a) for pure BNT while (b) for BNT with 0.03% Sb.

There is no significant change in the spectra for the prepared compositions. For better observation of the Raman spectra of BNT pure and Sb doped BNT (Sb = 0.03%) along with the curves fitted to individual peaks are shown in Fig. 4.4. The spectra of BNT (Sb = 0.03%) shows additional peaks around 151, 281, 585 and 853 cm^{-1} compared to the peaks observed in BNT. The occurrence of these bands splitting may be due to structural change at doping level 0. 03% of Sb, which are well in line with the studies of XRD phase analysis. However, from Fig. 4.5 it is possible to detect that all the Raman peaks are very broad in BNT and Sb doped BNT ceramics.

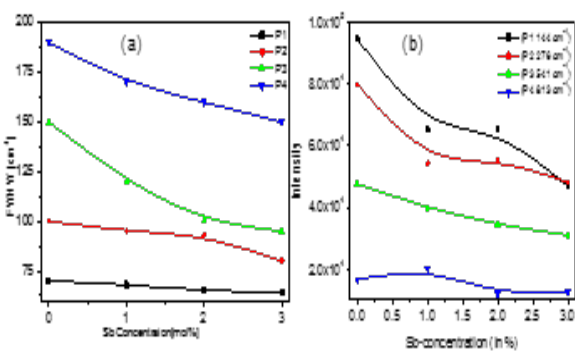

Fig.6. Variation of the FWHM and intensity of different modes in the Raman spectra versus Sb-concentration is shown in figure (a) and (b) respectively.

Dielectric studies

Pure BNT, shows two abnormal dielectric peaks which originate from phase transition from ferroelectric to anti-ferroelectric (at T_f) and anti-ferroelectric to paraelectric phase (at T_m), and is consistent with the previous reports of BNT, BNT–, BNT–PT lead based/lead-free ceramics systems.

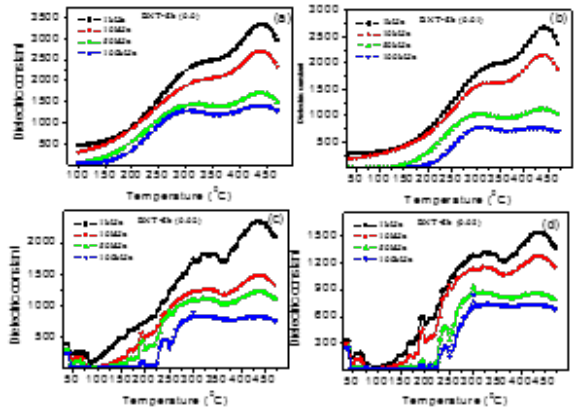

Fig.7. Shows dielectric response of BNT-Sb with different concentration of antimony at different frequencies. (a) for Pure BNT-Sb (0.0) (b) for BNT-Sb (0.01), (c) for BNT-Sb (0.02) and (d) for BNT-Sb (0.03).

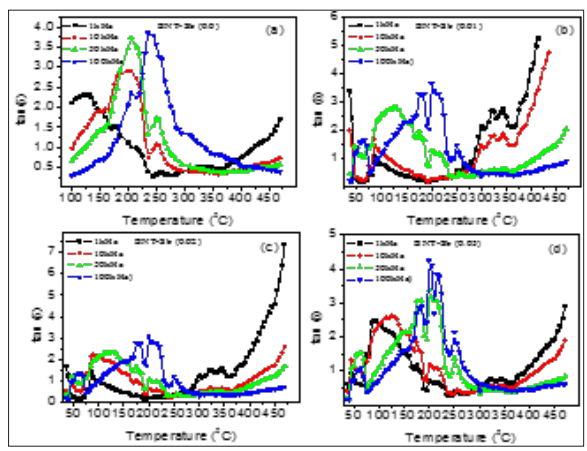

Fig.8. Shows tangent loss of BNT-Sb with different concentration of antimony at different frequencies. (a) for Pure

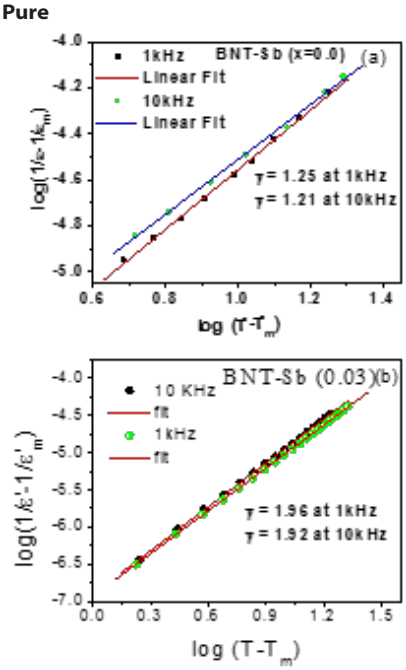

Fig. 9. log ($1/\varepsilon - 1/\varepsilon_m$) as function of log($T-T_m$) for different composition of BNT-Sb (x=0.0 and 0.03) at 1 and 10kHz. (a) for (0.0) and (b) for (0.03).

Impedance studies

$Z' = \frac{R}{1+(\omega RC)2}$ and $Z'' = \frac{\omega RC}{1+(\omega RC)2}$

and the impedance of constant phase element Z_Q = A (Macdonald, 1987). Variation of real part of impedance (Z') as a function of angular frequency is shown in Fig. 4.10 for different temperatures of different concentration of Sb.

The magnitude of Z' decreases with increase in frequency as well as temperature indicating an increase in ac conductivity with rise in temperature and frequency. The Z' values for all temperatures merge above 60 kHz for Sb(0.0 and 0.01) while for Sb (0.02 and 0.03) almost at 55kHz.

Fig.11. shows the variation of the imaginary part of the impedance (Z") with frequency at different temperatures. Z" peak starts appearing with increase in temperature ≥ 250°C with asymmetric broadening. For temperatures below 250°C, the peak was beyond the range of frequency measurement. The peak shifts towards higher frequency with increasing temperature indicating the spread of relaxation times and the existence of temperature dependent electrical relaxation phenomena. Probably, high temperature triggers grain boundary relaxation process as is also evident from the asymmetric broadening of the peaks (Cole and Cole, 1941).

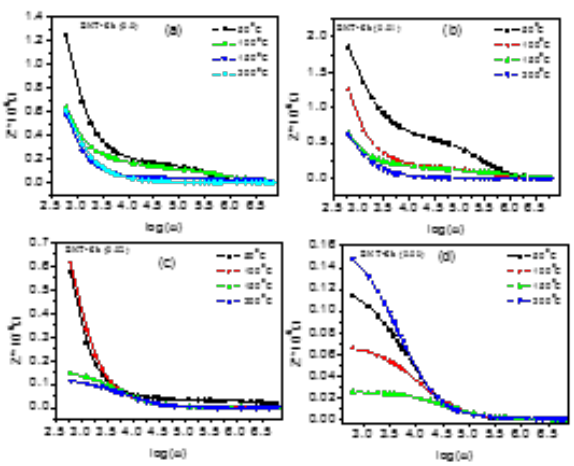

Fig.10.Frequency dependence of real part of impedance at different temperature with different concentration of antimony (Sb). (a) for Pure BNT-Sb (0.0) (b) for BNT-Sb (0.01), (c) for BNT-Sb (0.02) and (d) foe BNT-Sb (0.03).

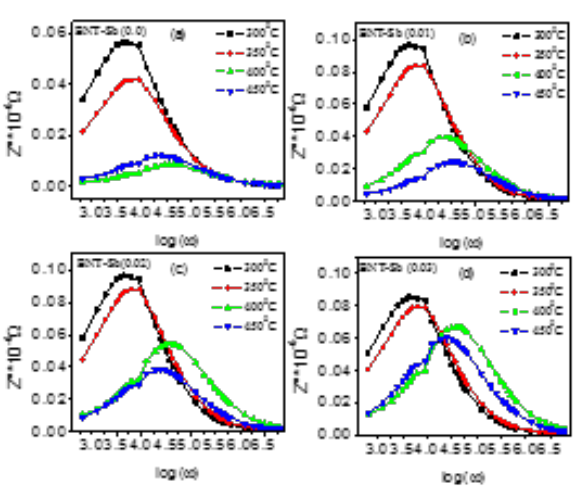

Fig.11.Frequency dependence of imaginary part of impedance at different temperature with different concentration of antimony (Sb). (a) for Pure BNT-Sb (0.0) (b) for BNT-Sb (0.01), (c) for BNT-Sb (0.02) and (d) foe BNT-Sb (0.03).

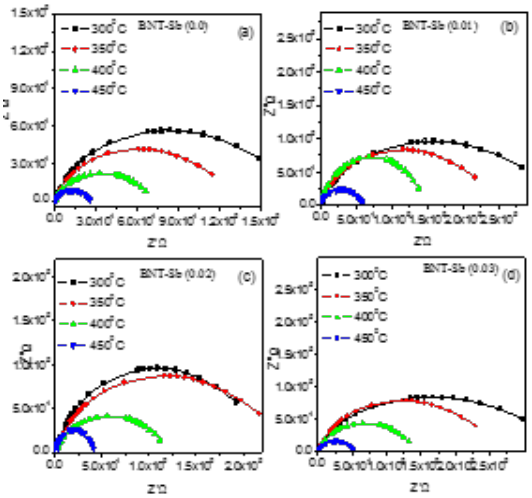

Fig.12.Cole-Cole plot of impedance at different temperature with different concentration of antimony (Sb). (a) for Pure BNT-Sb (0.0) (b) for BNT-Sb (0.01), (c) for BNT-Sb (0.02) and (d) for BNT-Sb (0.03).

The values of parameters Rs, R_g, C_g, R_{gb}, C_{gb}, are calculated and plotted for pure BNT shown in Fig.13. as a function of temperature. The value of C_g increases slowly with increase in temperature whereas the R_g show exponential decrease at higher temperatures. The behavior could be associated with the grain becoming conducting.The series resistance Rs also increases at high temperature (not shown) and reached maximum at 250°C, reflecting that the charges trapped at the bulk electrode interface is migrated into the bulk at this region. The value of R_{gb} decreases with increase in temperature whereas C_{gb} increases slowly with increase in temperature.

Conductivity Studies

The frequency variation of ac conductivity (σ_{ac}) at different temperatures is shown in fig.14. The behavior of σ_{ac} with frequency at room temperature exhibits both low and high frequency dispersion phenomena.

The conductivity obeys the Jonscher's power law;

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

where *n* is the temperature dependent frequency exponent (0 < *n*<1), *A* is a thermally activated quantity, hence electrical conduction of the materials is thermally activated process.

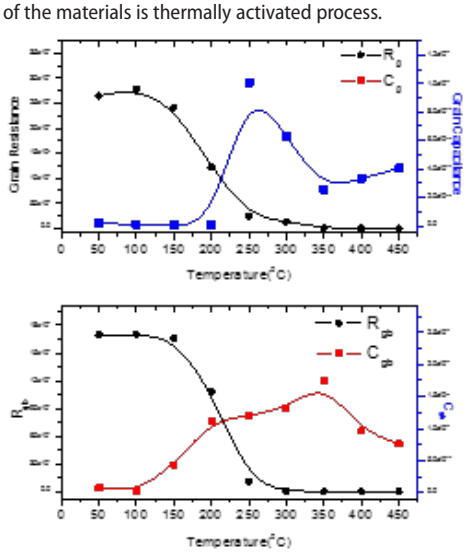

Fig.13. Shows variation of R_g, C_g, R_{gb} and C_{gb} as a function of temperature. Also, the conduction behavior of the materials obeys the power law $\sigma(\omega)$ $a\omega_n$ with a slope of σ_{ac} curve governed by n in the low temperature region.

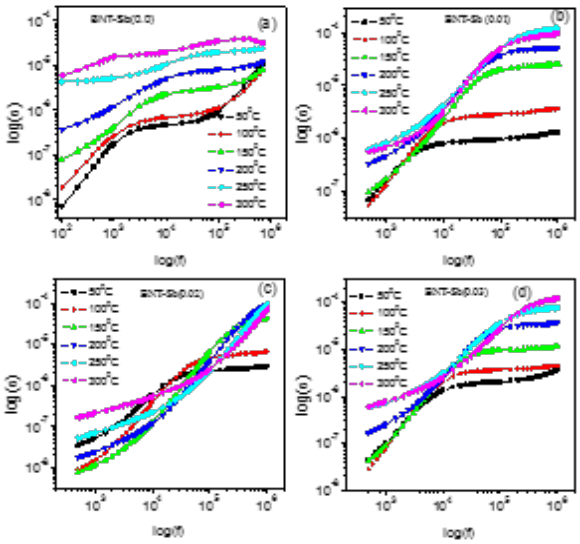

Fig.14. Frequency dependence of electrical conductivity at different temperatures. (a) for Pure BNT-Sb (0.0) (b) for BNT-Sb (0.01), (c) for BNT-Sb (0.02) and (d) foe BNT-Sb (0.03).

CONCLUSIONS

Pure and antimony doped BNT electro ceramics were successfully synthesized by a conventional solid state reaction route. From XRD analysis, it is evident that antimony (Sb) diffused into the BNT lattice and does not cause an obvious change in the phase structure. X-ray diffraction analysis showed that a probable structural change at the 0.03% Sb doped with the BNT. It may be possible that a morphotropic phase boundary (MPB) exists around $x = 0.03$. Analysis of peak positions, widths and intensities of Raman spectroscopy study also confirmed the existence of structural change around $x = 0.03$ composition. The dielectric response of lead free ferroelectric BNT-Sb, which indicates typical frequency dispersion, shift in dielectric maxima temperature (T_m) towards higher temperature side with increase in frequency. The value of γ estimated from the slope of the graph indicating that the material has almost complete diffuse phase transition characteristics when concentration of Sb reaches at 0.03.

REFERENCES

1. H. Nagata and T. Takenaka, "Lead-Free Piezoelectric Ceramics of (Bi0.5Na0.5)TiO3-0.5(Bi2O3-Sc2O3) System," Jpn. J. Appl. Phys., 36 [9B] 6055-7 (1997).
2. A.J. Moulson and J.M. Herbert, Electroceramics: Materials, Properties, Applications.,2nd ed. Wiley and Sons, West Sussex, England, 2003.
3. A.N. Soukhojak, H. Wang, G.W. Farrey, and Y.-M. Chiang, "Superlattice in Single Crystal Barium-Doped Sodium Bismuth Titanate," J. Phys. Chem. Solids, 61 [2]301-4 (2000).
4. G.O. Jones and P.A. Thomas, "Investigation of the Structure and Phase Transitions in the Novel A-site Substituted Distorted Perovskite Compound Na0.5Bi0.5TiO3," ActaCrystallogr., B 58 [2] 168-78 (2002).
5. P. Woodward, "Octahedral Tilting in Perovskites. I. Geometrical Considerations,"ActaCrystallogr.,B 53 [1] 32-43 (1997).
6. P. Woodward, "Octahedral Tilting in Perovskites. II. Structure Stabilizing Forces,"ActaCrystallogr.,B 53 [1] 44-66 (1997).64
7. G.O. Jones and P.A. Thomas, "The Tetragonal Phase of Na0.5Bi0.5TiO3 - a New Variant of the Perovskite Structure," ActaCrystallogr.,B 56 [3] 426-30 (2000).
8. M.E. Lines and A.M. Glass, Principles and Applications of Ferroelectrics and Related Materials. Oxford University Press, New York, 2001.
9. S.A. Sheets, A.N. Soukhojak, N. Ohashi, and Y.-M. Chiang, "Relaxor SingleCrystals in the (Bi1/2Na1/2)1-xBaxZryTi1-y)3 System Exhibiting High Electrostrictive Strain," J. Appl. Phys., 90 [10] 5287-95 (2001).
10. S. Kuharuangrong, "Studies on the Dielectric Properties and the Phase Transitions of the Bi0.5Na0.5TiO3 PbTiO3"; Ph. D. Thesis.Alfred University, Alfred, NY, 1994.
11. T. Takenaka, K.-I. Maruyama, and K. Kakata, "(Bi0.5 Na0.5)TiO3-BaTiO3 System for Lead-Free Piezoelectric Ceramics," Jpn. J. Appl. Phys., 30 [9B] 2236-9 (1991).
12. S. Kuharuangrong, "Effect of La and K on The Microstructure and Dielectric Properties of Bi0.5Na0.5TiO3-PbTiO3," J. Mater. Sci., 36 [7] 1727-33 (2001).
13. H. Ishii, H. Nagata, and T. Takenaka, "Morphotropic Phase Boundary and Electrical Properties of BisumuthSodiumTitanate - Potassium Niobate Solid- Solution Ceramics," Jpn. J. Appl. Phys., Part 1, 40 [9 B] 5660-3 (2001).
14. H. Nagata and T. Takenaka, "Lead-Free Piezoelectric Ceramics of (Bi0.5Na0.5)TiO3- KNbO3-0.5(Bi2O3-Sc2)3) System," Jpn. J. Appl. Phys., 37 [9B] 5311-4 (1998).