International Symposium of Research Students on Materials Science and Engineering
December 2002-04 Chennai India
Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras

EFFECT OF HETEROVALENT SUBSTITUTION OF Nd AND Nb AT B-SITE ON THE DIELECTRIC AND ELECTRICAL PROPERTIES OF $(Na_{0.5}Bi_{0.5})(Nd_xTi_{1-2x}Nb_x)O_3$ CERAMICS

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ABSTRACT

$(Na_{0.5}Bi_{0.5})(Nd_xTi_{1-2x}Nb_x)O_3$ ceramic samples with heterovalent substitution of Nd and Nb at B-site in $Na_{0.5}Bi_{0.5}TiO_3$ with varying concentration of Nd and Nb were prepared via solid-state double sintering route. Single-phase formation is confirmed through X-ray diffraction technique. Dielectric and Impedance measurements were made over a wide range of temperature and frequency. Simultaneous substitution of Nd and Nb has decreased the transition temperature and has drastic effect on the dielectric behaviour of Nd and Nb doped samples. The Effect of Nd and Nb concentration on the dielectric behaviour and electrical properties of doped NBT samples are presented in this paper.

Keywords: $Na_{0.5}Bi_{0.5}TiO_3$, heterovalent substitution, Dielectric properties and Impedance spectroscopy.

1. INTRODUCTION

ABO_3 perovskite type oxides are important for their electronic, magnetic and dielectric properties and are attractive materials for various applications [1]. Notable examples are $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Zn_{2/3}Nb_{1/3})O_3$, $(Pb_{1-x}La_x)(Zn_{2/3}Nb_{1/3})O_3$ etc. Most of these materials are lead based, which have more than one cation occupying the lattice sites A, and B. The toxicity of the lead and the degradation of the properties of these compounds due to volatility of lead have resulted in an increasing demand for environmental friendly materials.

NBT is one of such lead free ferroelectric materials with rhombohedral symmetry at room temperature. It undergoes a series of phase transitions: (1) ferroelectric rhombohedral to antiferroelectric tetragonal around 230^OC, (2) Antiferroelectric tetragonal to non polar tetragonal around 320^OC and (3) nonpolar tetragonal to cubic around 520^OC [2]. In this material the heterovalent cations Na^+, Bi^{+3} occupy the lattice site A and are randomly distributed. The distribution of these cations and the magnitude of these cationic disorders at lattice sites strongly influence the dielectric behaviour, temperature of dielectric maximum (T_m) and also the nature of phase transitions. Appropriate cationic modification at A site [3, 4] with (Pb, Sr, Pb+Sr, K etc) has resulted in good dielectric relaxor behaviour. There are few reports available [5] on NBT based relaxor dielectric material in which cationic modifications at B-site with homovalent ions have been tried and these materials exhibited high electrostrictive strain. In order to study the effect of heterovalent substitution at B-site, we investigated the effect of simultaneous heterovalent substitution of Nd and Nb at B-site in NBT.

2. EXPERIMENTAL PROCEDURE

Ceramic compositions $(Na_{0.5}Bi_{0.5})(Nd_xTi_{1-2x}Nb_x)O_3$ with x = 0.0125, 0.025, 0.05 were prepared through solid state double sintering route. Stoichiometric mixture of initial powder was calcined at 800^OC for 15 hrs and the pellets of calcined powder were final sintered in the temperature range 1100 to 1150^OC depending up on composition. The formation of single-phase compounds was confirmed by an X-ray diffraction technique using (PW3040/60 X'pert PRO) X-ray powder diffractometer with CuK_α radiation. Dielectric measurements on these samples were carried out over a wide range of temperature using HP4192A impedance analyzer. Impedance measurements were made over a wide range of frequency (100Hz-1MHz) at different constant temperatures using AUTOLAB (PGSTAT30) Low frequency impedance analyzer.

3. RESULTS AND DISCUSSION

Fig.1 shows the powder diffraction pattern for all compositions. At room temperature all the samples showed single phase with rhombohedral symmetry (see Table 1 For Lattice parameters a and α). The density of the samples was found to be between 86 to 92% of theoretical density depending up on the composition. Fig.2 shows the dielectric constant as a function of temperature for all compositions in the frequency range 10KHz to 1MHz. Frequency dependent dielectric behaviour is observed in the low temperature region between room temperature to 532 K for x = 0.0125. For temperatures between 532K and 650K (T_m) the dielectric dispersion with frequency narrowed. After dielectric maximum, frequency dependent broad dielectric peaks were observed and with increase in frequency dielectric maximum peak shifted characterizing relaxor like behaviour. Observed broad dielectric peaks may be attributed to the cationic disorder arising due to the heterovalent Na^+, Bi^{+3} ions occupying the lattice sites-A and Nd^{+3}, Ti^{+4}, Nb^{+5} occupying the lattice site-B. With increase of Nd and Nb concentration in NBT (i.e for x= 0.025), further broadening of peaks around dielectric maximum was observed. With further increase of Nd and Nb concentration (i.e. for x= 0.05), frequency dependent dielectric peaks in the low temperature region were dominating with T_m shifting towards higher temperature side. A hump corresponding to the transition to paraelectric phase was observed around 615K. Substitution of Nd and Nb at B-site has decreased the T_m (Table.1), which may be attributed to the steric effect [6] arising due to the partial replacement of Ti^{+4} ion with heterovalent ions Nd^{+3}, Nb^{+5} having different ionic radii.

For the temperatures higher than T_m, the variation of inverse of dielectric constant with temperature does not follow Curie-Weiss law and the dielectric constant varies according to the law $(1/\varepsilon'-1/\varepsilon'_m) = (T-T_m)^\gamma/(2\delta^2\,\varepsilon'_m)$ [7] where $1 \le \gamma \le 2$. Fig 3. shows $\log(1/\varepsilon'-1/\varepsilon'_m)$ Vs $\log(T-T_m)$. In the above relation γ is degree of dielectric dispersion and δ is a parameter characterizing the diffuseness of phase transition. The data on γ and δ are presented in Table 1.

Fig 4. shows cole-cole plots obtained for all compositions at 848K. Equivalent circuit modeling was done. The impedance data at 848K for x= 0.0125, 0.025 was found to fit to two RC circuits in series, one corresponding to grain and other corresponding to grain boundary. The impedance data for x = 0.05 at 848K was found to fit to three RC combination in series with each other. The third RC circuit corresponds to sample electrode interface effect. The data on grain, grain boundary and sample electrode resistance(capacitance)at 848K are presented in table 2. For x=0.05 increase in dielectric constant with temperature well above transition temperature was found at lower frequencies ≤ 10kHz (Fig.2). This increase may be attributed to development of large capacitance at highly resistive sample electrode interface due to accumulation of charge carriers at these interfaces. Fig. 5 shows $\log(\sigma'_{ac})$ Vs 1000/T(K) for composition x= 0.0125 at 10kHz, 50kHz and 100kHz. The ac conductivity increased with increase of frequency. For temperatures greater than T_m the data was found to fit to Arrhenius law. Activation energies for all compositions at 10kHz are presented in table 2.

4. CONCLUSION

Dielectric and electrical properties of ceramic compositions $(Na_{0.5}Bi_{0.5})(Nd_xTi_{1-2x}Nb_x)O_3$ (x= 0.0125, 0.025, 0.05) with heterovalent substitution at B site have been studied as a function of temperature and frequency. A relaxor like behaviour was observed around dielectric maximum temperature of NBT with heterovalent substitution. The broad dielectric peaks and the relaxor behaviour may be attributed to the cationic disorder at B site.

5. ACKNOWLEDGEMENT

The authors would like to thank DRDO, Delhi, India for financial support in carrying the present research work. Syed Mahboob would also like to thank Prof. S. V. Suryanarayana, Prof. T. Bhima Sankaram, Department of Physics, Osmania University, Hyderabad, India for constant encouragement.

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TABLES

Table.1

Composition → / Parameter ↓		x = 0.0125	x = 0.025	x = 0.05
Lattice parameter	a(A^O)	3.857	3.895	3.882
	α	89.908	89.907	89.950
Tanδ at RT (10KHz)		0.048	0.044	0.038
ε_{RT} (10KHz)		712	619	620
T_m (10KHz)		650 K	648 K	536 K
γ (10KHz)		1.754	1.989	1.456
δ (10KHz)		118	206	144

Table 2

Composition → / Parameter ↓	x = 0.0125	x = 0.025	x = 0.05
E_{act} at 10KHz (eV)	0.894	0.437	0.631
R_g (KΩ)	11.15	2.635	2.344
C_g (nF)	1.031	2.810	0.948
R_{gb} (KΩ)	111.4	274.2	37.4
C_{gb} (nF)	0.3070	0.2716	0.331
R_e (KΩ)	------	------	24.10
C_e (nF)	--------	------	2.500
R_s (Ω)	163.4	133.9	196.1

FIGURES

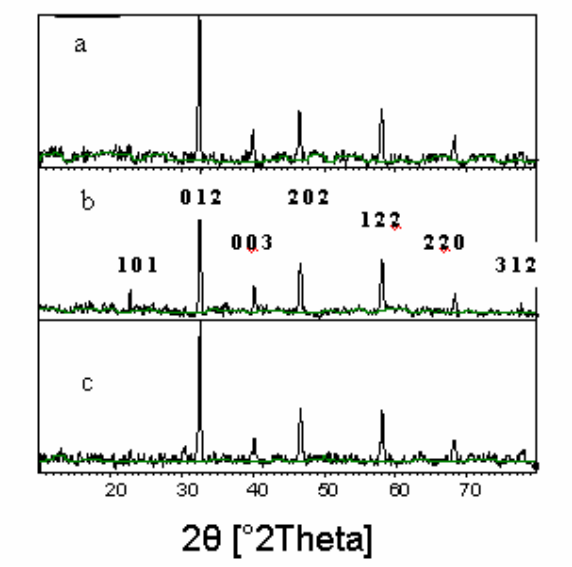

Fig. 1(a, b, c) shows XRD pattern for compositions x =0.0125, 0.025, 0.05 respectively

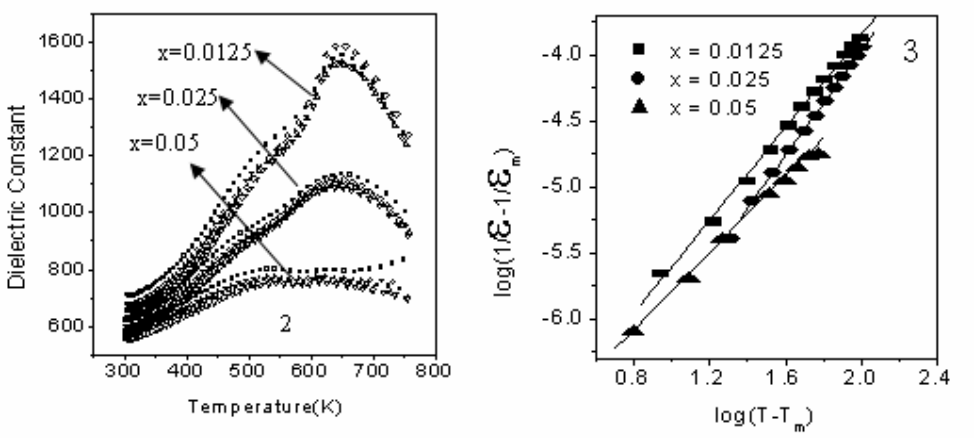

Fig. 2. shows variation of Dielectric constant Vs Temperature(K) for x = 0.0125, 0.025, 0.05 from top to bottom respectively at different frequencies. Fig.3 shows variation of $\log(T-T_m)$ Vs $\log(1/\varepsilon'-1/\varepsilon'_m)$

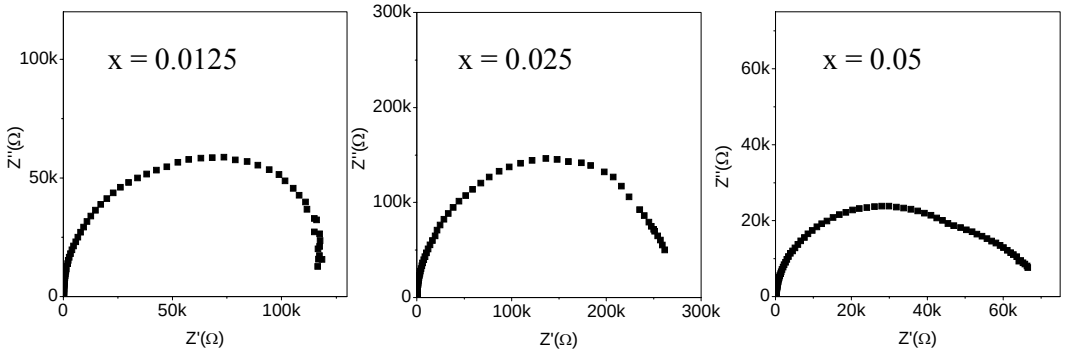

Fig. 4(a, b, c) shows plots Z'' Vs Z' 848K

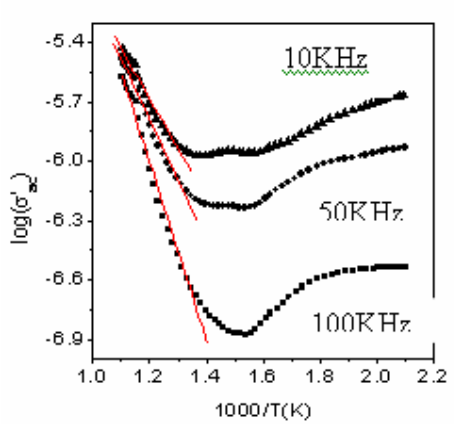

Fig.5 shows $\log(\sigma'_{ac})$ Vs 1000/T(K) for x= 0.0125 at different constant frequencies