EFFECT OF B SITE SUBSTITUTIONS OF Nb ON MICROSTRUCTURE, PHASE TRANSITION TEMPERATURES AND ELECTRICAL PROPERTIES OF (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ CERAMICS

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Niobium (Nb) substituted bismuth sodium barium titanate (BNBT) samples with general formula $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}$ $(Ti_{1-5x/4}Nb_x)O_3$, where x = 0, 0.003, 0.012 and 0.05 were prepared by solid state reaction method. The crystal phase, microstructure, electrical properties and phase transition temperatures of these materials were investigated. Samples consisted entirely of rhombohedral structure was formed. Scanning electron micrographs (SEM) revealed enhanced microstructure uniformity and retarded grain growth with increasing niobium content. Dielectric measurement as a function of temperature at variable frequency showed that the dielectric constant gradually decreases with niobium doping. The Curie temperature, $T_{\rm C}$ got shifted to lower temperature as the amount of dopant increases.

INTRODUCTION

Bismuth sodium titanate, Bi_{0.5}Na_{0.5}TiO₃ (BNT), a lead free ferroelectric with perovoskite structure, was first reported by Smolenskii et al. [1] in 1960 to have a relatively large remnant polarization ($P_r = 38 \ \mu \text{Ccm}^{-2}$) and Curie temperature ($T_c = 320^{\circ}$ C). However, because of their high coercive field ($E_c = 73 \text{ kVcm}^{-1}$) and relatively large conductivity pure BNT ceramics are difficult to be poled, which limits their application as a potential candidate to substitute PZT in ferroelectric and piezoelectric devices. To overcome this difficulty and enhance the intrinsic piezoelectric properties of BNT, several more studies have been made by forming solid solutions with BaTiO₃ [2], NaNbO₃ [3], KNbO₃ [4], K_{0.5}Bi_{0.5}TiO₃ [5], Ba(Ti,Zr)O₃ [6], Bi(Mg_{2/3}Nb_{1/3})O₃ [7] as well as by addition of modifiers like CeO₂ [8], Eu₂O₃ [9], and so on. Among the various solid solutions that are reported, bismuth sodium barium titanate, $(Bi_0 Na_0)_1$ "Ba, TiO₃ (BNBT) was found to exhibit a morphotropic phase boundary (MPB) at x = 0.06 with enhanced piezoelectric properties of $k_{33} = 0.55$, $k_{31} = 0.19$, $d_{33} = 125$ pC/N [10]. Zuo et al. [11] substituted Nb⁵⁺ in the B – site of BNT by compensating the increase in charge on B-site with corresponding decrease in charge on the A-site, $(Bi_{0.5}Na_{0.5})_{1-x/2}Ti_{1-x}Nb_x)O_3$ influenced densification and led to remarkable changes in dielectric, ferroelectric and piezoelectric properties. Since doping of Nb⁵⁺ has been found to yield somewhat better properties in BNT, the present work is undertaken to substitute Nb⁵⁺ in the B-site of BNBT at morphotropic phase boundary composition with complete charge compensation within the B-site and not on A-site as was done by Zuo et al.

EXPERIMENTAL

Samples of $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}(Ti_{1-5x/4}Nb_x)O_3$ with x = 0, 0.003, 0.012 and 0.05 were prepared through dry mixing followed by wet mixing with sufficient organic solvent in an agate mortar and pestle, and heated at 850° C for 3 hrs to get the better homogeneous samples.

The precursors used in this study were A.R. grade BaCO₃, Bi₂O₃, Na₂CO₃, TiO₂ and Nb₂O₅. The requisite amounts of raw powders as per stoichiometric ratios were thoroughly mixed, homogenized and subjected to calcination in platinum crucible at 850°C in air for 3 h and allowed to reach room temperature under controlled cooling. Completion of the reaction and the formation of desired phase were examined by x-ray diffraction method using XRD-PANalytical- X' Pert PRO, Japan equipped with CuK α radiation ($\lambda = 1.54059$ Å). The calcined samples were pelletized into discs using polyvinyl alcohol as binder and sintered at 1150°C for 2 h with an intermediate soak time 1 h at 500°C for organic binder removal. For electrical measurements, silver paste was

coated on the polished surface of pellets and fired at 600°C for 1 h. Microstructure investigations of the fractured surfaces of sintered pellets were obtained using a computer controlled scanning electron microscope, JEOL-JSM-6610LV, Tokyo, Japan. Capacitance (*C*), dielectric loss (*tan* δ), complex impedance (*Z**), resistance (*R*), phase angle(Φ), inductance (*L*) and quality factor (*Q*) in series and parallel were obtained by using phase sensitive LCR multi meter, N4L PSM 1700 Japan, in the temperature range from room to 400°C and frequency in the range of 100 Hz to 1 MHz. Samples with composition x = 0, 0.003, 0.012, 0.05 in (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06} (Ti_{1-5x/4}Nb_x)O₃ will be denoted in subsequent discussion as BNBT, BNBTN_{0.3}, BNBTN_{1.2}, BNBTN₅.

RESULTS AND DISCUSSIONS

Figure 1 show the X-ray diffraction patterns of BNBTN_x samples with x = 0, 0.003, 0.012 and 0.05 heat treated at 850°C for 3 hours. All XRD patterns in the figure are in good agreement with that of rhombohedral Bi_{0.5}Na_{0.5}TiO₃, (JCPDS file number 36-0340), indicating that pure phase samples resulted in all compositions under study. According to Zuo et al. [11], addition of $Nb^{5+} > 0.03$ mol with charge compensation on A-site resulted in appearance of a second phase and with increasing concentration of Nb5+, the amount of second phase became higher and higher. However, in the present study, no extra peaks were evident even for x = 0.05, indicating that all Nb⁵⁺ has gone into the crystal lattice. The lattice parameters of $BNBTN_x$ materials with x = 0, 0.003, 0.012 and 0.05 have been calculated by using a standard computer program "POWD", and tabulated in Table 1 with corresponding relative densities, crystallites size & lattice strain. The theoretical or X-ray density was calculated by using the relation $\rho = (1.66042 \ \Sigma A)/V$, where ρ is X-ray density (g/cc), ΣA is sum of all the atomic weights of the atoms in the unit cell and V, volume of the unit cell. The average crystallite size was estimated from the line width of intense powder diffraction line using Scherrer's formula ranges from 29.6 to 44.2 nm.

As shown in Figure 2, the SEM micrographs of fractured surfaces of sintered pellets of pure and niobium doped BNBT are very dense throughout the composition

range of $0 \le x \le 0.05$ as evidenced with their relative densities of 94.7 %, 96.1 %, 98.7 % and 99.2 %, respectively. However, from the grain size variations seen in SEM micrographs, it may be noticed that there is a slight decrease in grain size with increasing niobium concentration as it was reported for Nb⁺⁵ doping [11]. The average grain size for each composition was found to be in the range of 1.2 μ m, 1.4 μ m, 1.1 μ m and 1.0 μ m respectively. This decrease in average grain size can be explained by cation vacancies created by substitution of Nb⁵⁺ in Ti⁴⁺ sites in the lattice. Some large grains were observed in the SEM micrograph of BNBT doped with low concentration of niobium (or 0.003 mole), which might be due to sintering conditions. According to Yi et al. [12] the cation vacancy in the grain boundaries would attract positively charged cations through columbic interactions and restrain the mobility of grain boundaries, thus resulting in small grains. The increase of densification from undoped to doped (BNBTN, with x = 0.05) observed in SEM micrographs might be due to the increase of mass transportation ability to B-site vacancies



Figure 1. Powder X-ray diffraction patterns of $BNBTN_x$ for x = 0, 0.003, 0.012 and 0.05.

Table 1. Lattice parameters and densities of BNBTNx samples, where x refers to a dopant concentration of 0, 0.003, 0.012 and 0.05 respectively.

Composition	Lattice parameters		Density		
	a (Å)	α (°)	Crystallite size (nm)	Experimental (g·cm ⁻³)	% Relative
BNBT	3.899	89.79	44.2	5.67	94.4
BNBTN0.3	3.901	89.90	39.4	5.70	96.2
BNBTN1.2	3.903	89.94	29.6	5.82	98.7
BNBTN5	3.907	89.98	32.6	5.92	99.2

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Figure 2. SEM micrograph of fractured surface of sintered pellets of BNTBNx samples.

Figure 3 shows the variation of relative permittivity (ε') and dielectric loss (or tan δ) as a function of temperature for sintered $BNBTN_x$ samples with x = 0, 0.003, 0.012 and 0.05 measured at 1 KHz frequency. In the case of BNT, dielectric anomalies have been reported at two different temperatures corresponding to the depolarization temperature $T_{\rm d}$ and maximum temperature T_m respectively. Depolarization temperature denotes transition temperature at which rhombohedral phase transforms to tetragonal phase, while T_m is the temperature corresponding to the maximum value of dielectric constant. The addition of 6 % mole of BaTiO₃ to BNT increased the dielectric constant to 6500 at T_m according to the report of H. Wang et al. 2010 [13]. From Figure 3a, the magnitude of dielectric constant of $BNBTN_x$ at Tm decreases with increase in concentration of Nb⁵⁺, suggesting that high dopant level of Nb⁵⁺ acts

as a suppressor as reported by Zuo et al. for BNT [11]. The dielectric loss variation with temperature depicted in the Figure 4b shows an increase in *tan* δ with increasing concentration of Nb⁵⁺ below 100°C and a plateau between 200°C and 300°C followed by a steep increase. All BNBTNx samples showed relaxor behavior in terms of variation of ϵ ' with frequency as shown in the Figure 4. This is expected because of heterogeneity in both A-site and B-site ions in the lattice caused by Na⁺, Ba²⁺, Bi³⁺ and Ti⁴⁺, Nb⁵⁺ respectively.

BNBTN_x samples in the studied range of x, where $x = 0 \le x \le 0.05$, show dispersion throughout the frequency range studied, and Figure 4 shows the temperature and frequency dependence of dielectric constant and dielectric loss for BNBTN_{0.3} ceramic sample. Figure 5 shows the differential scanning calorimeter (DSC) curves of BNBTN_x for x = 0, 0.003, 0.012 and 0.05.



Figure 3. Temperature variation of permittivity and dielectric loss measured at the frequency of 1 KHz for $BNBTN_x$ sintered samples where x = 0, 0.003, 0.012 and 0.05.



Figure 4. Temperature dependence of relative permittivity and dielectric loss measured at 1, 10, 50 and 100 kHz frequencies for BNBTN_x sintered sample up to 400°C, where x = 0.003.



Figure 5. DSC measurements of BNBTN_x ceramics with x = 0, 0.003, 0.012 and 0.05 in the temperature range of 27°C to 600°C up on heating.



Figure 5. DSC measurements of BNBTN_x ceramics with x = 0, 0.003, 0.012 and 0.05 in the temperature range of 27°C to 600°C up on heating.

The powder samples were analyzed by DSC with the heating rate of 3°C per minute from room temperature to 600°C by DSC 823e (Mettler Toledo, Germany). In each case two endothermic peaks were observed which may be assigned to the antiferroelectic ferroelectric to (AFE-FE) and ferroelectric to paraelectric (FE-PE) phase transition temperatures. From this figure it can be noticed the FE-PE transition temperature decreases with increase in niobium concentration while the AFE-FE transition temperature remains unaffected by niobium doping. These results confirm the pattern of change observed in variation of dielectric constant with temperature.

CONCLUSIONS

Niobium substituted bismuth sodium barium titanate samples of composition (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}(Ti_{1-5/4x}Nb_x)O₃ for x = 0, 0.003, 0.012 and 0.05 were prepared by conventional solid state reaction method. X-ray diffraction patterns showed formation of single phase rhombohedral structure for all the investigated compositions. The powder samples were pressed into discs and sintered at 1150°C for 2 h for densification. Microstructure studies on the fractured surface of the sintered pellet revealed that niobium doping inhibits grain growth and improves densification behavior of the material. The dielectric investigation on the silver coated sintered pellets also showed that niobium substitution has lowered the dielectric properties of BNBT polycrystalline ceramic materials. Differential Scanning Calorimetric studies indicated a progressive shift of ferroelectric phase transition to paraelectric phase to lower temperature compared to the undoped BNBT.

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