Research Article

Structural, dielectric and piezoelectric properties of NaNbO₃-BaTiO₃ ceramic system

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Abstract

Ceramics (1-x)NaNbO₃-xBaTiO₃ for x = 0, 0.25, 0.50, 0.75 and 1.0 were synthesized using a standard solid state reaction method (sintering temperature: 870°C to 1300°C) and their unit cell structure, microstructure, dielectric and piezoelectric properties were investigated. All specimens are found to have single phase with perovskite type structure with crystal structure of NaNbO₃ was varied from orthorhombic to tetragonal with increasing BaTiO₃ content x. The effect of BaTiO₃-addition to NaNbO₃ is discussed in the light of structural, dielectric and piezoelectric properties. Results show that the phase transition has diffusive character. The piezoelectric constant (d_{33} = 63 pC/N) was found to be maximum for x = 0.50.

Keywords: Ceramic, Structure, Dielectric constant, Lead free, Microstructure

1. Introduction

[1]Ceramics with perovskiteABO_3-type structures have received considerable attention due to their excellent functional properties and technological relevance. They are widely used in various electronic and microelectronic devices such as in capacitors, piezoelectric transducers, pyroelectric detectors/sensors, memory devices, SAW substrates, MEMS, *etc.* Recently they are also employed in high-power applications such as defibrillators, detonators, power electronics and in intravascular imaging applications via intravascular ultrasounds, *etc.* Materials used for the fabrication of such devices were mostly lead-based but lead-free piezoelectric materials have recently attracted significant attention from the viewpoint of environmental safety. Among them alkali niobates, $ANbO_3$-based materials, are considered as one of potential candidates for a lead-free ferroelectric and/or piezoelectric applications (Y. Saito *et al*, 2003). Sodium niobate $NaNbO_3$ (NN) is a well-known dielectric material with a perovskite-type structure exhibiting good piezoelectric properties. At room temperature it shows anti-ferroelectric behavior and undergoes a phase transition at high temperature (J. Gervais *et al*, 1982; S. Lanfredi *et al*, 2002; J. Koruza *et al*, 2010; S.K. Roy *et al*, 2013). Recently some NN-based *perovskite* solid solutions (1-x)NaNbO₃-xABO₃ with small amount of *x* such as: $Na_{1-x}Ba_xNb_{1-x}Ti_xO_3$ (J.T. Zeng

et al, 2006) and $Ba_{0.06}(Na_{1/2}Bi_{1/2})_{0.94}TiO_3$-NaNbO₃ (S.K. Roy *et al*, 2016a; S.K. Roy *et al*, 2016b) show excellent dielectric and ferroelectric properties and they can be easily used to obtain dense ceramics. Besides, BaTiO₃ (BT) is a typical ABO_3 perovskite structure ferroelectric material that can transform through the cubic-paraelectric, ferroelectric-tetragonal, orthorhombic and trigonal phase for temperatures in descending order. Recently, Zuo *et al*. reported the dielectric and electrostrictive properties of NaNbO₃-BaTiO₃ ceramics for *x* = 0.15–0.25 (R. Zuo *et al*, 2016) and the large exhibit a high electrostrictive coefficient Q_{33} of 0.046 m⁴/C² . The microstructure and electrical properties of same ceramic system were evaluated for *x* = 0.04–0.20 (S. Xie *et al*, 2009) and upto 0.45 mol% (W.Q. Cao *et al*, 2016). However, detailed report on structure, dielectric and piezoelectric properties of (1-x)NaNbO₃-xABO₃ ceramics have not yet been investigated. In this work, (1-x)NaNbO₃-xABO₃; 0 ≤ x ≤ 1 (NN-BTx) ceramics synthesized using standard solid-state reaction method and their crystal structures, dielectric and piezoelectric properties are reported.

2. Experimental details

The compositions selected for the present study were of the type (1-x)NaNbO₃-xBaTiO₃ for *x* = 0, 0.25, 0.50, 0.75 and 1.0. Figure 1 shows the detatils of the procedure adopted for the prepraton of ceramic samples using high temperature 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. For preliminary structural studies, X-ray diffractograms (XRD) were recorded at room temperature by X-ray diffractometer Bruker, D8-Advance using nickel filtered CuK_α - radiation (λ = 1.5406Å) at a scanning rate of 2°(2θ)/min. The angular range 2θ covered was 10° - 80°. The surface morphology of the ceramic samples was taken by scanning electron microscope (JEOL JSM-7600F, Japan). To measure the dielectric properties of the compounds, air drying silver paint was applied on both the large faces of the samples to serve as electrodes. Measurements of dielectric constant (ε) and dielectric loss (tanδ) were carried out as a function of frequency (20 Hz - 1MHz) and temperature (25°C - 300°C) using an 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.
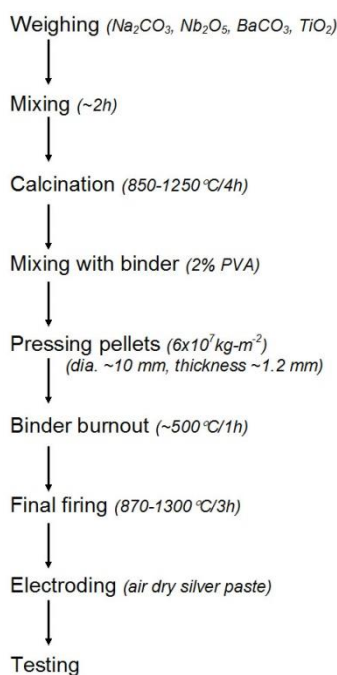

Weighing *(Na₂CO₃, Nb₂O₅, BaCO₃, TiO₂)*

↓

Mixing *(~2h)*

↓

Calcination *(850-1250 ℃/4h)*

↓

Mixing with binder *(2% PVA)*

↓

Pressing pellets *(6x10⁷kg-m⁻²)*
(dia. ~10 mm, thickness ~1.2 mm)

↓

Binder burnout *(~500℃/1h)*

↓

Final firing *(870-1300 ℃/3h)*

↓

Electroding *(air dry silver paste)*

↓

Testing

Fig. 1 Procedure for sample preparation

3. Results and discussion

With an aim to study the effect of BaTiO₃ addition to NaNbO₃ on the unit cell structure, XRD analysis of (1-x)NaNbO₃-xBaTiO₃; x = 0, 0.25, 0.50, 0.75 and 1.0 have been carried out. Figure 2 shows the XRD profiles for NN-BTx ceramic system. The XRD-pattern analyses indicated that all specimens are of single-phase with perovskite-type structure. The crystal structure of NaNbO₃ and BaTiO₃ at room temperature are found to be orthorhombic and tetragonal respectively, which are consistent with the earlier reports (S.K. Roy *et al*, 2013; A.K. Jha and K. Prasad, 2010a; A.K. Jha and K. Prasad, 2010b). The lattice parameters (Table 1) were estimated using a standard computer program (least

squares refinement method). Experimentally observed and calculated *d*-values for these compounds were compared and were found to be in good agreement. The shift in diffraction peaks towards higher Bragg's angle indicated the decrease in lattice parameters as well as unit cell volume with increasing x (Figure 3, Table 1). A second order polynomial fitting to concentration (x) dependence of unit cell volume data yielded a relation: $V = 242.25297 - 278.33897x + 97.17257x^2$ with r^2 = 0.9855. Furthermore, the XRD results clearly indicated the formation of perovskite type single phase NN-BTx solid solutions for the whole range (x).
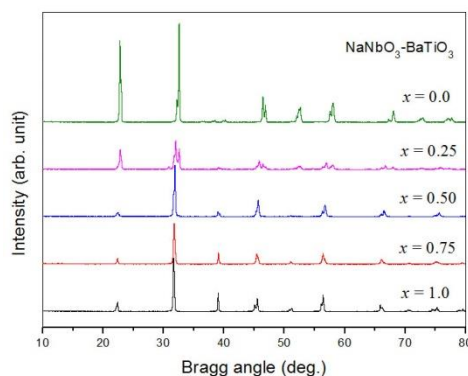

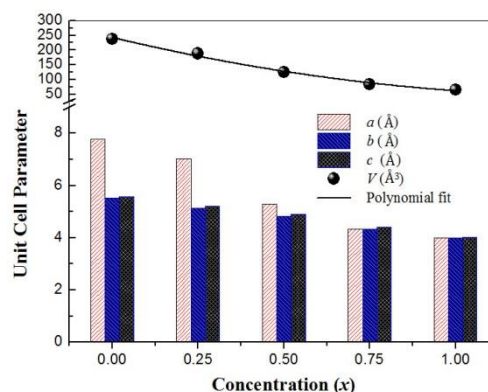**Fig. 2** X-ray diffraction patterns of NaNbO₃-BaTiO₃ ceramics

**Fig. 3** Compositional dependence of lattice constant (*a*, *b*, *c*) and unit cell volume of NaNbO₃-BaTiO₃ ceramics

The SEM-photographs for NN-BTx are shown in Figure 4. The black regions represent low intensity of secondary electrons and white regions, high intensity. The photograph contains a very few voids or cavities, suggest that the density of the material is high and all the particles are uniformly and homogeneously distributed. The grains of unequal sizes (2 – 4 *μm*) were found for the chosen compositions. It is also observed that a few grains are agglomerated and appear larger in size compared to the average size which is termed as an abnormal grain growth or secondary crystallization.

Table 1 Unit cell parameters of NaNbO$_3$-BaTiO$_3$ ceramics

Materials → Unit Cell Parameters ↓	$x = 0$	$x = 0.25$	$x = 050$	$x = 0.75$	$x = 1.0$
Structure	O	O	O	T	T
a (Å)	7.76(3)	7.021(4)	5.284(1)	4.322(8)	3.995(7)
b (Å)	5.51(3)	5.133(6)	4.821(5)	4.322(8)	3.995(7)
c (Å)	5.568(3)	5.216(2)	4.892(4)	4.416(2)	4.031(1)
V (Å^3)	238.07	188.018	124.645	82.524	64.359

O : Orthorhombic; T : Tetragonal
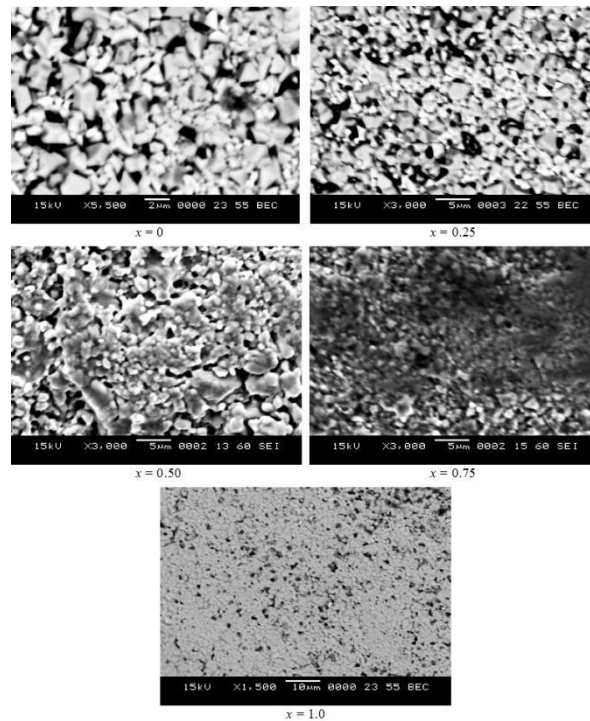
Fig. 4 Scanning electron micrographs of NaNbO$_3$-BaTiO$_3$ ceramics
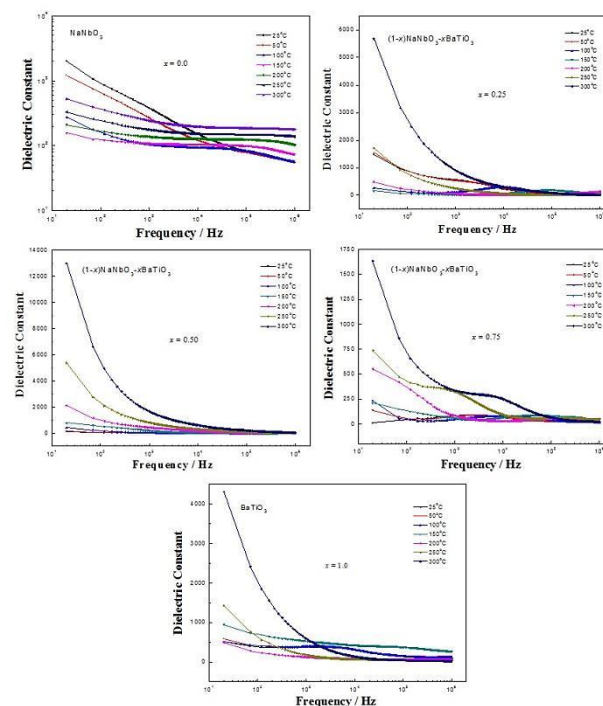
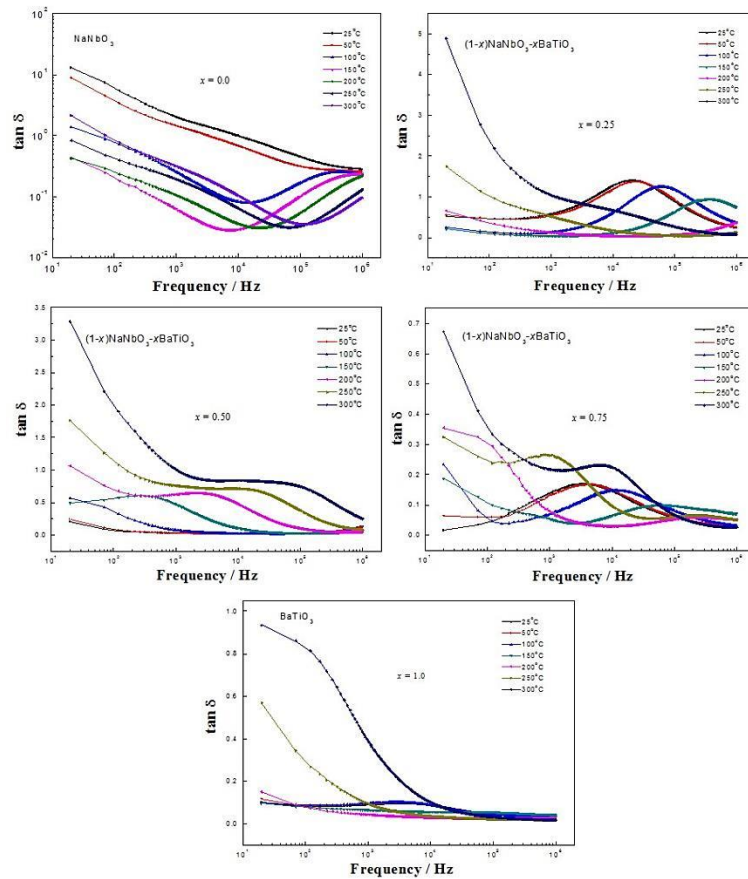**Fig. 5** Frequency dependence of dielectric constant of NaNbO$_3$-BaTiO$_3$ ceramics at different temperatures

Fig. 6 Frequency dependence of loss tangent of NaNbO₃-BaTiO₃ ceramics at different temperatures

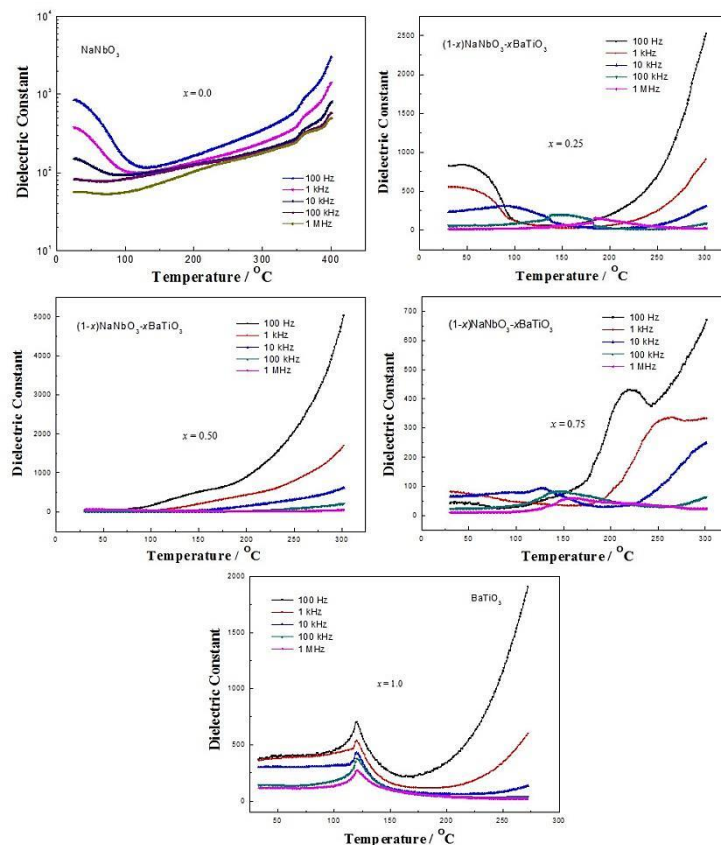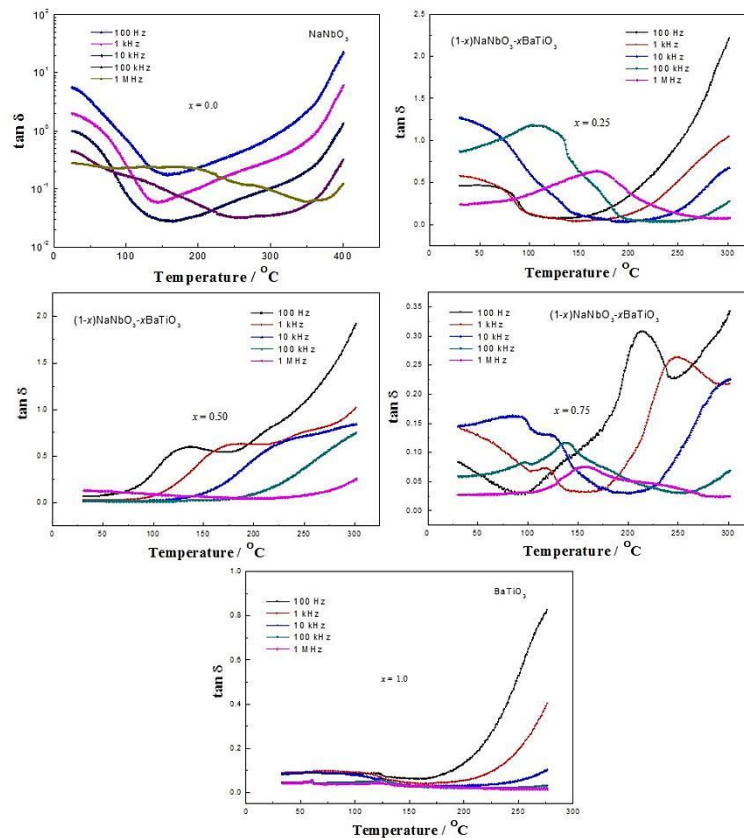**Fig. 7** Temperature dependence of dielectric constant of NaNbO₃-BaTiO₃ ceramics at different frequencies

Fig. 8 Temperature dependence of loss tangent of NaNbO₃-BaTiO₃ ceramics at different frequencies

The frequency dependence of dielectric constant (ε) and loss tangent ($\tan\delta$) for NN-BTx ceramics at different temperatures are shown in Figure 5 and Figure 6, respectively. It is observed that the values of both ε and $\tan\delta$ decrease with increasing frequency. However, $\tan\delta$-f graphs show peaks for $x \geq 0.25$ whose maximum values decrease as well as shift toward higher frequency side with the increasing temperature. This clearly shows that the dielectric relaxation present in the system. A relatively high dielectric constant at low frequencies is a characteristic of almost all dielectric materials. This is due to the fact that dipoles can no longer follow the field at high frequencies. It is known that the variations in ε and $\tan\delta$ are attributed to different types of polarizations *e.g.*, ionic, electronic, dipolar and space charge or interfacial which arise at different stages of material's response on varying temperature and frequency of the applied alternating field. Each of which involves a short range displacement of charges and contributes to the total polarization and hence to the permittivity of the material.

Figures 7 and 8, respectively, show the variation of ε and $\tan\delta$ with temperature at different frequencies. As typical of normal ferroelectrics, ε increases gradually with increment in temperature up to the transition temperature (T_m) and then decreases. It is seen that the partial substitution of BT with NN decreases the value of T_m, the value of ε_{RT} and $\tan\delta_{RT}$ (RT denotes values at room temperature) increase while maximum value of ε (ε_{max}) decreases, dielectric

peak shifts towards lower temperature side and ε-T curve flattens *i.e.* the phase transition becomes more diffuse. In other words, the ferro-paraelectric phase becomes more disordered. This can be explained on the basis of the fact that the delicate balance of short-range forces (favouring the non-polar cubic phase) and long-range Coulomb forces (favouring the ferroelectric state) makes the transition sensitive to defects (substitutions) that modify the short-range interactions and to carriers (*e.g.* photoelectrons) that screen the long-range field. The decrease in ε_{max} implies that the substitution of BT reduces the dipole moment of the lattice and lowers the peak dielectric constant. In all the materials $\tan\delta_{RT}$ was found to be of the order of 10^{-2}. The low $\tan\delta$ of this kind can be advantageous when improved detectivity is required. The diffuse phase transition in the material may be due to compositional fluctuations where the local curie points of different microregions are statistically distributed around the mean Curie temperature. It is possible to explain the results considering an increasing disorder on the arrangement of different ions in the lattice that should produce some kind of heterogeneities. The values of d_{33} were found to be 22 pC/N, 31 pC/N, 63 pC/N, 48 pC/N and 52 pC/N, respectively for x = 0, 0.25, 0.50, 0.75 and 1.0.

Conclusions

Lead-free (1-x)NaNbO₃-xBaTiO₃; (0 ≤ x ≤ 1) ceramics prepared using a high-temperature solid-state reaction technique, were found to have a perovskite-type

orthorhombic structure upto x = 050 thereafter it become tetragonal. Increase of $BaTiO_3$ content significantly reduces the dielectric constant as well as loss tangent values and improve the frequency and temperature stability of the dielectric properties of system. The compositional fluctuations are the main cause for diffusivity. The piezoelectric constant (d_{33} = 63 pC/N) was found to be maximum for x = 0.50.

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