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Effects of Nb-doping on the micro-structure and dielectric properties of $(Bi_{0.5}Na_{0.5})TiO_3$ ceramics

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Abstract

Bismuth sodium titanate [$(Bi_{0.5}Na_{0.5})TiO_3$ or BNT] ceramics incorporated with 0, 1, 5, 10, 15 and 20 mol% niobium were prepared by conventional solid state reaction method. The green bodies were sintered at 1050 °C for 2 h to obtain dense ceramics. The effects of substitution of niobium ion for titanium ion in BNT ceramics on micro-structure and dielectric properties were investigated. X-ray diffraction analysis showed the presence of a secondary phase when more than 5 mol% niobium was added. Within the solubility limit, Nb doping caused the grain size of BNTNb to be smaller than the undoped sample. The investigation of the dielectric properties showed that the transition temperature (T_c) was found to shift towards lower temperature as the content of Nb increased. In this research, the donor-type behavior and induced charged defects had significant influence on the electrical properties of Nb-doped BNT ceramics.

Keywords: A. Sintering; B. X-ray methods; C. Dielectric properties

1. Introduction

Nowadays, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is considered to be a potential candidate for lead-free ferroelectric and piezoelectric materials [1]. It is an A-site complex compound of ABO_3-type perovskite ferroelectrics with rhombohedral symmetry at room temperature [2]. The temperature of phase transition includes (i) ferroelectric rhombohedral to antiferroelectric tetragonal around 230 °C, (ii) antiferroelectric tetragonal to non-polar tetragonal around 320 °C with broad maximum of dielectric permittivity, which may originate from dielectric relaxation due to the response of electromechanical interaction between polar regions and non-polar matrix [3], (iii) tetragonal to cubic symmetry occurs in the temperature range of 520–540 °C, where it is superparaelectric [4]. Furthermore, the BNT shows strong ferroelectric properties of large remanent polarization ($P_r = 38\ \mu C/cm^2$) and large coercive field ($E_c = 73$ kV/cm) at room temperature. The latter was the main reason for poling difficulties of this material. Nevertheless, its properties could be tailored by either using acceptor or donor dopants [5]. It has been known that aliovalent ionic substitution had only limited solubility in host material. Hence, in this work, the aim is to prepare a donor-doped system i.e., $(Bi_{0.5}Na_{0.5})Ti_{1-x}Nb_xO_3$ ceramics when $x = 0$, 0.01, 0.05, 0.10, 0.15 and 0.20. The influence of excess Nb^{5+} doping on micro-structure and temperature dependence of dielectric properties of the ceramics are investigated and discussed.

2. Experimental

The starting materials i.e., powders of Bi_2O_3 ($>98\%$, Carlo Erba), Na_2CO_3 (99.5%, Fluka), TiO_2($>99\%$, Aldrich) and Nb_2O_5 (99.9%, Aldrich) were weighed according to the formula $(Bi_{0.5}Na_{0.5})Ti_{1-x}Nb_xO_3$ (BNTNb) when $x = 0$, 0.01, 0.05, 0.10, 0.15 and 0.20. The prepared powders were milled with zirconia balls in anhydrous ethanol for 24 h. The mixed

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powder was then dried and calcined at 800 °C for 2 h. The calcined powders were mixed with polyvinyl alcohol 3 wt%, as a binder and then uniaxially pressed to form pellets having 10 mm in diameter and 1 mm in thickness. The green bodies were sintered in air atmosphere on an alumina plate at 1050 °C for 2 h.

The relative densities of sintered BNTNb ceramics were measured using the Archimedes method. Microstructural characterization of the ceramics was performed using scanning electron microscopy (SEM, JEOL JSM-6335F). For preparing SEM samples, ceramics were polished with sand paper and alumina abrasive. Then they were thermally etched at 900 °C for 30 min to reveal their grain boundaries. The phase purity of sintered ceramics was checked using an X-ray diffractometer (XRD, Phillip Model X-pert) using Cu K_α radiation ($\lambda = 1.54$ Å). Silver paste was fired at 700 °C for 15 min on both surfaces of the disc as electrodes for electrical measurement. Temperature dependence on dielectric constant, ε_r and loss tangent, tanδ was measured for the determination of Curie temperature (T_c) with a frequency of 1 kHz using an LCR meter (LCR, GW INSTEK LCR-821).

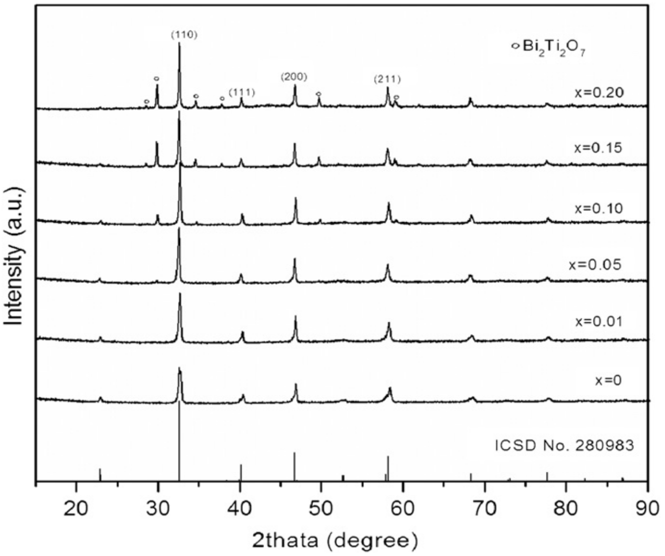

Fig. 1. X-ray diffraction patterns of $(Bi_{0.5}Na_{0.5})Ti_{1-x}Nb_xO_3$ ceramics sintered at 1050 °C for 2 h.

3. Results and discussions

3.1. XRD Analysis

X-ray diffraction patterns of $(Bi_{0.5}Na_{0.5})Ti_{1-x}Nb_xO_3$ ($x = 0$, 0.01, 0.05, 0.10, 0.15 and 0.20) ceramics sintered at 1050 °C for 2 h with 2θ values from 10° to 90° are presented in Fig. 1.

It was obvious from Fig. 1 that major X-ray peakswere found to be well matched with standard file ICSD No. 280983 with rhombohedral structure as reported by different researchers [6–8]. When $x > 0.5$, the structure exhibited secondary phase, meaning that the solubility limit of Nb^{5+} in the BNT was about $x = 0.05$. The amount of the secondary phase increased with increasing amount of Nb content. This secondary phase was found to be $Bi_2Ti_2O_{7,}$ which was also observed in previous study of La-doped BNT by Zuo et al. [8] and Yi et al. [9]. Moreover, substitution of Nb^{5+} in BNT shifted peak position towards lower angles without changing relative peak intensities which suggested that the rhombohedral structure was maintained while the volume of unit cell was increased with increasing amount of Nb content. The substitution of Nb^{5+} ($r_{Nb^{5+}} = 0.64$ Å) into Ti^{4+} ($r_{Ti^{4+}} = 0.61$ Å) lattice site was believed to be the cause of the expantion of the unit cell of BNT.

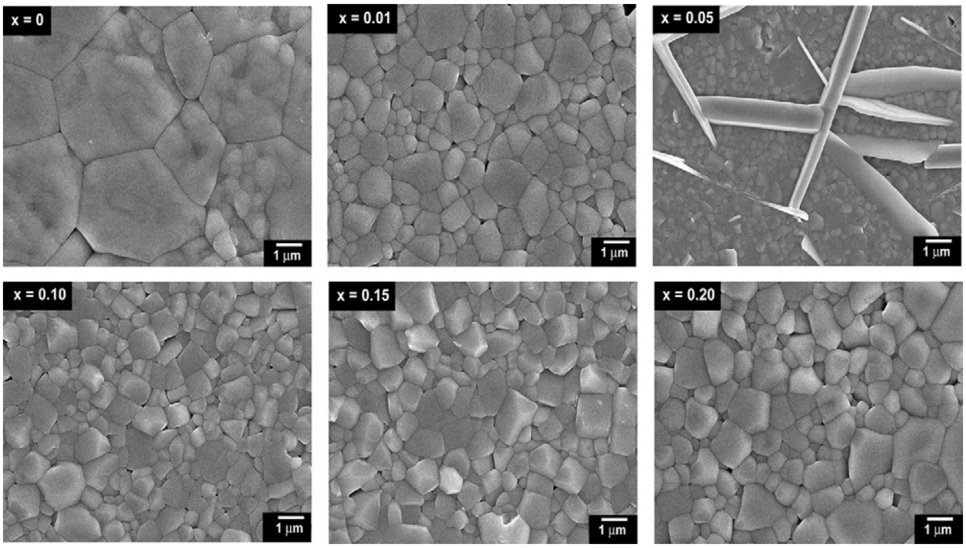

Fig. 2. SEM of the surfaces of $(Bi_{0.5}Na_{0.5})Ti_{1-x}Nb_xO_3$ ceramics sintered at 1050 °C for 2 h.

3.2. SEM and EDS

In this study, experimental density of Nb-doped BNT ceramics was found to be more than 97% of the theoretical density. Fig. 2 shows the micro-structure of BNTNb ceramics. The result showed that the grain size of ceramics decreased with Nb doping up to the solubility limit and then slightly increased as listed in Table 1. The decrease in grain size in the case of Nb donor doping could be explained by A-site cation vacancies created as required to maintain charge neutrality in the lattice. These cation vacancies existed along grain boundaries, which was thermodynamically more stable, rather than inside grain. Grain boundaries would be pinned by these defects, inhibiting grain growth and resulting in relatively small grains in the case of donor doping [9–11]. In this study, spherical shape grains with an average grain size of less

Table 1
Density and average grain size of $(Bi_{0.5}Na_{0.5})Ti_{1-x}Nb_xO_3$ ceramics sintered at 1050 °C for 2 h.

x	Density (g/cm^3)	Avg. grain size (μm)
0	5.82 ± 0.04	3.45 ± 1.59
0.01	5.88 ± 0.01	0.98 ± 0.36
0.05	5.90 ± 0.01	0.70 ± 0.14
0.10	5.89 ± 0.02	0.83 ± 0.31
0.15	5.88 ± 0.01	1.00 ± 0.27
0.20	5.87 ± 0.03	0.95 ± 0.37

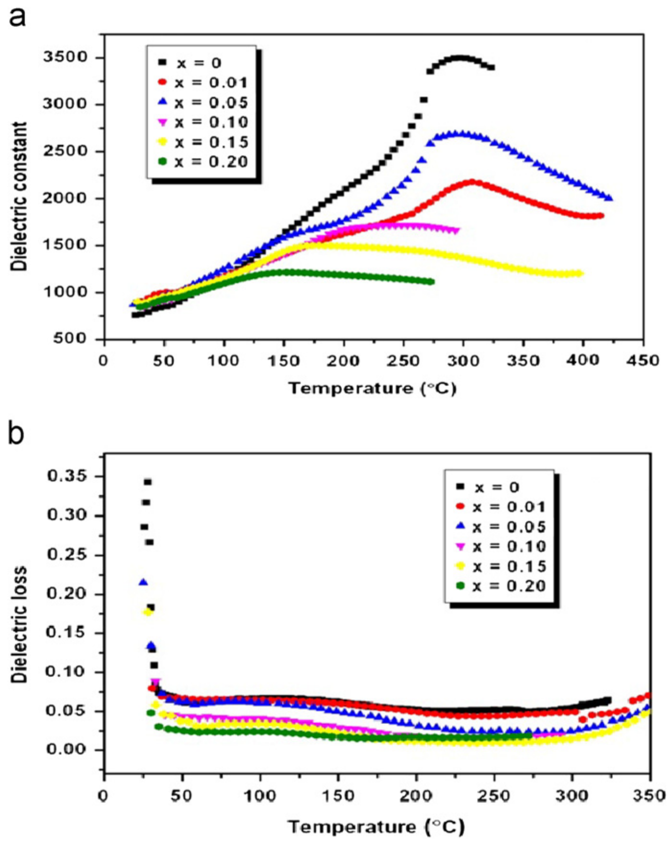

Fig. 4. (a) dielectric constant and (b) dielectric loss at 1 kHz of $(Bi_{0.5}Na_{0.5})Ti_{1-x}Nb_xO_3$ ceramics as a function of temperature.

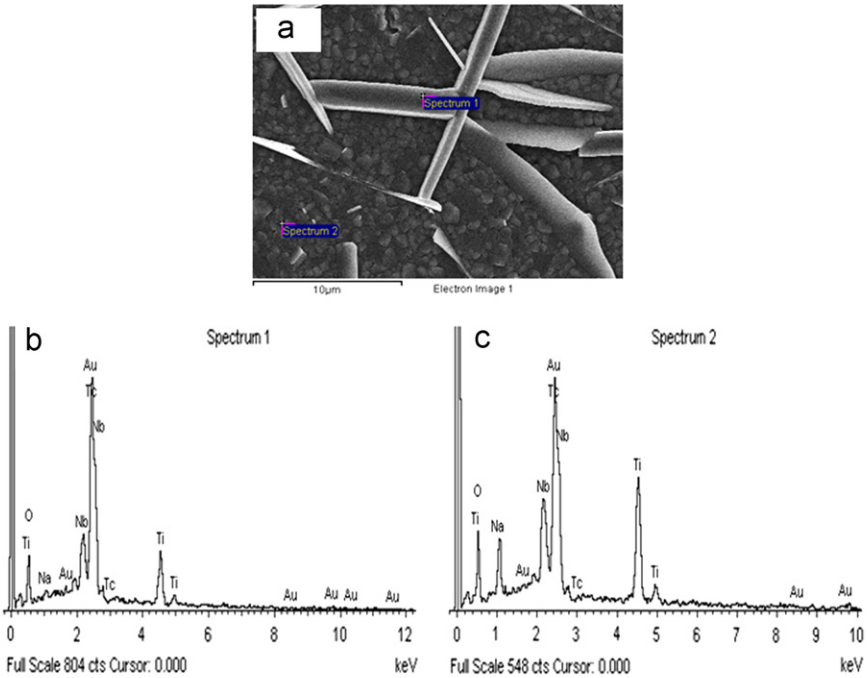

Fig. 3. The $(Bi_{0.5}Na_{0.5})Ti_{0.95}Nb_{0.05}O_3$ ceramics sintered at 1050 °C for 2 h: (a) the micro-structure with plate-like grain, (b) the EDS analysis result of plate-like grain, and (c) the EDS analysis of normal grain.

Table 2
Dielectric properties of $(Bi_{0.5}Na_{0.5})Ti_{1-x}Nb_xO_3$ ceramics at 1 kHz.

x	T_c (°C)	Dielectric constant (ε_r)		Dielectric loss (tanδ)	
		RT	T_c	RT	T_c
0	298	773	3500	0.0838	0.0533
0.01	310	920	2191	0.0701	0.0416
0.05	295	872	2690	0.0944	0.0242
0.10	245	851	1718	0.0884	0.0162
0.15	179	885	1501	0.0582	0.0139
0.20	154	852	1215	0.0337	0.0167

* RT = room temperature, T_c = Curie temperature

than 1 μm were observed in Nb-doped BNT ceramics. Above 5 mol% Nb, the average grain size becomes larger but some of these grains belonged to second phase, i.e., $Bi_2Ti_2O_7$, whose crystal structure was cubic. Since Bi^{3+} and Ti^{4+} precipitated out as second phase, there would also be compositional change in Nb-doped BNT matrix phase which would also change grain growth characteristics of these ceramics.

Such phase decomposition has been observed for the composition Nb 5 mol% as shown in Fig. 3(a) where some large and plate-like second phase appeared. Plate-like grains were characterized for chemical composition compared with normal grain and the result was shown in Fig. 3. The result indicated that the amount of Bi and Na elements in the plate-like grain are less than that in the normal grains. It is demonstrated that Na and Bi component could be lost during sintering process at high temperature.

The density and average grain size of the ceramics are shown in Table 1. It could be seen that the temperature of 1050 °C was high enough to produce dense ceramics. Using the density of BNT as reference, the relative densities of all samples were found to be greater than 95% in agreement with the observed micro-structure.

3.3. Dielectric properties

The temperature dependence of dielectric constant (ε_r) and dielectric loss (tanδ) of the ceramics were measured at a frequency of 1 kHz and the results are shown in Fig. 4.The result indicated that at room temperature, dielectric constant of the Nb-doped sample was higher that of undoped sample as shown Table 2. However, the dielectric constantat T_c of undoped ceramic decreased with Nb doping.

Two explanations for this phenomenon were introduced by Schmidt et al. [12]. The first explanation may be due to superparaelectric cluster polarization reorientation. This orientation was limited because of the exchangeable site of Bi^{3+} and Na^+ cations, when these cations were carriers. The second explanation is from the Maxwell–Wagner effect. This explanation could be used to describe this phenomenon only if the electrode and crystal resistances remain nearly equal, whereas both change considerably as temperature rised.

In addition, the T_c becomes lower with increasing amount of Nb dopant. This suggested that the donor-doping and charge compensation effects could still be observed up to maximum Nb doping content. In addition, in highly-doped BNTNb ceramics, Nb preferred to substitute Ti and caused Bi vacancies which induced the only mentioned second phase. X-ray study indicated that rhombohedral perovskite structure could still be maintained even in the sample containing high Nb concentration. This fact suggested that single phase of highly-doped Nb was possible if compositional variation was carried out during ceramic processing.

4. Conclusions

The $(Bi_{0.5}Na_{0.5})Ti_{1-x}Nb_xO_3$, where x = 0, 0.01, 0.05, 0.10, 0.15 and 0.20 were prepared by conventional solid-state reaction. X-ray diffraction analysis indicated the solubility limit of Nb in BNT to be less than 5 mol% Nb. Above solubility limit, the presence of $Bi_2Ti_2O_7$ secondary phase appeared indicating that Nb substitution could replace Ti site and induced Bi vacancies. Dielectric measurement showed an apparent decrease in T_c when Nb content in BNT increased. This suggested that donor-type doping and charged defects still played a role in BNTNb ceramics. Single phase Nb-doped BNT could be obtained if compositional adjustment was carried out during ceramic processing.

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