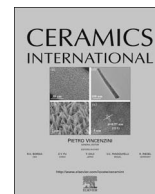




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Effect of Ce on structural and dielectric properties of lead-free ($\text{Bi}_{0.5}\text{Na}_{0.5}$) TiO_3 ceramics

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ABSTRACT

The structural, microstructural and dielectric properties of the Ce doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNTC) lead-free piezoelectric ceramics prepared by a conventional solid state reaction process have been investigated. Rietveld refinement of the BNTC ceramics shown that the volume of the unit cell increased with the concentration of Ce up to $x = 0.015$ and decreases further with the excess Ce doping ($\geq x = 0.025$). The average grain size of the BNTC ceramics found to be increased linearly up to $x = 0.015$ and higher concentration of Ce inhibited the grain growth. The dielectric response of the Ce doped BNT ceramics improved significantly and the optimum dielectric properties ($\epsilon_r = 672$ and $\tan \delta = 0.206$ at 1 MHz) were obtained for the composition of $x = 0.025$. For the low concentration of x , the Ce^{3+} was substituted in Ti^{4+} site, which enhanced the diffuseness coefficient ($\gamma = 1.83$). Conversely, the γ value was found to be decreased when $x \geq 0.025$, which is due to the substitution of Ce^{3+} in Na^+ site instead of Ti^{4+} site and weakens the relaxor behavior. The temperature dependent of AC-conductivity of BNTC ceramics was analyzed using Arrhenius's law and the variable range hopping (VRH) model and the corresponding density of states ($N(E_F)$), hopping length (R_H), and hopping energies (W_H) were calculated. The obtained results indicate that BNTC ceramics are suitable for promising industrial high performance piezoelectric applications.

1. Introduction

Lead based ceramics have been widely used for sensors, actuators and other applications due to their excellent piezoelectric properties [1,2]. However, the toxicity of lead oxide is hazardous to human health and environment; therefore, the development of lead-free piezoelectric ceramics to replace the lead based materials is now has become a goal for the research community. The lead-free piezoelectric ceramics ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) [3], BaTiO_3 (BT) [4] and $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN) [5] have been widely studied because of their excellent piezoelectric properties. Among the lead-free materials, BNT based ceramics have been considered as a good candidate due to its large remnant polarization ($P_r = 38 \mu\text{C}/\text{cm}^2$), coercive field ($E_c = 73 \text{ kV}/\text{cm}$) at room temperature and a high Curie temperature ($T_C = 320 \text{ }^\circ\text{C}$). Further, it also represents long range ferroelectric ordering and shows several structural phase transitions [3]. BNT ceramics with relaxor behavior have attracted in industrial applications due to their larger dielectric constant in the broad temperature range and diffuse phase transition [6]. The origin of the relaxor behavior is might be due to the compositional disorder that arises from the substitution of different ions occupying the equivalent crystallographic sites [7]. It is observed

that rare-earth doped lead-free piezoelectric ceramics have shown the relaxor behavior by inducing the crystallographic distortion with improved dielectric properties [8]. A high dielectric constant (ϵ_r) and low dissipation factor ($\tan \delta$) are the crucial parameters for the high performance piezoelectric applications. However, there are only few reports available on the rare-earth doped BNT ceramics. According to the author's knowledge, there is no systematic study on the dielectric and AC-conductivity analysis of Ce doped BNT ceramics. In the current study, the effect of Ce on the structural, microstructural and electrical properties of BNT ceramics have been studied systematically.

2. Experimental details

Lead-free $\text{Bi}_{0.5}(\text{Na}_{(1-x)}\text{Ce}_x)_{0.5}\text{TiO}_3$ (BNTC; $x = 0.00\text{--}0.035$) piezoelectric ceramics have been prepared by using conventional solid state reaction method. The high purity chemicals of Bi_2O_3 (M/s Alfa-Aesar, 99.975%), Na_2CO_3 (M/s Sigma Aldrich, 99.99%), TiO_2 (M/s Sigma-Aldrich, 99.99%) and CeO_2 (M/s Sigma-Aldrich, 99.99%) were used as starting materials and weighted according to their stoichiometry. These powders were mixed for 10 h using a planetary ball mill (M/s Fritsch GmbH, Pulverisette 6) and distilled water used as a grinding media.

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The mixed slurry was dried at 120 °C and calcined at 850 °C for 3 h. These calcined powders were again grounded for 10 h to reduce the initial particle size. Then, the organic binder poly vinyl alcohol (PVA) was added to the fine powders of all BNTC ceramics and pressed into pellets with the dimensions of 10 mm in diameter and 1 mm of thickness. Further, these samples were sintered in the range of 1050–1200 °C for 3 h to obtain maximum density. The density of sintered pellets was measured by using Archimedes's principle. However, the BNTC ceramics sintered at 1100 °C showed maximum density and better electrical and dielectric properties. As a result, the BNTC ceramics with $x = 0.00$ – 0.035 , sintered at 1100 °C were chosen for further studies. For electrical measurements, silver paste was used as electrodes for both sides of the samples and heated at 150 °C for 10 min to dry the samples.

The crystal structure and phase of the BNTC ceramics have been characterized by using x-ray diffractometer (M/s Rigaku, TTRAX III 18 kW) with Cu-K α radiation ($\lambda=1.5406$ Å). Raman spectra of the BNTC ceramics were collected using (M/s Horiba Jobin Yvon, LABRAM HR) Raman spectrometric analyzer with 632.8 nm as the excitation wavelength. Microstructure and surface morphology of the ceramics were examined using field emission scanning electron microscope (FESEM) (M/s Sigma Zeiss, Germany). The temperature (30 °C to 400 °C) dependent dielectric properties were measured using LCR meter (M/s Wayne kerr, Model 4300).

3. Results and discussion

3.1. Structural properties

The room temperature XRD patterns along with the Rietveld refinement of the BNTC ceramics sintered at 1100 °C for 3 h have shown in Fig. 1. All the BNTC ceramics exhibited a pure perovskite phase with rhombohedral crystal symmetry, which indicates that the Ce ions diffused into the BNT lattice and formed a solid solution. The lattice parameters (a , b , and c) and atomic positions of the Bi, Ce, Na, Ti, and O atoms were refined using Fullprof software by considering the $R3c$ space group (JCPDS No. 01-085-0530) [9]. The obtained lattice parameters and unit cell volumes were listed in Table 1. It is observed

Table 1

Rietveld refinement parameters of Bi_{0.5}(Na_{1-x}Ce_x)_{0.5} TiO₃ ceramic samples.

x	χ^2	$a = b$ (Å)	c (Å)	Volume (Å ³)
0	5.43	5.49	13.45	405.38
0.005	5.38	5.50	13.45	406.19
0.015	6.10	5.50	13.44	406.85
0.025	2.35	5.48	13.43	406.13
0.035	5.19	5.49	13.43	404.78

that the unit cell volume found to be increased up to $x = 0.015$ and further it decreases above $x = 0.025$ sample. The expansion and compression of the unit cell volume with Ce doping might be due to the occupation of Ce ions in different sites of perovskite structure at different concentrations.

Crystalline size of all the samples was calculated by using Scherrer equation. It is found to be increased from 47.01 nm to 48.16 nm with increasing Ce concentration up to $x = 0.015$ and further decreased to 46.21 nm for $x = 0.035$ sample. Similar trend was observed for the lattice parameters, density and grain size. From the Fig. 1(f), it can be clearly seen that as the Ce concentration increases, the position of the (110) diffraction peak shifted towards lower Bragg angle side up to $x = 0.015$, then after it shifted back to higher Bragg's angle side. It can be attributed to Ce occupancy. Initially, Ce occupied in the B (Ti) site, then after it occupied in A (Na) site due to mismatch of the ionic radii and valance. For the low concentration of x (≤ 0.015), the Ce³⁺ (1.01 Å) ions occupied the Ti⁴⁺ (0.605 Å) site, whereas the Ce³⁺ ions occupied the Na⁺ (1.02 Å) site at higher concentrations of x (≥ 0.025) [10]. These obtained results are also co-related with microstructural analysis.

3.2. Raman analysis

The back-scattered Raman spectra of BNTC ceramics recorded at room temperature were depicted in Fig. 2. All the BNTC ceramics exhibited the rhombohedral crystal symmetry with $R3c$ space group. In this work, nine Raman active modes observed and were fitted with Lorentz function using Magic plot software. According to the group theory, $R3c$ space group consists of 13 Raman active modes ($\Gamma_{\text{Raman}} =$

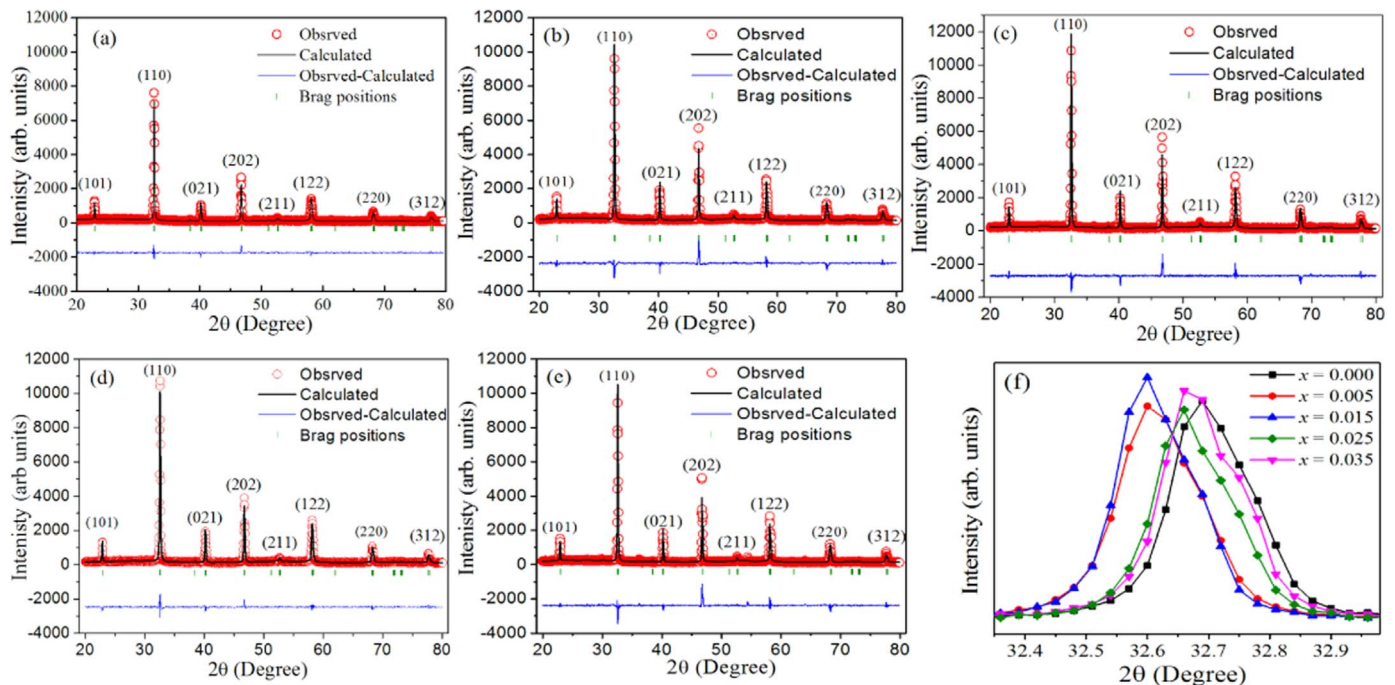


Fig. 1. Rietveld refined XRD pattern of the BNTC ceramics for (a) $x = 0.00$, (b) $x = 0.005$, (c) $x = 0.015$, (d) $x = 0.025$, (e) $x = 0.035$ and (f) magnified image of (110) diffraction peak of all BNTC samples.

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