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Dielectric behavior and impedance spectroscopy in lead-free BNT–BT–NBN perovskite ceramics for energy storage

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ABSTRACT

The dielectric behavior, impedance spectroscopy and energy-storage properties of $0.85[(1-x)Bi_{0.5}Na_{0.5}TiO_3–xBaTiO_3]–0.15Na_{0.73}Bi_{0.09}NbO_3$ [(BNT–xBT)–NBN] ternary ceramics were investigated. Temperature dependent permittivity curves displayed two depressed anomalies, resulting in significantly improved dielectric temperature stability. (BNT–9BT)–NBN showed a permittivity of 1680 at 150 °C with $\Delta\varepsilon/\varepsilon_{150\,°C}$ varying no more than ±10% up to 340 °C. From the complex impedance analysis, grain and grain boundary shared the same time constant. The high temperature resistivity followed the Arrhenius law with $E_a = 1.7–2.0$ eV, suggesting intrinsic band-type electronic conduction. The maximum energy-storage density of all the samples reached 1.1–1.4 J/cm^3, accompanied with good temperature stability in the range of 25–140 °C. These results indicate that (BNT–xBT)–NBN system should be a promising lead-free material for energy-storage capacitor applications.

1. Introduction

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT)-based ceramics for energy-storage application have received great attention in recent years [1–7]. Compared to other linear dielectrics, BNT-based dielectric ceramics possess higher permittivity and polarization. Consequently, a relatively large energy-storage density can be obtained even under medium electric field, which is an advantage for maintaining highly reliable capacitor operation. Pure BNT is strongly ferroelectric with large remnant polarization $P_r = 38\ \mu C/cm^2$ at room temperature [8], which is unavailable for energy release. However, in BNT-based binary and ternary systems, the energy-storage properties have been greatly enhanced due to suppressed ferroelectricity. Gao [9] first reported $Bi_{0.5}Na_{0.5}TiO_3–BaTiO_3–K_{0.5}Na_{0.5}NbO_3$ (BNT–BT–KNN) ceramics with a competitive energy-storage density of 0.46 J/cm^3 at 5.6 kV/mm and room temperature. Thereafter, in the investigations of $Bi_{0.5}Na_{0.5}TiO_3–BaTiO_3–KNbO_3$ (BNT–BT–KN) [10], $(Bi_{1/2}Na_{1/2})TiO_3–(Bi_{1/2}K_{1/2})TiO_3–SrTiO_3$ (BNT–BKT–ST) [11] and $(Bi_{0.5}Na_{0.5})TiO_3–(Bi_{0.5}K_{0.5})TiO_3–(K_{0.5}Na_{0.5})NbO_3$ (BNT–BKT–KNN) [12] systems, the optimal maximum energy-storage density reached 0.89 J/cm^3, 0.97 J/cm^3 and 1.20 J/cm^3 respectively. All of these reports indicate a potential for BNT-based ceramics used for energy storage.

BNT-based ceramics are considered as a relaxor ferroelectric by a majority of researchers instead of an anti-ferroelectric, although the real identity is still in dispute [13–15]. They differ from classical relaxors in that two kinds of polar nano-regions (PNRs) co-exist in a wide temperature range and their combined action contributes to the specific temperature dependent dielectric performance. Therefore, clarifying the dielectric behavior in BNT-based ceramics would be interesting and meaningful. Additionally, as a capacitor material, the electrical conductivity at elevated temperature is of critical importance. Impedance spectroscopy analysis has been widely employed to study BNT-based ceramics as a powerful tool in investigating the different electrical regions in electroceramics [16–18]. However, the mechanism of electrical conductivity differs in literature reports [19,20], which needs further detailed study.

Niobates have been reported to be good members to modify the ferroelectric properties of BNT-based ceramics [2,9,21,22]. Ma [23] systematically investigated $Na_{1-3x}Bi_xNbO_3$ ($0 \le x \le 0.30$) ceramics and found that the compositions with $x = 0.09$ exhibited excellent dielectric temperature stability. Therefore, we chose $Na_{0.73}Bi_{0.09}NbO_3$ (NBN) as the third member. In this study, we prepared a group of $0.85[(1-x)Bi_{0.5}Na_{0.5}TiO_3–xBaTiO_3]–0.15Na_{0.73}Bi_{0.09}NbO_3$ [(BNT–xBT)–NBN] ceramics around the morphotropic phase boundary (MPB) of BNT–BT [24] and comprehensively investigated the dielectric behavior, impedance spectroscopy and energy-storage properties. It was demonstrated that (BNT–xBT)–NBN system was promising as a dielectric for high-temperature energy-storage application.

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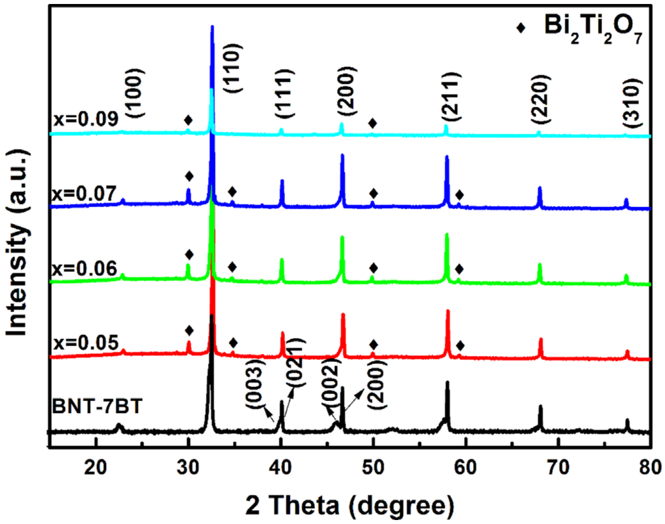

Fig. 1. XRD patterns of BNT–7BT and (BNT–xBT)–NBN ceramics.

2. Experimental procedure

(BNT-xBT)-NBN ($x=0.05$, 0.06, 0.07, 0.09) bulk ceramics were fabricated by a traditional solid-state processing route. First, Bi_2O_3, Na_2CO_3, TiO_2, $BaCO_3$ and Nb_2O_5 (purity > 98.5%) were mixed according to the stoichiometric formula and ball milled with zirconium media in ethanol for 24 h. After drying at 100 °C, the powder mixture was calcined at 850 °C for 2 h and subsequently ball-milled again for 24 h. Then, the powders were pressed into pellets of 12 mm in diameter and 1mm in thickness under a uniaxial pressure of 200 MPa. Sintering was performed at 1150 °C for 2 h. To minimize the evaporation of Bi and Na elements, the pellets were embedded in self-source powder.

Phase structure was determined using X-ray powder diffraction (Cu Kα radiation, PANalytical X'Pert PRO, Holland). Microstructure was studied by scanning electron microscope (Quanta 450 FEG, USA). Electrodes were fabricated with fire-on silver paste at 500 °C for 15 min. Dielectric measurements were carried out with a precision LCR meter (E4980A, Agilent, USA) using a customer designed furnace and computer-controlled data collection system at a heating rate of 2 °C/min. Impedance spectroscopy data was obtained stepwise from 400 °C to 440 °C at intervals of 10 °C. Before testing, the samples were kept at the measurement temperature for 20 min to reach thermal balance. To determine the ferroelectric properties, the sintered samples were polished to a thickness of 0.3–0.4 mm and then the test was performed using a ferroelectric material test system (HVI0403-239, Radiant Technology, USA) in a silicone oil bath at a frequency of 10 Hz.

3. Results and discussion

3.1. Phase structure and microstructure

Fig. 1 shows the XRD patterns of BNT–7BT and (BNT–xBT)–NBN ceramics with $2\theta=15°–80°$. A weak superlattice reflection was found near $2\theta=38.5°$ due to the antiphase oxygen octahedral tilting of BNT [25,26]. BNT–7BT possessed split (003)/(021) and (002)/(200) peaks at $2\theta=40°$ and 46.5°, representing coexistence of rhombohedral and tetragonal phases respectively, which is in good accordance with reports on MPB of BNT–BT ceramics [27]. All the (BNT–xBT)–NBN samples displayed the symmetry related to a typical perovskite structure with no obvious non-cubic distortion, indicating a pseudo cubic phase. The XRD data are consistent with literature reports on other BNT-based ternary systems [28–30]. This is considered to be related to the phase identity of BNT-based ceramics, which is a host cubic non-polar phase decorated with two PNRs of different symmetry, R3c and P4bm [15]. Additional diffraction peaks indicated the presence of a secondary phase, $Bi_2Ti_2O_7$, which was also found in other BNT-based systems [31,32]. The formation of the minor impurity may related to the deficiency of sodium in the system [33].

Fig. 2 illustrates the thermally etched cross-sections of (BNT–xBT)–NBN samples at 1050 °C for 30 min. A dense microstructure with no pores could be observed inside the ceramics. The grain size ranged from 0.8 to 2.9 μm with an average grain size around 1.4 μm.

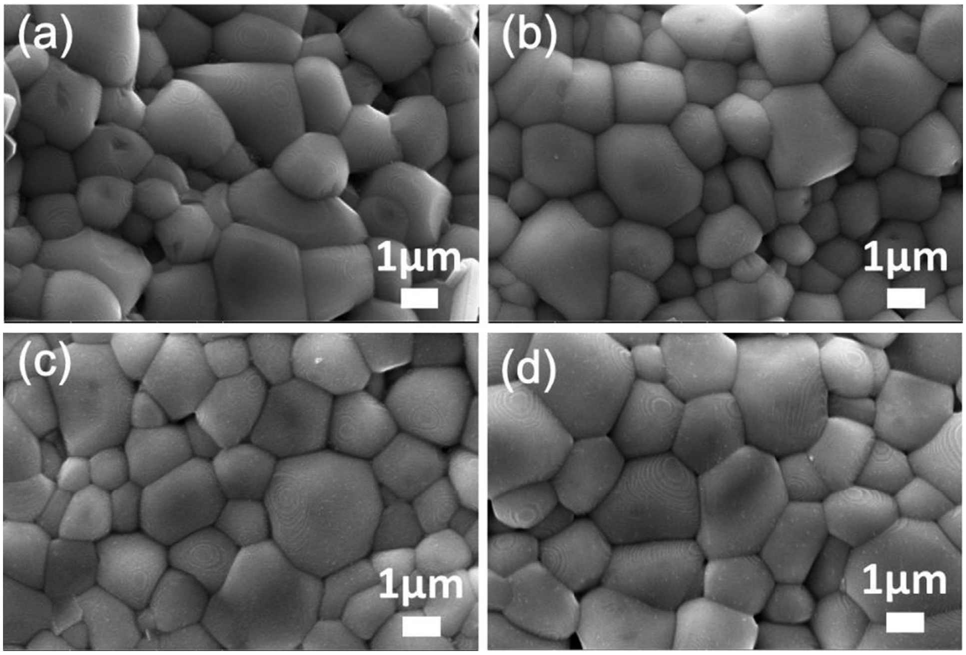

Fig. 2. SEM images of (BNT–xBT)–NBN ceramics thermal etched at 1050 °C.