



# The effect of composite $(\text{Li}_{0.5}\text{Nd}_{0.5})^{2+}$ ions substitution on microstructure, dielectric behavior and electrical properties of $0.95\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.05\text{BaTiO}_3$ ceramics

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## Abstract

New lead-free  $0.95(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}(\text{Li}_{0.5}\text{Nd}_{0.5})_x\text{TiO}_3-0.05\text{BaTiO}_3$  (BNTLN<sub>x</sub>-BT5) ceramics with  $x=0, 0.01, 0.03, 0.05, 0.07, 0.1$  have been fabricated by conventional solid-state method. The effect of composite  $(\text{Li}_{0.5}\text{Nd}_{0.5})^{2+}$  ions substitution on microstructure, dielectric behavior and electrical properties was investigated. A morphotropic phase boundary (MPB) separating the rhombohedral phases and pseudocubic phases is observed at the compositions  $x=0.01-0.03$ . The grain size increases at compositions  $x=0-0.07$  and decreases at composition  $x=0.1$ . At room temperature, the frequency dispersion of dielectric constant  $\epsilon_r$  strengthens with increasing  $x$ . The temperature stability coefficient  $f_\epsilon$  of dielectric constant  $\epsilon_r$  at  $T=23-230$  °C decreases from 28.35 to 6.18 with increasing  $x$ . The ceramics exhibit a largest dispersion coefficient ( $\gamma=1.90$ ) and a largest piezoelectric constant ( $d_{33}=135\text{pC/N}$ ) at  $x=0.07$ .

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## 1. Introduction

In recent years, perovskite-structured piezoelectric ceramics have been attractive in fields of applied electronic devices such as actuators, transducers and sensors [1,2]. The Pb-based piezoelectric ceramics have long played a leading role for the piezoelectric commercial applications [1]. However, with respect to legislation, lead is considered to be toxic and has been expelled from many commercial applications [2]. Hence, the considerable effort has been devoted to the development of lead-free piezoelectric ceramics [3]. Lead free  $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{BaTiO}_3$  (BNT-BT) ceramic, of which the research has been frequently done, is a promising outlook to replace the lead-based ceramics

due to their good electromechanical performance and distinct degree of the diffuse phase transition behavior [4]. The  $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{BaTiO}_3$  (BNT-BT) ceramics exhibit a morphotropic phase boundary (MPB) at  $x=0.05-0.07$ , which have relatively good electrical properties [5]. In many reported literatures, [6–9] the A-site substitution for piezoelectric ceramics is one of the effective methods to improve the electrical properties. Mixed perovskite ceramics often display diffuse dielectric anomalies at low frequencies ( $f < 10^4$  Hz) [10].  $\text{Li}^+$  ion substitutes for one or more cations in many piezoelectric systems, which is studied about piezoelectric, dielectric behavior and diffuse phase transition [11–14]. The rare earth oxide ( $\text{Nd}_2\text{O}_3$ ) is often used as an excellent additive to enhance remanent polarization  $P_r$  and electrical properties of piezoelectric ceramics [15–18]. Pure  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  ceramics exhibit large remnant polarization ( $P_r=38\text{ }\mu\text{C/cm}^2$ ), high Curie temperature ( $T_c=320$  °C) and large dispersion coefficient  $\gamma$  due to the A-site composite ions substitution [5]. It can be inferred that the A-site composite

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ions substitution of BNT–BT ceramics may possess large remnant polarization, large dispersion coefficient  $\gamma$  and optimal electrical properties.

Few literatures about A-site composite ions substitution have been reported in the past many years. As far as I know, the composite  $(\text{Li}_{0.5}\text{Nd}_{0.5})^{2+}$  ions substitute for  $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$  in A-site for BNT–BT ceramics has not been reported. Therefore, this work is of great significance to research.

The radius (1.34 Å) of  $(\text{Li}_{0.5}\text{Nd}_{0.5})^{2+}$  ions ( $\text{Li}^+$ :1.41 Å, 12CN and  $\text{Nd}^{3+}$ :1.27 Å, 12CN) is very close to the radius (1.375 Å) of  $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$  ions ( $\text{Bi}^+$ :1.36 Å, 12CN and  $\text{Na}^{3+}$ :1.39 Å, 12CN) [14,19]. The  $(\text{Li}_{0.5}\text{Nd}_{0.5})^{2+}$  ions will substitute for  $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$  ions in A-site successfully.

In present work, the effect of composite  $(\text{Li}_{0.5}\text{Nd}_{0.5})^{2+}$  ions on microstructure, dielectric behavior and electrical properties of  $0.95\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.05\text{BaTiO}_3$  was investigated. The temperature stability coefficient  $f_e$  of dielectric constant  $\epsilon_r$  and the frequency dependence of  $\epsilon_r$  as a function of temperature for  $0.95(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}(\text{Li}_{0.5}\text{Nd}_{0.5})_x\text{TiO}_3\text{--}0.05\text{BaTiO}_3$  ceramics were studied intensively. The complicated mechanisms of composite  $(\text{Li}_{0.5}\text{Nd}_{0.5})^{2+}$  ions substitute for  $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$  ions in A-site are also explored and discussed.

## 2. Experiment procedures

The  $0.95(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}(\text{Li}_{0.5}\text{Nd}_{0.5})_x\text{TiO}_3\text{--}0.05\text{BaTiO}_3$  ceramics (BNTLN $_x$ –BT5) were prepared by conventional solid-state reaction technique. Raw materials of  $\text{BaCO}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$  (>99%, Analytically pure) were mixed according to a predetermined ratio with addition of alcohol for 24 h. After drying at 100 °C, the powders were calcined at 860 °C for 4 h. After the calcination, the mixture was ball-milled again for 24 h and mixed thoroughly with a PVA binder solution, then pressed into disk samples (12 mm diameter and 1 mm thickness) under 100 MPa uniaxial pressure. Following removal of binder at 600 °C for 2 h, bulks were sintered at 1100 °C in air atmosphere for 2 h.

X-ray diffraction (XRD) (D8 Advance, Bruker Inc, Karlsruhe, Germany) was used to determine the formation of the crystalline phases. Surface microstructures of the ceramics were observed using a scanning electron microscopy (SEM) (JSM-5610LV /Noran-Vantage, JEOL, Tokyo, Japan). The surfaces of disk-shaped specimens were covered with a thin layer of silver paint and fired at 600 °C for 30 min. The samples were poled at room temperature in a silicone oil bath under a dc field of 60 kV/cm for 30 min. The piezoelectric coefficient  $d_{33}$  of poling sintered ceramics was measured after 24 h by using a Berlincourt  $d_{33}$  meter (ZJ-3 A, CAS, Shanghai, China). Dielectric properties were measured using an impedance analyzer (Agilent 4294 A, Agilent Inc., Bayan, Malaysia). Temperature-dependent of capacitance and dielectric loss were measured in the range from 23 to 450 °C. Each data point was extracted in an interval of 3 °C. The room temperature polarization-electric field ( $P$ – $E$ ) loops were observed at 1 Hz using a ferroelectric tester (Radiant Technologies Inc., Albuquerque, New Mexico, USA).

## 3. Results and discussion

Fig. 1 shows the XRD diffraction patterns of BNTLN $_x$ –BT5 ( $x=0, 0.01, 0.03, 0.05, 0.07, 0.1$ ) sintered bulks in the  $2\theta$  range of 20–80°. All samples are detected as single perovskite structure, which means that  $(\text{Li}_{0.5}\text{Nd}_{0.5})^{2+}$  ions have entered into crystalline lattice structure of 0.95BNT–0.05BT solid solution.

Detailed XRD diffraction patterns of BNTLN $_x$ –BT5 sintered bulks in the  $2\theta$  range of 38–48° have been shown in Fig. 2. The most used piezoelectric materials display a phase transition region in their composition phase diagrams, defined as a morphotropic phase boundary (MPB) where shows excellent properties [20]. The BNTLN $_x$ –BT5 sintered bulks possess a perovskite structure with rhombohedral symmetry at  $x=0$ , which is corresponding to the reported literature [21]. The XRD diffraction patterns of BNTLN $_x$ –BT5 sintered bulks show pseudocubic symmetry at  $x=0.05$ –0.1. This is evidenced by the obvious merging of the (0 0 3) and (0 2 1) diffraction peaks to (1 1 1) peak, as observed in the BNTLN $_x$ –BT5 sintered bulks at  $x=0.01$ –0.03. The morphotropic phase boundary (MPB) is located at  $x=0.01$ –0.03. With the increasing content of  $(\text{Li}_{0.5}\text{Nd}_{0.5})^{2+}$  ions substitution, the diffraction peaks shift to higher diffraction angles in Fig. 2. The ionic radius of  $(\text{Li}_{0.5}\text{Nd}_{0.5})^{2+}$  (1.34 Å) is smaller than the ionic

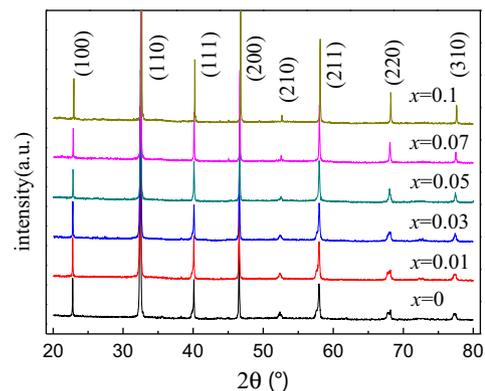


Fig. 1. X-ray diffraction patterns of BNTLN $_x$ –BT5 sintered bulks in the  $2\theta$  range of 20–80°.

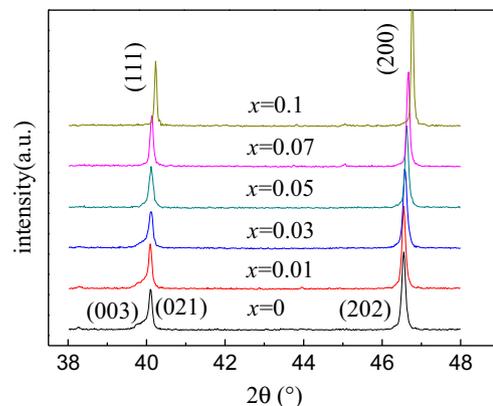


Fig. 2. X-ray diffraction patterns of BNTLN $_x$ –BT5 sintered bulks in the  $2\theta$  range of 38–48°.

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