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Microstructure and impedance properties of La, Ce multi-rare earth ions doped $Na_{0.5}Bi_{2.5}Nb_2O_9$ Aurivillius type ceramics

Zhihang Peng*, Xiangxiong Zeng, Feng Cao, Xiang Yang

Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, College of Aerospace and Materials Engineering, National University of Defense Technology, Changsha 410073, Hunan, China

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(Li, Ce, La) multi-doped $Na_{0.5}Bi_{2.5}Nb_2O_9$ ceramics were prepared by a conventional solid state sintering method. Microstructure of sintered ceramics was examined by the X-ray diffraction and scanning electron microscopy. The introduction of voluminous La^{3+} cations decreases the degree of lattice distortion, leading a lower Curie-temperature. The detailed electrical conduction behaviors were determined by the electrochemical impedance spectra (EIS). The electrical properties were investigated as a function of frequency (10^2–10^6 Hz) at various temperatures (350–750 °C). The underlying physical mechanism of electrical properties at high temperature for multi-rare-earth doping NBN-based was studied via an assistance of EIS techniques. There were a set of Debye-like relaxation peaks in the imaginary part of impedance and electric modulus data. Oxygen vacancies are responsible for both *ac* conduction and dielectric relaxation processes. A discontinuous variation of the exponent parameter *n* is found owing to a ferroelectric-ferroelastic phase transition around 550 °C.

1. Introduction

Based on the superior piezoelectric, dielectric, and ferroelectric properties, Pb(Ti, Zr)O_3-based (PZT) ceramics are the heart of piezoelectric transducers, sensors, resonators and actuators [1]. The aerospace, aircraft and nuclear power industries have an imperative demand for sensors which can operate at 500 °C or higher with a long mean time between failures (MTBF) [2–4]. Unfortunately, PZT-based ceramics cannot satisfy the applications in such fields because of their relatively low Curie-temperature (T_C < 380 °C). Aurivillius type compounds (bismuth layered structural ferroelectrics, BLSFs) have high Curie-Temperature (T_C), large *dc* resistivity and fatigue-free properties [2,4–7]. In recent years, BLSFs have attracted much attention because of potential applications for high temperature piezoelectric accelerometers and ferroelectric random access memories (FeRAMs). BLSFs possess the general formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, built up of $(Bi_2O_2)^{2+}$ layers between which $(A_{m-1}B_mO_{3m+1})^{2-}$ perovskite-like slab is inserted, where *m* is the number of octahedral layers in the perovskite slab [8,9].

Sodium bismuth niobate, $Na_{0.5}Bi_{2.5}Nb_2O_9$ (NBN), is a typical two-layered Aurivillius-type compound with a high Curie temperature of 790 °C [10]. However, the piezoelectric coefficient d_{33} of NBN ceramics is relatively low (~6pC/N) prepared through the conventional solid state sintering process owing to the restriction of spontaneous polarization in *a-b* planes. Much work was attempted to improve piezoelectric activity of NBN ceramics using chemical-modifications [11], or other texturing technologies [10]. It is an effective way to enhance the piezoelectric properties via rare-earth element modifications. Li, Ce and A-site vacancies modified NBN-based ceramics have a large d_{33} value (~27 pC/N), together with a high T_C value (~809 °C) [12]. Ce, Ta multi-dopants can also improve the piezoelectric activity of NBN-based ceramics [13]. Long et al. reported the effects of LiLn (Ln = La, Ce, Nd, Y) on piezoelectric, ferroelectric and thermal aging properties of NBN-based ceramics [14]. However, two or more kinds of rare-earth modified NBN-based, or BLSFs ceramics have been scarcely reported. In our previous work, (Li, Ce, Pr) multi-dopants can significantly improve the piezoelectric properties of $CaBi_2Nb_2O_9$-based ceramics without sacrificing the Curie temperature. The d_{33} and T_C values for the optimum composition are found to be ~17.3 pC/N and ~939 °C, respectively [15].

Therefore, it is of interest to investigate the effects of multi rare-earth doping on the piezoelectric, dielectric, *dc* conduction and impedance properties of BLSFs. It is well known that the impedance

* Corresponding author.
E-mail address: chemiepengzh@gmail.com (Z. Peng).

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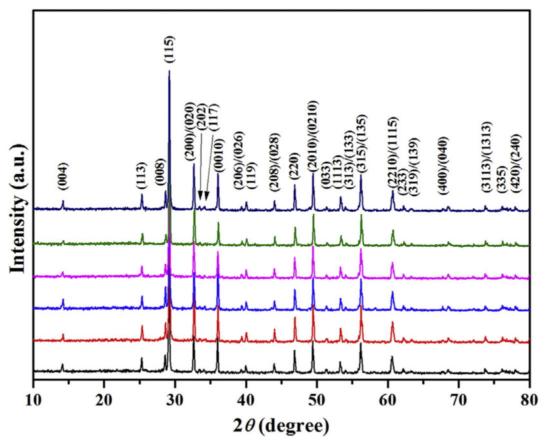

Fig. 1. XRD patterns of NLCL-100x sintered ceramics.

analysis is a powerful approach to characterize the conductive process and the relaxation mechanism of materials [16–18]. In this paper, we aim to investigate the electrical conduction process of La, Ce multi-rare-earth elements modified NBN-based ceramics. The effects of (Li, Ce, La) substitutions on the microstructure and electrical properties of NBN ceramics were studied and underlying physical mechanisms were also addressed. The impedance analysis is invoked to understand the mechanisms of electrical conduction and dielectric relaxation, and also to clarify the relationship between both processes.

2. Material and methods

Multi-rare-earth doped Aurivillius type $(Na_{0.45}Li_{0.05})(Bi_{0.45-x}Ce_{0.05}La_x)Bi_2Nb_2O_9$ ceramics (abbreviated as NLCL-100x, where the x values are equal to 0, 0.01, 0.02, 0.05, 0.07 and 0.10, respectively) were prepared by a conventional solid-state reaction route. The metal oxides, Bi_2O_3 (99%), Na_2CO_3 (99.8%), Li_2CO_3 (98%), Nb_2O_5 (99.5%), La_2O_3 (99.99%) and CeO_2 (99.99%) were used as starting raw materials. All powders were weighed according to the stoichiometric compositions and then mixed by ball milling in ethanol for 24 h with ZrO_2 balls as milling media. The slurry was dried at 80 °C to remove the ethanol and then calcined at 800 °C for 3 h. The calcined powders were milled again in the same condition, and granulated with polyvinyl alcohol (PVA) as a binder. The powders were finally pressed into disks of ~10 mm in diameter and ~1 mm thick in a steel die at a press of about 5 Tf. After burning out the binder at 650 °C, the green pellets were sintered at 1050–1100 °C for 2 h according to x contents.

The crystal structure of sintered ceramics was determined by an X-ray diffractometer (X'Pert Pro MPD, PANalytical, Netherlands) employing Cu-Kα radiation (λ = 1.5418 Å) at a step of 0.02°. Surface morphologies of the ceramics were observed using a field-emission scanning electron microscope (S4800, Hitachi, Japan). Both surfaces of sintered ceramics were grinded and polished, and then fired Ag/Pd paste at 850 °C for 10 min as the electrodes. The dielectric and impedance behavior as a function of temperature was performed using an LCR analyzer (IM3536, Hioki, Japan) attached to a programmable furnace. The temperature dependence of impedance spectra was measured from 350 to 750 °C at a heating rage 3 °C/min.

3. Results and discussion

Fig. 1 shows XRD patterns for NLCL-100x sintered ceramics in the 2θ range of 10–80°. X-ray results indicate that all compositional ceramics have a single Aurivillius phase structure. No secondary phase is detected under the measurement condition. Single phase structure suggests that the La^{3+} cations diffuse into the lattice of NBN-based ceramics and form the solid solution due to the high

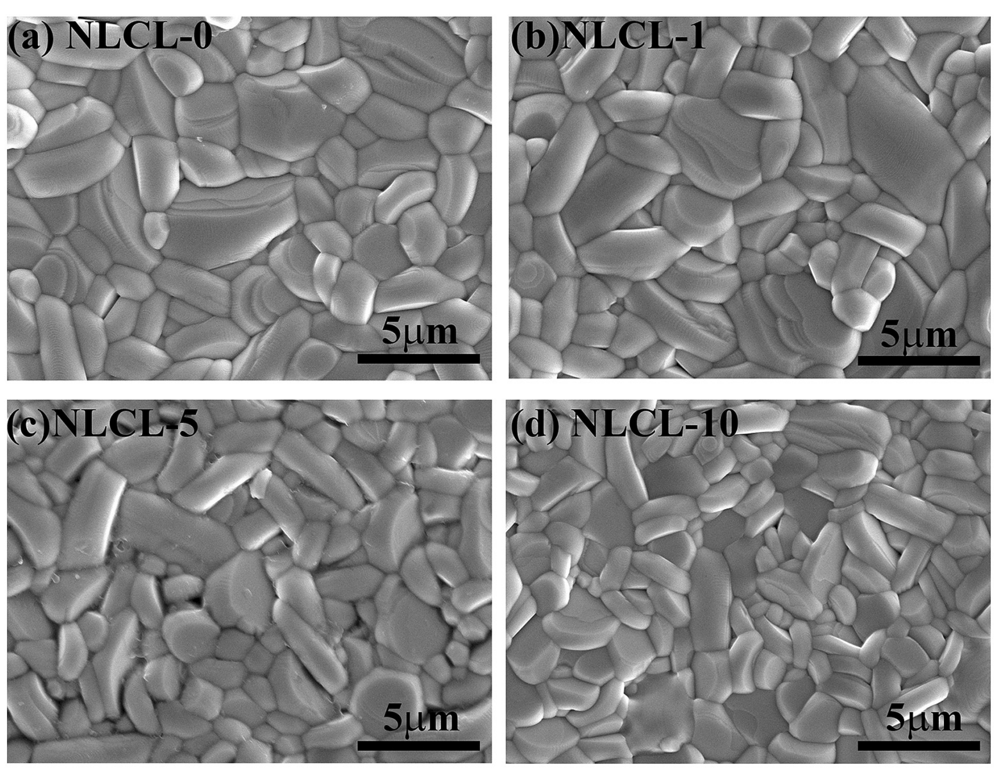

Fig. 2. SEM images of natural surfaces of NLCL-based ceramics.