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Microstructure and electrical properties in W/Nb co-doped Aurivillius phase $Bi_4Ti_3O_{12}$ piezoelectric ceramics

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ABSTRACT

Aurivillius-type $Bi_4Ti_{3-x}W_{x/2}Nb_{x/2}O_{12}$ ceramics were prepared by a conventional solid-state sintering method. The XRD patterns demonstrated that all compositions were a single three layered crystalline structure, involving a reduction of lattice distortion with an increase in W/Nb doping level. The electrical properties including dielectric, electrical conduction and piezoelectric properties were tailored by W/Nb additives. The Curie-temperature decreased, whereas the electrical resistivity drastically increased with introduction of W/Nb donor dopants. As a result, a high electric field can be applied during the poling process. The $Bi_4Ti_{2.9}W_{0.05}Nb_{0.05}O_{12}$ ceramics exhibited optimum piezoelectric coefficient (d_{33} ~22.8 pC/N), large remnant polarization ($2P_r$ ~26.8 μC/cm^2@200 °C) together with a high Curie temperature (T_C ~635 °C). Furthermore, this composition possessed a wide sintering window with outstanding piezoelectric properties. These parameters indicate that $Bi_4Ti_{2.9}W_{0.05}Nb_{0.05}O_{12}$-based ceramic is a promising candidate for high temperature piezoelectric applications.

1. Introduction

Aurivillius phase compounds, as called bismuth layer-structured ferroelectrics (BLSFs), are a large family of important and interesting ferroelectrics. These compounds have attracted more and more attention in recent years due to their fascinating properties. BLSFs possess a high Curie temperature and fatigue-free properties, being promising candidates for high-temperature piezoelectric sensors in some hazardous environments and non-volatile ferroelectric random access memory (FeRAM) devices [1–4]. In addition, photoluminescence property was found in rare-earth elements modified BLSFs [5,6]. The structure of these compounds can be described by a general formula:

$$(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-},$$

where A is mono-, di-, trivalent ion or a mixture allowing dodecahedral coordination, B is a combination of transition metal cations well suited for octahedral coordination, and m is the number of octahedral layers in the perovskite slab in the range of 1–6 [7,8].

$Bi_4Ti_3O_{12}$ (BIT) is one of classic BLSFs, because of its high Curie temperature (T_C ~675 °C), large spontaneous polarization (P_r ~37 μC/cm^2) and excellent fatigue endurance properties [4,9–11]. However, it is difficult to obtain well-poled BIT ceramics due its high leakage current [12]. As a result, a low piezoelectric coefficient (d_{33} ~3.5 pC/N) hinders its application in piezoelectric sensors [13]. Efforts have been made to enhance the piezoelectric properties using grain orientation techniques, such as spark plasma sintering [14], hot-forging [15] and tape casting methods [16]. However, these methods are not as cost effective as the traditional ceramic sintering method. Thus, it is favorable to optimize piezoelectric properties via appropriate chemical modifications. It has been shown that donor dopants such as V^{5+}, Nb^{5+}, Ta^{5+} and W^{6+} ions reduce oxygen vacancies, decrease leakage current and improve the piezoelectric properties of BIT-based ceramics [17–19].

It was reported that d_{33} value was 26 pC/N for Nb/Ta co-modified BIT ceramics which was fabricated via a conventional solid-state reaction method [19]. Unfortunately, reports on W/Nb-doped BIT-based ceramics are scarce. It is of interest to further study the influence of W/Nb-doped on BIT ceramics. In this paper, W/Nb-doped BIT ceramics were prepared by the conventional solid-state sintering route. The influence of W/Nb additive on the microstructure and electrical properties was investigated. Furthermore, the ferroelectric properties and the influence of

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sinter temperature on $Bi_4Ti_{2.9}W_{0.05}Nb_{0.05}O_{12}$ ceramics were also conducted.

2. Experimental

Aurivillius type $Bi_4Ti_{3-x}W_{x/2}Nb_{x/2}O_{12}$ (abbreviated as BWNb-100*x*, where the *x* values vary from 0 to 0.10) ceramics were prepared by a conventional solid-state reaction route. The metal oxides, Bi_2O_3 (99%), TiO_2 (98%), WO_3 (99%) and Nb_2O_5 (99.5%) were used as raw materials. All powders were weighed according to the stoichiometric compositions and then mixed for 24 h using ethanol as solvent and zirconia balls as the milling media, and then the dried mixtures were calcined at 850 °C for 2 h. The calcined powder was milled again in the same condition, and granulated with polyvinyl alcohol (PVA) as a binder. The pellets were prepared by pressing powder in 10 mm diameter die using a uniaxial press under 8 tonnes-forces. After burning out PVA at 550 °C, the green pellets were sintered in a temperature range of 1000–1120 °C for 2 h, depending on the *x* content.

The crystal structure of sintered ceramics was determined by an X-ray diffractometer (DX2700, Dandong, China) employing Cu-Kα radiation (λ = 1.5418 Å). The experimental density of sintered ceramics was measured by using the Archimedes method. The relative density was calculated according to the experimental density and estimated theoretical density, calculated from XRD data. Both surfaces of sintered ceramics were polished and fired silver paste at 700 °C for 10 min as the electrodes. The dielectric behavior as a function of temperature was performed using an LCR analyzer (HP 4980A, Agilent, US) attached to a programmable furnace. A high-resistance meter (6517B, Keithley, USA) was used to obtain the resistance of the sample. After stabilizing the temperature for about 15 min, the sample was applied voltages of 100 and 10 V for 1 min at various temperatures and then measured the resistance. Samples were polarized in a silicon oil bath at 180 °C under a DC electric field of 5–12 kV/mm for 5–30 min. The piezoelectric coefficient d_{33} was measured using a quasi-static d_{33} meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, China). The ferroelectric properties of BWNb-10 ceramics were measured by using a ferroelectric analyzer at 1 Hz (TF-2000, Aix ACCT, Aachen, Germany).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of BWNb-100*x* sintered ceramics in the 2θ range of 20–60°. The main peaks are indexed according to the JCPDS-89–7501, which belongs to the *B*2*ab* space group. No secondary phase is found in all patterns, which suggests that the substitution of Nb^{5+} and W^{6+} cations enter into the B-site of pseudo-perovskite and form the solid solution, corresponding to the similar ionic radii and electrical valence. The most intensive peak refers to the (1 1 7) plane, which is consistent with the fact that the most intensive reflection is of the type of (1 1 2*m*+1) plane. It is noted that (0 0 1 2)/(2 0 0)/(0 2 0) diffraction peaks slightly shift to lower angles, involving an expansion of crystal lattice with an increase in W/Nb doping level. To further evaluate the variation of the crystal structure, the lattice parameters were calculated and shown in Fig. 1(b). It is noted that the lattice parameter, *a*, slightly increases, however, other parameters, *b* and *c*, increase obviously, resulting in an expansion of the lattice. This expansion implies that the incorporation of Nb/W dopants reduce the lattice distortion in the pseudo-perovskite block [20]. Moreover, it could be concluded that the introduction of Nb^{5+} and W^{6+} ions enter into the B-site of pseudo-perovskite structure and substitute the Ti^{4+} ions, giving rise to a corresponding variation of electrical properties.

Fig. 2(a) and (b) shows the SEM images of natural surfaces of pure- or W/Nb modified-BIT based ceramics. It can be clearly seen that both ceramics reveal an anisotropic plate-like microstructure, which is a characteristic of BLSFs. This microstructure arises from the highly anisotropic grain growth rate, which is much higher in the direction perpendicular to the *c*-axis than that along *c*-axis [21]. In addition, it is noted that an evolution of microstructure occurs with introduction of W and Nb additives. The average length of plate-like grain significantly increases from ~2.58 μm to ~5.62 μm, but the thickness varies from ~0.50 μm to ~0.38 μm (Fig. 2(c)), for pure BIT and BWNb-10 ceramics, respectively. This means that the aspect ratio *L*/*T* (length/thickness) is controlled by the W/Nb dopants. The W/Nb modifications increase the grain growth rate in the direction perpendicular to the *c*-axis and result in a highly anisotropic microstructure of BWNb-10 ceramic.

Temperature dependence of dielectric permittivity of BWNb-100*x* ceramics is shown in Fig. 3. The Curie temperature (T_C) for pure BIT is found to be 670 °C, which is in agreement with other literatures. Moreover, it is noted that the T_C value gradually decreases with introduction of Nb^{5+}, W^{6+} dopants. It is well known that the T_C value for BLSFs is intensively correlated with the lattice distortion in pseudo-perovskite interior. In consideration of analogous ionic radii of Ti^{4+} (0.61 Å), Nb^{5+} (0.64 Å) and W^{6+} (0.60 Å) ions, this substitution does not make a significant contribution to the variation of lattice distortion. Hence, it is of interest to find another explanation to interpret this evolution of T_C. It should be noted that the transition metal ions in the B-sites possess the marked difference of electronic configuration, that is, nd^0 configuration [22]. For an instant, the Nb and Ta possess the same ionic radii (~0.64 Å), the higher T_C (~440 °C) in $SrBi_2Nb_2O_9$ ($4d^0$) could be attributed to the B site of $4d^0$ configuration, whereas $SrBi_2Ta_2O_9$ possesses the $5d^0$ configuration and lower T_C(~300 °C).

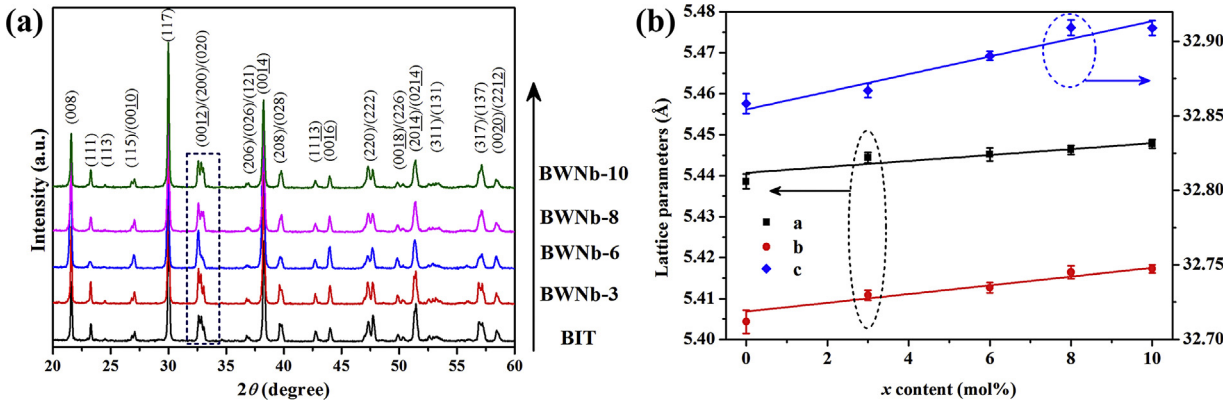

Fig. 1. (a) XRD patterns for BWNb-based ceramics in the 2θ range of 20–60°; (b) lattice parameters *a*, *b* and *c* vs. the *x* content.