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Ceramics International 38 (2012) 2679–2684
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Ordered domains in lead free $0.94(Na_{0.5}Bi_{0.5})TiO_3$–$0.06BaTiO_3$ ceramics

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Received 1 November 2011; received in revised form 14 November 2011; accepted 14 November 2011
Available online 22 November 2011

Abstract

The microstructure of lead-free $0.94(Na_{0.5}Bi_{0.5})TiO_3$–$0.06BaTiO_3$ (BNBT-6) piezoelectric ceramics was investigated by different analysis techniques. X-ray diffraction (XRD) result reveals the coexistence of rhombohedral and tetragonal symmetry in the structure of BNBT-6 ceramics at room temperature. Selected area electron diffraction (SAED) patterns reveal the presence of ordered domains in BNBT-6 ceramics. The superlattice reflections $\{h + 1/2\,k + 1/2\,0\}$ and $\{h + 1/2\,k + 1/2\,l + 1/2\}$ of ordered domains mainly come from the octahedral tilt and chemical ordering of A-site atoms. High-resolution transmission electron microscopy (HRTEM) combined with image processing is an effective method to investigate the defects and the size of ordered domains in BNBT-6 ceramics. One-dimensional fringe images of superlattice reflections indicate that there are significant local Na and Bi atomic layer displacements and anti-phase boundaries as a result of chemical ordering, which provide a driving force for order–disorder transformation. A filtered HRTEM black/white image shows the size of ordered domains to be about 5–10 nm.

Keywords: HRTEM; Superlattice reflection; Ordered domain; Antiphase boundary

1. Introduction

In recent years, much interest has been focused on lead-free piezoelectric materials based on the viewpoint of environment impact. Since Smolenskii [1] reported that the A-site complex perovskite compound $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) has piezoelectric properties, this material as a key lead-free piezoelectric ceramics to substitute PZT based materials and PMN based relaxor ferroelectrics, has aroused extensive interest of researchers [2–8]. Most of the previous researches about NBT or NBT based complex perovskite ceramics, however, concentrated on the improvement of piezoelectric properties and the temperature induced phase transitions. Takenaka et al. reported that $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ (BNBT) showed the highest piezoelectric constant with composition close to the morphotropic phase boundary (MPB) [2]. Yilmaz [3] synthesized textured BNBT (5.5 mol% $BaTiO_3$) ceramics using templated grain growth method (TGG) showing piezoelectric constant $d_{33} = 520$ pC/N (high field) which is higher than that of single crystal of BNBT (6.0 mol% $BaTiO_3$, $d_{33} = 450$ pC/N) [4]. Summarizing previous studies, NBT and NBT based complex perovskite ceramics undergo two-phase transitions, i.e., cubit ↔ tetragonal at ~540 °C and tetragonal ↔ rhomborhombohedral at ~250 °C [2,4,5]. Liu et al. also reported that BNBT ceramics experience one structural phase transition and two ferroelectric phase transitions under 400 °C: tetragonal paraelectric phase ↔ tetragonal antiferroelectric phase ↔ rhombohedral (or rhombohedral plus tetragonal) ferroelectric phase [6].

It is well known that BNBT ceramics are relaxor ferroelectrics, which show diffuse phase transition and a frequency dependent dispersion behavior with suitable $BaTiO_3$ contents [9]. Most of the relaxor ferroelectrics having the general formula $A(B'B'')O_3$ show high dielectric and piezoelectric constants, which indicates that the behaviors and properties of these materials have a very close relationship with the order–disorder transition and the ordering degree of the complex perovskite structure [10]. Wang et al. summarized that the formation of ordered structure is strongly dominated by the differences in both valence and ionic radii between the B' and B'' cations in most complex $A(B'B'')O_3$ perovskites [11]. Previous researches ascribed the origin of ordered domains due to the localized chemical ordering in relaxor materials, such as

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doi:10.1016/j.ceramint.2011.11.035

lead scandium tantalite (PST) and lead magnesium niobate (PMN) [12,13]. Since BNBT ceramics with the general formula $(A'A'')BO_3$ are regarded as the relaxor ferroelectrics, they may have ordered structure in theory. But the difference in ionic radii between Na^+ and Bi^{3+} is insignificant based on Wang report [11], the tendency for ordering is slight. Consequently the microstructure of BNBT ceramics needs to be investigated in detail to reveal whether it has ordering characteristics or not.

In this study, BNBT ceramics for the composition of the MPB (6.0 mol% $BaTiO_3$) were synthesized by solid-state preparation method. The microstructure, including ordered domain, displacement, anti-phase boundary and so on, was investigated by a combination of XRD, SAED, and HRTEM techniques. The mechanism of superlattice reflection formation in BNBT ceramics was discussed by virtue of HRTEM images and SAED patterns.

2. Experimental procedure

To synthesize the BNBT-6 ceramics, high purity raw materials Bi_2O_3 (99.9%), TiO_2 (99.0%), Na_2CO_3 (99.8%), and $BaTiO_3$ (99.0%) were mixed with composition $0.94(Bi_{0.5}Na_{0.5})TiO_3$–$0.06BaTiO_3$ by ball milling for 20 h. Then the dried powders were calcined at 850 °C for 2 h in air. The calcined powders were re-milled for 16 h and dried, and then were cold-pressed at 160 MPa into discs of approximately Ø13 mm diameter and 2 mm thickness. Finally, the discs were sintered at 1150 °C for 2 h.

The structure characteristics and phase purity of the sintered BNBT-6 ceramics were identified by XRD using an ARL X'TRA diffractometer (Themo Electron Co., Ecublens, Switzerland) with CuKα ($\lambda = 1.5406$ Å) radiation, in continuous scan mode with 0.5°/min in the range of 10–80° (2θ). For HRTEM and SAED observation, the specimen was first polished to about 100 μm in thickness and ultrasonically cut into a disc of Ø3 mm in diameter, and then the disc was dimple grinded to about 20 μm in thickness. The final perforation in the disc center was performed using argon ions from both sides via Precision Ion Polishing System (PIPS, Model 691, GATAN Co., Pleasanton, CA). The microstructure characteristics and SAED were conducted with a HRTEM (JEM-2010, JEOL) equipped with a side-entry double-tilting specimen holder. Image filtering and processing were conducted by DigitalMicrographa software (GATAN).

3. Results and discussion

3.1. XRD characterization

Fig. 1 shows the XRD pattern of BNBT-6 ceramics that exhibits a single perovskite structure, and there are no other phases like pyrochlore structure. All reflections in the case were indexed on the basis of the pseudocubic perovskite unit cell. The pattern clearly shows rhombohedral split (see inset of Fig. 1), which means that the structure of BNBT-6 ceramics is pseudocubic with a very small deviation from ideal cubic symmetry. In other words, under the effect of the excess $BaTiO_3$ (6.0 mol%), the structure of BNBT-6 is the coexistence of rhombohedral and tetragonal symmetry at room temperature. Measurement results show that rhombohedral structure has cell parameter $a = 3.9013$ Å, $\alpha = 89.688°$, and tetragonal structure has cell parameter $a = 3.9028$ Å, $c = 3.9205$ Å, respectively.

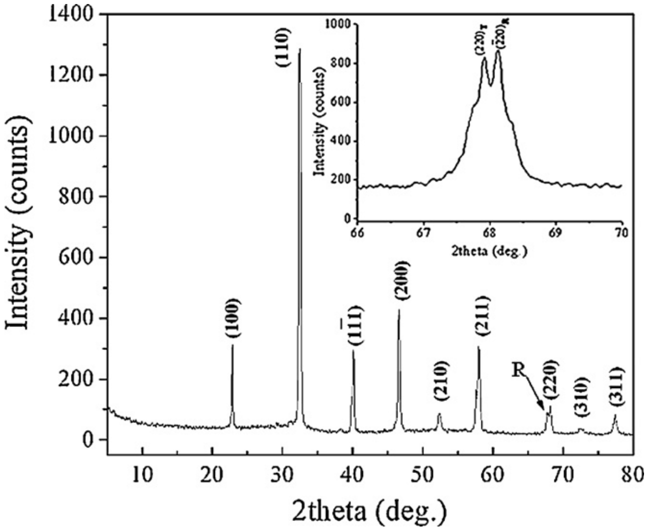

Fig. 1. XRD pattern of BNBT-6 ceramics, R denotes rhombohedral split.

Based on Soukhojak report [14], ordered domains occur in BNBT crystal. No ordered domain reflections, however, can be observed in the XRD pattern of BNBT-6 ceramics besides rhombohedral split. There are two possible reasons for the limitation of ordered domain reflections. One is the heavy X-ray absorption that masks the weak ordered domains lines, and the other is the small size of ordered domains that cannot be detected by XRD. Therefore, in order to validate whether there are ordered domains in BNBT-6 ceramics or not, the electron microscopy was processed.

3.2. SAED characterization

Fig. 2 shows three kinds of SAED patterns from the studied specimen that were observed along [0 0 1], [1 1 1], and [0 1 1] zone axis directions via rotating the double-tilting specimen holder, respectively. In [0 0 1] and [1 1 1] zone axis directions, Fig. 2(a) and (b), the diffraction patterns show the existence of $\{h+1/2\,k+1/2\;\;0\}$ superlattice reflections (indicated by the empty arrow). And in [0 1 1] zone axis diffraction pattern, Fig. 2(c), the diffraction pattern shows another kind of superlattice reflections $\{h+1/2\,k+1/2\,l+1/2\}$ in all three directions, and the intensities of superlattice reflections are stronger than $\{h+1/2\,k+1/2\;\;0\}$ superlattice reflections. The presence of superlattice reflections confirmed that there are ordered domains in BNBT-6 ceramics.

For the origin of superlattice formation in complex perovskite, there are mainly three possible mechanisms [14]: (1) chemical ordering of the species, (2) octahedral tilt, (3) anti-parallel displacement of ions. For chemical ordering, the characteristic is that the intensities of superlattice reflections do not change significantly with temperature [13]. For NBT single