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The kinetic effect on formation of disordered intergrowth structures in mixed bismuth-layered $(Bi_3NbTiO_9)_2(Bi_4Ti_3O_{12})_1$ compounds

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Abstract

A series of intergrowth bismuth-layered $(Bi_3TiNbO_9)_2(Bi_4Ti_3O_{12})_1$ ceramics were reactive-sintered to infer their structural characters and microstructural relationship. Combined with XRD and STEM analysis, the long-range-disordered structures were found in this compound accompanied by obvious kinetic effect. Detail study showed that the inhomogeneous liquid phase composition before grain growth-interface induces the emergence of various intergrowth structures. The further epitaxial growth of these potential structures along *c*-direction builds up the long-range-disordered intergrowth grains. Meanwhile, such growth features make it hard for the $(Bi_3TiNbO_9)_2(Bi_4Ti_3O_{12})_1$ system to obtain long-range-ordered intergrowth structure by a conventional solid-state reaction method.

Keywords: Bismuth-layered ferroelectrics; Intergrowth structure; Kinetic effect; Bi_3TiNbO_9; $Bi_4Ti_3O_{12}$

1. Introduction

The layered intergrowth structures commonly exist in inorganic solid compounds and have long been widely interested because of a variety of novel properties, such as high-temperature superconductivity, high-temperature piezoelectricity, colossal magnetoresistance and low thermal conductivity[1–5]. The intergrowth bismuth-layered structures are one of the most important systems among these compounds, which are built up by the regular stacking of two different bismuth layered blocks $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$ and $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$, always with $n=m+1$ and mainly with Bi to occupy A sites[6–8]. The values of m and n determine the numbers of perovskite layers within adjacent $(Bi_2O_2)^{2+}$ layers. As shown in Fig. 1, the intergrowth $(Bi_3TiNbO_9)_1(Bi_4Ti_3O_{12})_1$ compound is formed by equal number of Bi_3TiNbO_9 ($m=2$, abbreviated as BTN) and $Bi_4Ti_3O_{12}$ ($n=3$, abbreviated as BiT) blocks [9], or simplified as BTN_1BiT_1 with perovskite sequences in –23– [10]. Such unique intergrowth relationships provide opportunities to tailor and design novel electrical properties. Earlier studies have indeed found that combinations of two ferroelectric modules can optimize the ferroelectric properties [9,11–13]. And such synergistic effects open new chances to further couple the multi-functionalities in intergrowth compounds.

The desire to optimize ferroelectric/piezoelectric properties promotes the designing of new intergrowth structures, and the focuses are also drawn to the frequently observed stacking faults [11,14,15] which may further affect the performance [16]. Such defects are generally regarded as local disorders, but they may also be considered as new intergrowth orders. The detailed study of Gao [17] on BTN_1BiT_1 system in –23– order shown that various types of BTN or BiT stacking faults could be found in changing populations, while locally high density of stacking faults can induce new orders such as –223– and –233– sequences. This provides a new idea for us to design novel intergrowth compounds, such as the BTN_2BiT_1 intergrowth compound reported in our previous work [10]. The long-range-ordered –223– structure was demonstrated to be an

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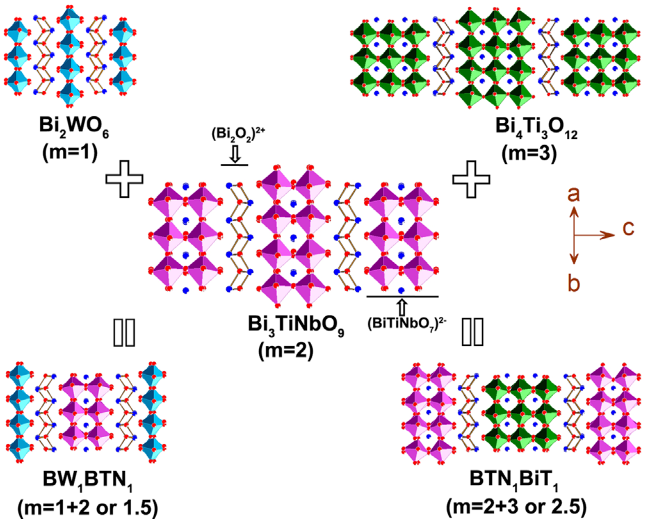

Fig. 1. The formation of intergrowth structures by two Aurivillius phases: left $m=1$ and $n=2$ ($BiWO_6+Bi_3TiNbO_9=Bi_4WTiNbO_{15}$ (BW_1BTN_1)); right $m=2$ and $n=3$ ($Bi_3TiNbO_9+Bi_4Ti_3O_{12}=Bi_7TiNbO_{21}$ (BTN_1BiT_1)).

independent structure and its crystals were successfully synthesized by a self-flux method. However, we also found this structure could not be achieved in the ceramic prepared by a conventional solid-state reaction method, instead the compounds are built up by mixtures of –23–, –223–, –2223–, and –22– intergrowth orders. Actually, the local ordering in random or recurrent matrix is not an uncommon phenomenon in the intergrowth systems [18–21]. The nanometer-sized building blocks of intergrowth compounds make their order–disorder structures dissimilar to alloy systems, and quite different kinetic processes should take place. In this context, we will follow the previous study and focus further on the formation mechanism of intergrowth BTN_2BiT_1 compounds. This will be benefit to the understanding of the order–disorder phenomenon in intergrowth structure.

2. Experiment

A series of BTN_2BiT ceramic compounds were prepared by the conventional solid-state reaction method with simple oxides Bi_2O_3 (99.9%), TiO_2 (99.3%), and Nb_2O_5 (99.5%). An additional 2 mol% Bi_2O_3 was added into the nominal composition to compensate for its volatilization during the sintering process. The starting powders were mixed by planetary milling and pre-sintered at 820 °C for 7 h, then crushed for further planetary milling before pressed into pellets and reactive-sintered at 950 °C, 1000 °C, 1050 °C, 1100 °C, and 1125 °C for 2 h in air, hence abbreviated as PS820, RS950, RS1000, RS1050, RS1100, and RS1125 respectively.

The powder XRD patterns of these samples were performed with a D/max-2500 V diffractometer (Rigaku Co., Japan) using Cu-K radiation (Å), in a 2θ range of 5–55° with a scanning step of 0.02°. Microstructure observation was performed in a scanning electron microscope (SEM, Model JSM-5800, JOEL, Japan) on polished surfaces in the back-scattered electron (BSE) mode. The study of intergrowth structures was carried out in a field-emission electron microscope (TECNAI F20, FEI, USA) in the scanning transmission electron microscopy mode (STEM), because the high-resolution high-angle annular-dark-filed (HAADF) images are ready to expose the detailed structures.

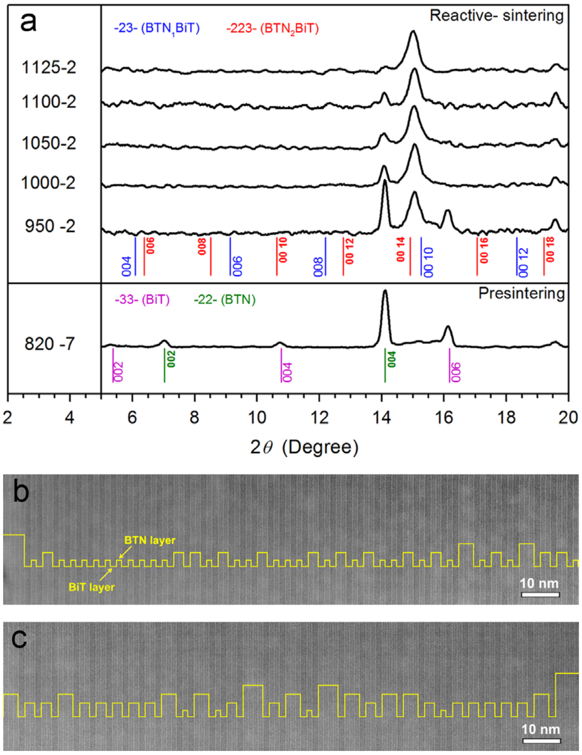

Fig. 2. The possible co-existence of BTN_1BiT_1 with BTN_2BiT_1 structures in reactive-sintered ceramics at temperatures up to 1125 °C as revealed by (a) XRD patterns, which also detect the starting BTN phase [10]; (b, c) HAADF images show locally different ordered sequences observed from two areas in a same grain, the yellow bar heights correspond to the repeating number of BTN blocks.

3. Results and discussion

3.1. Kinetic effect to dictate sintering

The XRD patterns of the as-sintered BTN_2BiT_1 samples are given in Fig. 2a [10]; the pre-sintering pattern is also shown for comparison with the starting parent phases BTN ($m=2$) and BiT ($n=3$). Whether the final sintered phase is the expected BTN_2BiT_1 or the known BTN_1BiT_1 phase could not be determined directly by XRD since their reflections overlap strongly. In contrast, reflections from the remnant BTN phase could be easily identified, revealing its decrease with increasing sintering temperatures. This gradual and imbalanced consumption of the starting materials indicates that the kinetic process may influence significantly the reaction process to form the intergrowth orders.

Meanwhile, this influence can also be found in grain structures. An apparent change between two areas of a grain