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Local orderings in long-range-disordered bismuth-layered intergrowth structure

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ABSTRACT

A series of intergrowth bismuth-layered $(Bi_3TiNbO_9)_2(Bi_4Ti_3O_{12})$ (2_23) ceramics were prepared by conventional solid-state reaction to study the characteristics of the local orderings in long-range-disordered intergrowth structures. High-resolution high-angle annular dark-field (HAADF) imaging reveals the intergrowth structure composed of mixtures of -23-, -223-, -2223- and -22- sequences, while the -223- structure is the thermodynamic stable state of this intergrowth system. It was confirmed by the crystals of recurrent -223- structure prepared by self-flux method and the nature of the local ordering was discussed from their differences in repeating units. The statistics show that when repeating units reach 4 or higher, the independent -223- intergrowth ordering emerges clearly among the competing associated orderings. We infer it is the kinetic factor that induces local compositional variance to result in long-range disordered intergrowth structures.

1. Introduction

Intergrowth in solids becomes increasingly common while gaining greater interest, thanks to the large variety of inorganic materials exhibiting novel structures and properties due to random or recurrent intergrowth [1–7]. However, the order and disorder intergrowth phenomenon has not been fully understood. On the one hand, local-disordered intergrowth structures (DOIS) are found even in systems forming ordered intergrowth structures (OIS) with long periodicities [8–10]. On the other hand, there is always a marginal degree of orders in DOIS [11–15]. There is little doubt that the OIS are equilibrium structures while many questions focus on the nature of the DOIS. Generally, the DOIS are considered as special solid solutions of two or more different components [1]. Although, in this description, the DOIS are understood as a phase, the existence of various local orderings in DOIS makes it difficult to identify its unit cell as for traditional solid solutions. Consequently, the nature of the local orderings becomes a key to understand the DOIS. Kohn and Eckart [16,17] considered that the local ordering could be recognized as an independent structure if it repeats more than five times. In contrast, Rao [1] stipulated that the structure expected from the periodicities observed in HREM lattice images should be consistent with the unit cell dimensions from diffraction measurement. Although these two criterions are acceptable to a certain extent, they are somewhat subjective and could not be combined or even unified to understand the nature of local ordering in DOIS.

Meanwhile, the bismuth layer-structured ferroelectrics (BLSF) have attracted increasing attention due to its broad application prospect in high temperature piezoelectrics [18], non-volatile ferroelectric random access memories (FeRAM) [19,20], multi-ferroic fields [21], oxide ion conductors [22] and photocatalysts [23]. These materials have the Aurivillius-type structures with a general formula of $(Bi_2O_2)^{2+}$ $(A_{m-1}B_mO_{3m+1})^{2-}$ where the perovskite slabs, $(A_{m-1}B_mO_{3m+1})^{2-}$, m octahedra layers, are interleaved by $(Bi_2O_2)^{2+}$ interlayers. As a typically OIS, the recurrent intergrowth bismuth layer-structured ferroelectrics (iBLSF), formed by two constituent structures (m and $m+1$) alternating along the common c-axis, were synthesized to enable further tailoring of the ferroelectric properties [24–26]. Bi_3TiNbO_9–$Bi_4Ti_3O_{12}$ (BTN$_1$BiT, $m=2+3$) is one such iBLSF formed by equal numbers of Bi_3TiNbO_9 (BTN, $m=2$) and $Bi_4Ti_3O_{12}$ (BiT, $m=3$) [27,28]. Same with other intergrowth systems, disorder is also a phenomenon commonly encountered in iBLSF. In this family, the disorder is closely related to the stacking faults that are caused by the uninterrupted sequences of one parent structure or constituent layer, and such disorders do cause widespread concerns of researchers. For example, Gao [8] frequently observed the local BTN and BiT stacking faults in the ordered -23- stacking sequence

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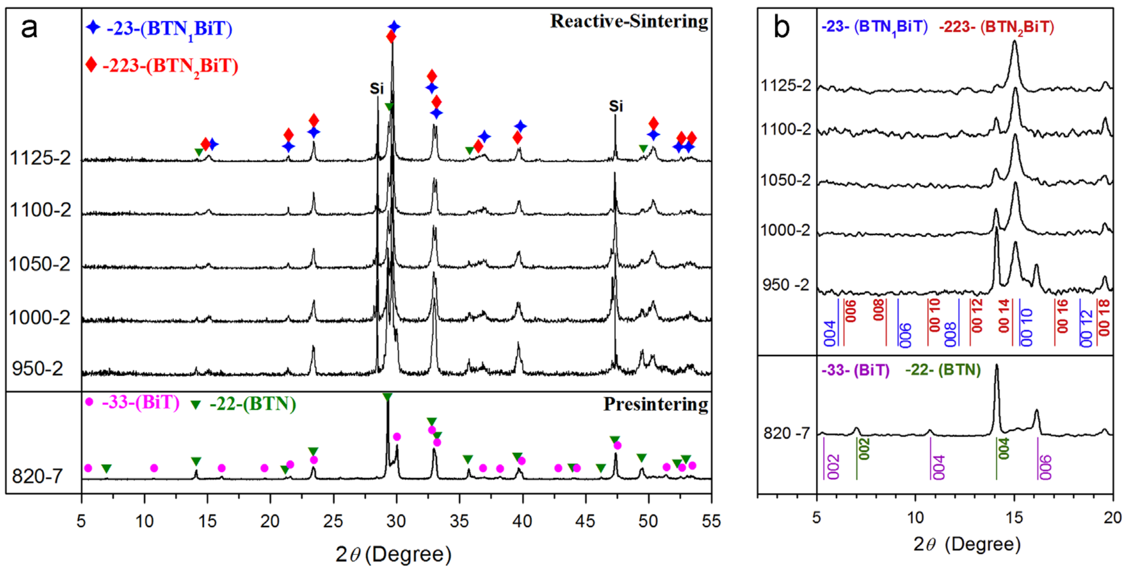

Fig. 1. (a) XRD patterns of the BTN_2BiT ceramics reactive-sintered at the temperatures between 950 and 1125 °C; the two starting phases BTN and BiT were prepared at 820 °C and also presented here. (b) XRD patterns at low angle ($2\theta < 20°$) obtained by slowly scanning (1°/min). The theoretical cell parameters along *c*-axis of -22-, -33-, -23- and -223- structures that we used to calculated the (0 0 *l*) peaks are 2.5099 [30], 3.28111 [31], 5.7990 [32] and 8.300 nm [29], respectively.

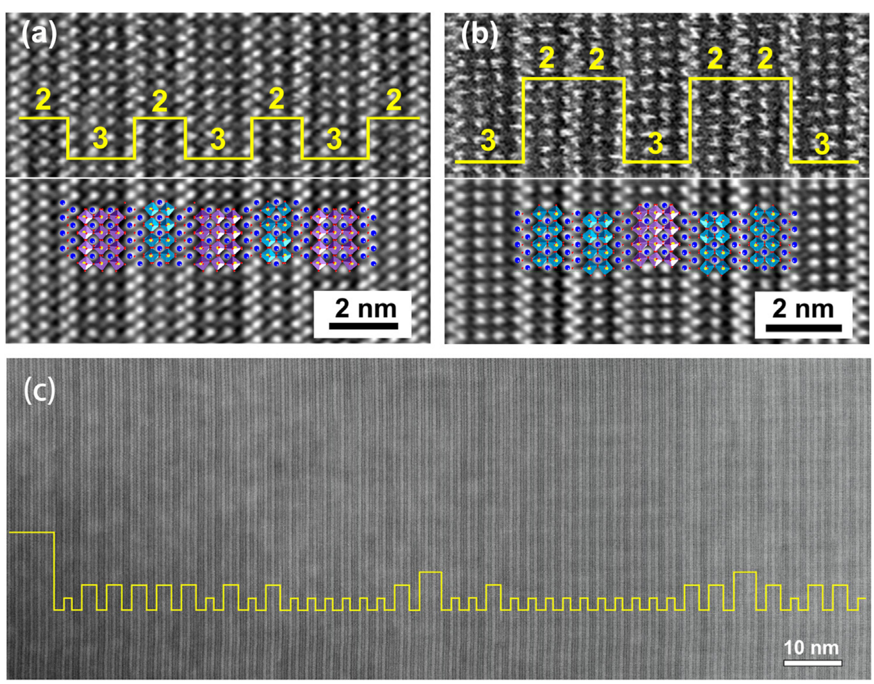

Fig. 2. ((a) and (b)) High-resolution HAADF images of local -23- and -223- sequences, the corresponding FFT filed images and structural models are also given in the lower parts. (c) Medium-magnification HAADF image of a long-range-disordered structure in a BTN_2BiT grain (RS1125). The difference in stacking sequences of BTN and BiT constituent layers are labeled by increasing heights for repeated BTN layers.

of BTN_1BiT structure by HRTEM. In their opinion, the stacking faults may also represent new stacking orders and the local orderings of -223- and -233- with 2–3 repeats may be the signs of new recurrent iBLSF. Actually, in earlier studies, Shibuya [29] have already successfully prepared the recurrent iBLSF film with -223- stacking sequence by pulsed-laser deposition (PLD) method, but it is worth noting that the PLD target they used was BTN_1BiT rather than BTN_2BiT pellet, and the structural changes with the oxygen pressure and substrate temperature make it difficult to directly connect this recurrent -223- structures with the local -223- ordering in ceramics. Besides, Boullay [11] carried out related research on BTN_2BiT and $BTNBiT_2$ systems. In their study, the structures of these two systems did not show expected long-range-ordered -223- and -233- stacking sequences, but the local orderings of these two sequences were frequently observed. Consequently, as a typically intergrowth system, the iBLSF system generally also has the question of order or disorder. However, due to the limits of experiments and concerns, the fundamental questions about the order and disorder have not been systematically answered. Furthermore, there are still the questions of whether the