

Centrosymmetric crystal structure of BiMnO₃ studied by transmission electron microscopy and theoretical simulations

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Abstract

In this paper, electron diffraction (ED), high-resolution transmission electron microscopy (HRTEM), and theoretical simulations have been used to study the room-temperature structure of the multiferroic BiMnO₃ synthesized under high pressure. The electron diffraction data reveal that BiMnO₃ crystallizes in the centrosymmetric *C2/c* structure, not in the non-centrosymmetric *C2* structure. This is confirmed by further calculations of ED patterns and HRTEM images. The present work is very important for the further studies of BiMnO₃.

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1. Introduction

Multiferroic materials, displaying simultaneously more than one of (anti)ferromagnetism, (anti)ferroelectricity and ferroelasticity, are currently attracting growing interests due to their novel physical phenomena and potential applications [1]. In recent years, BiMnO₃ with a highly distorted perovskite-type structure has been extensively studied as a multiferroic material. The initial interest in the study of BiMnO₃ is mainly because it displays unexpected ferromagnetic behaviors with a Curie temperature (T_C) of ~ 105 K [2]. The ferromagnetism has been confirmed by many works [3–7]. BiMnO₃ is also expected to be ferroelectric according to the first-principle calculations [8,9]. Experimentally, dielectric hysteresis loops have been measured on BiMnO₃ [5,10]. However, the measured ferroelectric polarization [5,10] is much smaller than the result calculated from first principle [11], making it difficult to associate the measured hysteresis loops to bulk ferroelectricity.

Multiferroic materials are rare in nature because the physical/structural/chemical conditions for a material to display simultaneously more than one of (anti)ferromagnetism, (anti)ferroelectricity, and ferroelasticity are generally difficult to be achieved [9,12]. Especially, ferroelectricity requires that the crystal structure be non-centrosymmetric and the ferroelectric transition is directly related to the structural phase transformation. Therefore, in such intriguing multiferroics, structural characterizations are extremely important. At room temperature, BiMnO₃ has a highly distorted perovskite-type structure, and was primitively reported to be of a triclinic lattice with $a=c \approx 3.935$ Å, $b \approx 3.989$ Å, $\alpha = \gamma \approx 91.47^\circ$, and $\beta \approx 91.97^\circ$ [13]. Later, ED observation by Chiba et al. [14] suggested a 4-fold periodicity along the $[1\ 1\ 1]_p$ direction (where the subscript ‘p’ refers to the fundamental perovskite-type cell). The reciprocal lattice of BiMnO₃ reconstructed from the ED observation [14] is schematically shown in Fig. 1. Based on the electron diffraction information, the crystal structure of BiMnO₃ was refined from powder neutron diffraction data to be a *C2* monoclinic superstructure with $a = 9.53$ Å, $b = 5.61$ Å, $c = 9.85$ Å, and $\beta = 110.67^\circ$ [15]. This structure was commonly accepted and used as a fundamental model for interpretation of the observed

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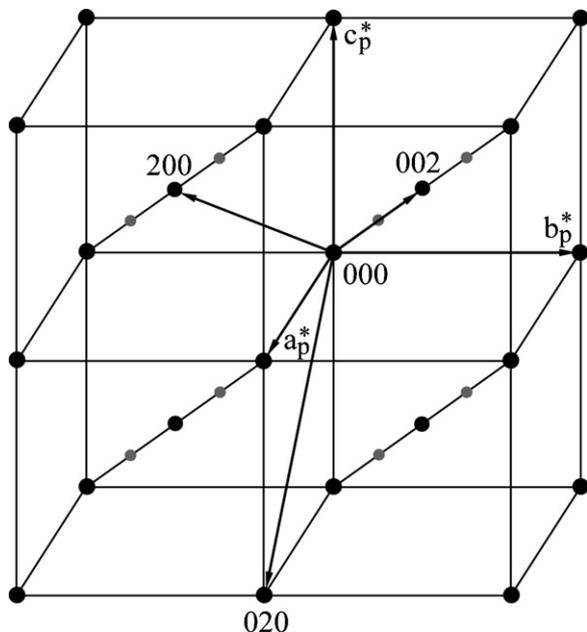


Fig. 1. Reciprocal lattice of BiMnO₃ reconstructed from the ED observation by Chiba et al. [14], suggesting a 4-fold periodicity along the $[1\ 1\ 1]_p$ direction.

physical phenomena. However, very recently Belik et al. [16] observed the $[0\ 1\ 0]$ zone-axis ED pattern of BiMnO₃ in which the $h0l$ reflections with $l=2n+1$ are absent (hereinafter the indices and zone axis without the subscript ‘p’ are given in the monoclinic supercell), and suggested that this extinction is due to the existence of the c -glide plane perpendicular to the b^* -axis. They also used convergent beam electron diffraction (CBED) to confirm this dynamical extinction. The space group of BiMnO₃ was therefore determined to be $C2/c$ based on the transmission electron microscopy (TEM) observation, and the structural data were also refined from neutron powder diffraction [16]. Thus, two space groups, $C2$ and $C2/c$ were assigned to BiMnO₃, and the former one is non-centrosymmetric while the latter one is centrosymmetric. In terms of crystallography, the non-centrosymmetric $C2$ structure is expected to be ferroelec-

tric. However, the ferroelectric polarization calculated using the $C2$ structural parameters [17], giving $0.52\ \mu\text{C}/\text{cm}^2$ [11], is much larger than the experimentally measured result ($\sim 0.06\ \mu\text{C}/\text{cm}^2$ at room temperature [10]). In addition, the first-principle calculations on BiMnO₃ showed that the centrosymmetric $C2/c$ structure with zero polarization is more stable than the non-centrosymmetric $C2$ structure at 0 K [18]. If BiMnO₃ crystallizes in the $C2/c$ structure, the observed ferroelectric properties of BiMnO₃ possibly originate from other mechanisms, such as an electronic phase transition triggered by an electric field, and the local structural distortion from centrosymmetric to non-centrosymmetric caused by the tiny changes of the stoichiometry and the appearance of Mn⁴⁺ or Mn²⁺ ions [16]. To further reveal the origin of the ferroelasticity in BiMnO₃, it is very important to clarify its room-temperature structure.

Below room temperature, the monoclinic structure of BiMnO₃ appears to be stable [15,17,19]. Two high-temperature structure changes have been reported to occur at 450 and 770 K [3,7,19,20]. The phase transformation at 450 K is monoclinic-to-monoclinic without any detectable change in the symmetry [19,20]. The phase transformation at 770 K is monoclinic-to-orthorhombic [19,20]. The origin of both the high-temperature phase transitions has not been determined yet. In this paper, we mainly focus on the investigation of the room-temperature structure of BiMnO₃ by means of ED, HRTEM, and the theoretical simulations.

2. Experimental

Polycrystalline BiMnO₃ ceramic was prepared by a high-pressure synthesis method described in Ref. [3]. A stoichiometric mixture of Bi₂O₃ (Alfa Aesar 99.99%) and Mn₂O₃ (Alfa Aesar 98%) was ground intimately in an agate mortar followed by calcination in alumina crucible at 600 K for 24 h, and then subjected to high-pressure synthesis (5 GPa and 1173 °C for 30 min) using a cubic-anvil-type apparatus. Thin foils for TEM studies were prepared by crushing BiMnO₃ ceramic in an agate mortar filled with alcohol, and then dispersing the fine fragments suspended in alcohol on a microgrid. A Tecnai F20 field-emission transmission electron microscope was used for ED and HRTEM experiments. All the TEM studies were carried out at an acceleration voltage of 200 keV.

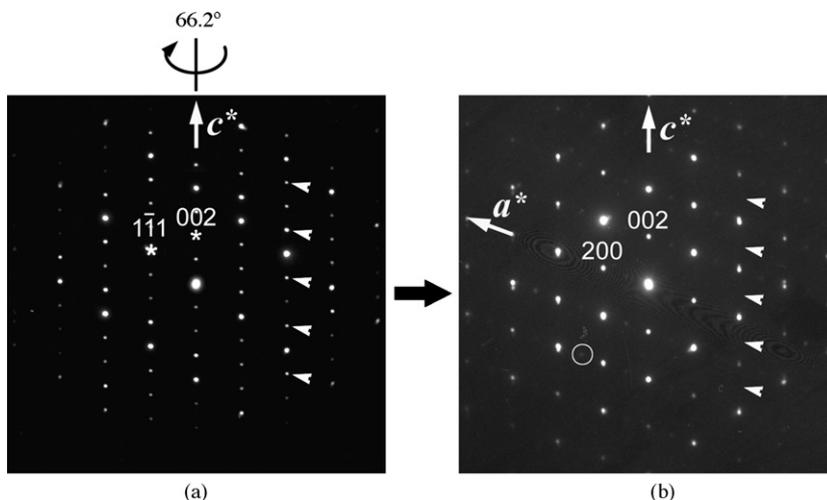


Fig. 2. (a) ED pattern taken along the $[1\ 1\ 0]$ zone-axis direction, (b) $[0\ 1\ 0]$ zone-axis ED pattern obtained by tilting the $[1\ 1\ 0]$ zone axis about 66.2° around the c^* -axis clockwise. Note that the $00l$ reflections with $l=2n+1$ are absent on the $[0\ 1\ 0]$ zone axis, while such reflections are clearly visible on the $[1\ 1\ 0]$ zone axis.

3. Results and discussion

The important differences in electron diffraction between the proposed $C2$ and $C2/c$ structures of BiMnO_3 [15,16] would be shown on the $[0\ 1\ 0]$ zone axis. To see which one of the two structural models is valid, it is extremely important to investigate the $[0\ 1\ 0]$ ED pattern. As there are a number of very similar ED patterns in BiMnO_3 , we conducted systemic tilting experiments to assign the correct zone axis. Fig. 2(a) shows the ED pattern taken along the $[1\ 1\ 0]$ zone-axis direction. The ED pattern shown in Fig. 2(b) was recorded by tilting the $[1\ 1\ 0]$ zone axis about 66.2° around the c^* -axis clockwise, and is therefore confirmed to be the $[0\ 1\ 0]$ zone-axis ED pattern. It can be seen that the $00l$ reflections with $l=2n+1$ are clearly visible on the $[1\ 1\ 0]$ zone axis, but are absent on the $[0\ 1\ 0]$ zone axis (as indicated by arrows). This extinction condition is attributed to the existence of the c -glide plane perpendicular to the b^* -axis. The electron diffraction data clearly suggest that BiMnO_3 crystallizes in the $C2/c$ structure [16], not in the $C2$ structure [15]. The observation of rather strong $00l$ reflections with $l=2n+1$ on the $[1\ 1\ 0]$ zone axis, as well as on some other c^* -lying ED patterns such as the $[1\ 0\ 0]$ one [16], is due to the intrinsic properties of the $C2/c$ structure. This can be verified from the following calculations of electron diffraction patterns. In the $[0\ 1\ 0]$ ED pattern of Fig. 2(b), very weak $h0l$ reflections are seen to appear for $h=2n+1$ (one of the reflections is marked by the white open

circle). The appearance of those weak reflections is likely due to the double diffraction.

In order to further confirm that BiMnO_3 crystallizes in the $C2/c$ structure instead of in the $C2$ structure, electron diffraction patterns were calculated from both the structural models. Fig. 3(a and b) shows, respectively, the $[1\ 1\ 0]$ and $[0\ 1\ 0]$ zone-axis ED patterns calculated from the $C2/c$ structural model [16], and Fig. 3(c and d) shows, respectively, the $[1\ 1\ 0]$ and $[0\ 1\ 0]$ ED patterns calculated from the $C2$ one [15]. From Fig. 3(a and b), it can be seen that the $00l$ reflections with $l=2n+1$ are absent on the $[0\ 1\ 0]$ zone axis, while such reflections appear clearly on the $[1\ 1\ 0]$ zone axis (as indicated by arrows). In addition, the calculated $[0\ 1\ 0]$ diffraction pattern (Fig. 3(b)) also presents the weak $h0l$ reflections with $h=2n+1$ (one of which is marked by the open circle). These results clearly show that the ED patterns calculated from the $C2/c$ structural model nicely reproduce the experimental ED patterns. However, none of the ED patterns calculated from the $C2$ structural model demonstrates the extinction of the $00l$ reflections with $l=2n+1$.

To further confirm that BiMnO_3 indeed forms the $C2/c$ structure, we also carried out the HRTEM studies. The most informative images are obtained along the $[1\ 1\ 0]$ zone axis. Fig. 4 shows the calculated images along this zone axis as function of thickness for several defocus values to be used for the analysis of HRTEM images. The experimental images, taken from regions in different thickness, are perfectly in agreement

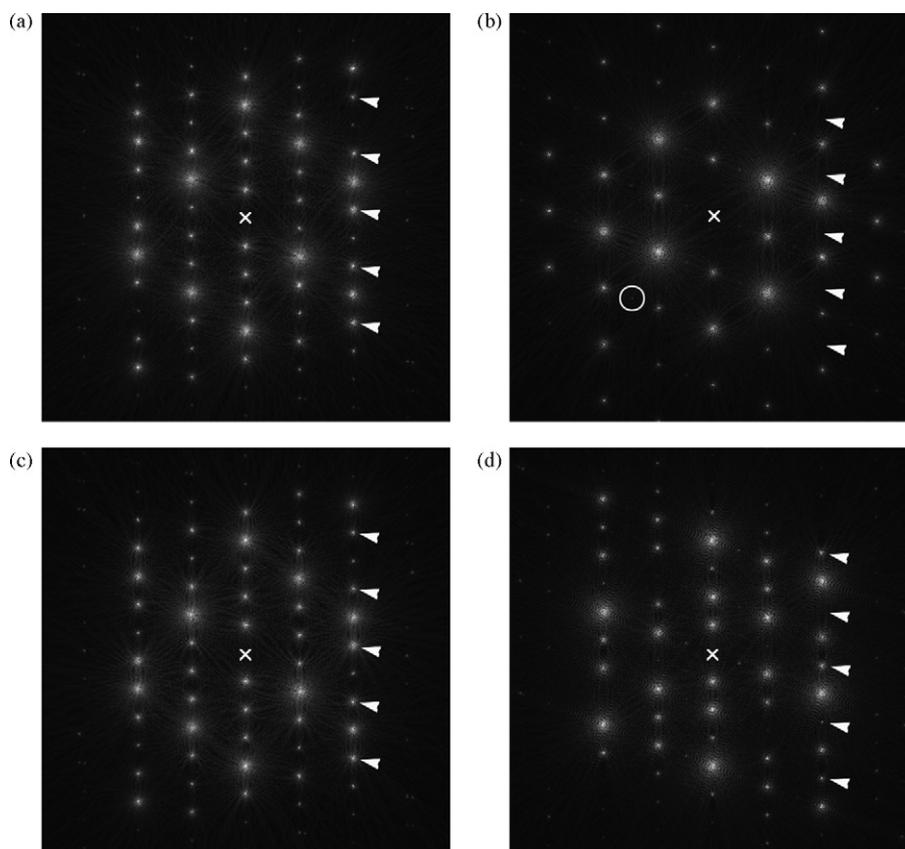


Fig. 3. (a and b) $[1\ 1\ 0]$ and $[0\ 1\ 0]$ zone-axis ED patterns calculated from the $C2/c$ structural model. (c and d) $[1\ 1\ 0]$ and $[0\ 1\ 0]$ ED patterns calculated from the $C2$ structural model.

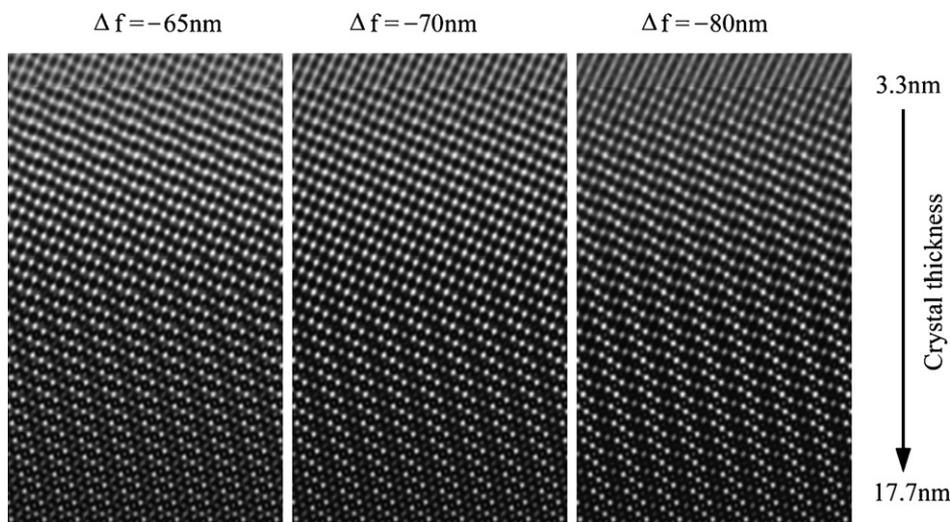


Fig. 4. Calculated [1 1 0] zone-axis images as function of thickness for several defocus values.

with these simulated images. An example of an image, taken under the defocus value of approximately -70 nm, is given in Fig. 5. A simulated image for a thickness of 15.4 nm and a defocus value of -70 nm is superimposed onto the experimental image to produce the good agreement.

Our experimental and theoretical studies demonstrate that at room temperature BiMnO_3 crystallizes in the centrosymmetric $C2/c$ structure but not in the non-centrosymmetric $C2$ structure. This work is very important for the further studies of BiMnO_3 and structurally related compounds. In addition, we would point out that no trace of other polymorphs of BiMnO_3 was detected in our as-prepared sample by TEM investigation, but under strong

and long-time electron beam irradiation the $C2/c$ structure was found to be able to transform to other modulated superstructures, and such phase transformations have been revealed to be the loss of oxygen caused by irradiation [21–23].

4. Conclusions

Selected area ED, HRTEM and theoretical simulations have been used to characterize the structure of the high-pressure synthesized perovskite-type BiMnO_3 . The experimental and theoretical data reveal that at room temperature BiMnO_3 forms the centrosymmetric $C2/c$ structure instead of in the non-centrosymmetric $C2$ structure. This work is very important for the further studies of BiMnO_3 and structurally related compounds.

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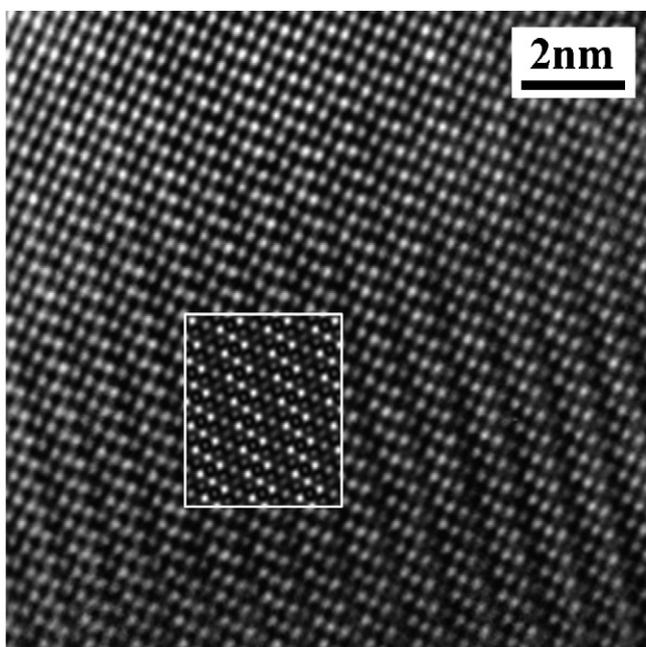


Fig. 5. [1 1 0] HRTEM image taken under the defocus value of approximately -70 nm. A simulated image for a thickness of 15.4 nm and a defocus value of -70 nm is superimposed onto the experimental image to produce the good agreement.

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