2030
doi:10.1017/S1431927622007875
Microsc. Microanal. 28 (Suppl 1), 2022

Evolution of Superstructure Demarcated with Heterointerface and Polymorphic Transformation in $BiMnO_3$ Compounds

Satyam Choudhury*, Vishnumahanthy Mohan, Avnish Singh Pal, Rajiv Kumar Mandal* and Joysurya Basu*

Department of Metallurgical Engineering, Indian Institute of Technology (BHU), Varanasi, Uttar Pradesh, India

* Corresponding authors: satyamchoudhury.rs.met18@iitbhu.ac.in, rkmandal.met@iitbhu.ac.in, jbasu.met@iitbhu.ac.in

Self-assembled 2D superstructures with long range periodicity have attracted research interest due to their exciting physical properties in oxide based pervoskites. Bismuth transition metal oxides (BMO, M = Fe, Cr, Mn) gained immense importance as functional materials due to their multiferroic properties [1]. In Bi-Mn-O ternary phase diagram $BiMnO_3$ phase has been reported to be a high pressure compound [2]. As we vary the partial pressure of oxygen, either oxygen vacant sites are created or annihilated in combination with the change in the oxidation state on Mn-ion in order to maintain the charge neutrality in the compound. That is how these materials may find application in oxygen sensing devices [3]. The motivation of this work is to elucidate the assembly of superstructure, its constituents and interface characteristics at atomic scale in $BiMnO_3$ through transmission electron microscopy [4].

Synthesis of Bi-Mn-O compounds has been carried out through hydrothermal process. Equimolar amounts of bismuth nitrate pentahydrate [$Bi(NO_3)_3.5H_2O$] and manganese acetate [$Mn(CH_3COO)_2$] were dissolved in nitric acid and de-ionised water to form solution. After homogenisation, ammonia stock solution was added drop wise under continuous stirring until the solution reaches the desired pH value of 11. The resultant mixture was filled into a Teflon lined chamber with 70% filling capacity and then was loaded into a stainless steel autoclave. It was placed inside a muffle furnace and was heated at 180°C under autogenous pressure for 72 h. As synthesised powder was collected by centrifuge, washed with repeated cycles of de-ionised water and ethanol followed by vacuum filtration than drying at 50°C on a hotplate overnight. X-ray diffraction (XRD) studies on selected sample reveal signature of orthorhombic $BiMnO_3$ phase with lattice parameter a = 5.391 Å, b = 7.499 Å, c = 5.365 Å as reported earlier by Calestani et al. in 2014. Excessive peak splitting could be observed resulting from polymorphic variants of orthorhombic $BiMnO_3$ phase. Additionally, peaks corresponding to non-stoichiometric Bi-Mn-O phase have been observed. However, unique indexing of the XRD pattern is difficult due to multiple phases.

To establish better correlation with XRD data, studies through complementary statistical sampling approach has been carried out to have better understanding about the structure confined to nano regime down to atomic scale. Electron diffraction with varying probe size coupled with diffraction contrast imaging (DCI) on synthesised sample confirms the signature of in-plane rotated orthorhombic $BiMnO_3$ phase projected along [010] axis with lattice parameter in well correlation with XRD data. DCI reveal signature of lattice fringes corresponding to superstructure acquired at relatively lower magnification along [010] zone axis (ZA). High resolution phase contrast image reveals signature of three distinct polymorphs of $BiMnO_3$ phase with slight deviation in lattice parameter. Assembly of 4a×4c superstructure is clearly observed along [010] ZA. Signature of strain field could be observed at the interface of consecutive superstructure along [100] and [001]. This may be due to polymorphic transformation at the interface supported with octahedral distortion. In depth analysis along with high

resolution simulation through JEMS confirms octahedral tilt ordering within the superstructure assembly [5].

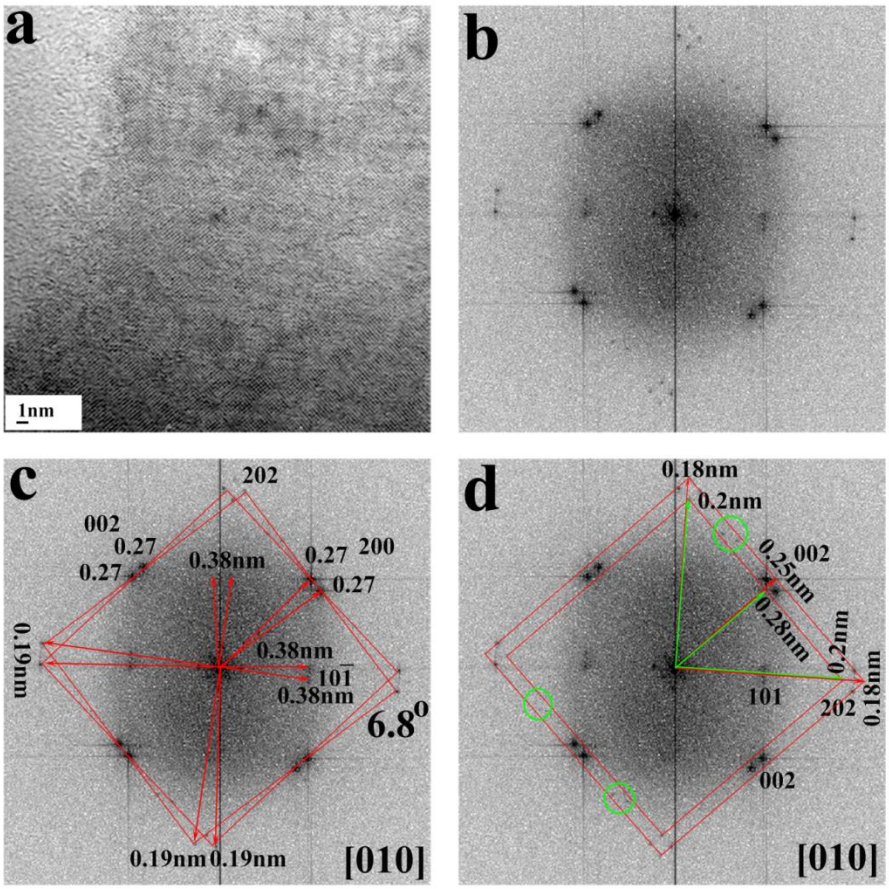

Figure 1. (a) Illustrate high resolution phase contrast image where atomic column is resolved, revealing signature of superstructure assembly. (b) Illustrate fast Fourier transformed (FFT) image acquired from phase contrast image. Analysis of FFT (c) reveal signature of in-plane rotated orthorhombic phase along [010] ZA and (d) signature of two distinct polymorphs of $BiMnO_3$.

References:

[1] Calestani et al., *Inorganic chemistry* 53, no. 16 (2014): 8749-8754.

[2] Sugawara et al., *Journal of the Physical …*, vol. 25. pp. 1553–1558, 1968.

[3] Meera et al., *J. Nucl. Mater.*, vol. 487, pp. 174–185, 2017.

[4] D. B. Williams and C. B. Carter, *Transmission Electron Microscopy*, vol. 5, no.721. 2009.

[5] The authors would like to acknowledge the financial support from UGC-DAE-CSR by the award number CSR-KN/CRS-94/2017-18/282.

[6] The author would like to acknowledge the support from Department of Science & Technology for FIST programme.

https://doi.org/10.1017/S1431927622007875 Published online by Cambridge University Press