Decrypting commensurate modulation, superstructure and inversion domain boundary in bismuth transition metal oxide through transmission electron microscopy

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Bismuth transition metal oxides (BMO, M = Cr, Mn) gained immense importance as functional materials due to their multiferroic properties [1]. In B-M-O ternary phase diagram BiCrO₃ and BiMnO₃ phases have been reported to be high pressure compounds [2], which are unstable at ambient temperature and pressure condition and transform to new structure with little variation in chemistry. This response is preferentially tuned by compositional fluctuation of one of its constituent element to impose changes onto sub-lattice of other two constituent elements, leading to redistribution of the atoms in 3D space. Phases specific to these systems exhibit wide range interesting functional properties such as fast oxygen ion conduction [3], candidate oxygen sensor material [4], etc. The motivation of this work is to elucidate the underlying short range order pervading through the bulk phase in Bi-Cr-O and Bi-Mn-O compounds.

Synthesis of Bi-Cr-O & Bi-Mn-O compounds were carried out through solid state and wet chemical synthesis route. Characterization of synthesised samples was carried out by X-Ray diffraction (XRD) and Transmission Electron Microscopy (TEM), which enabled us to correlate studies at different length scale implementing bulk and statistical sampling methods. XRD studies validated the presence of orthorhombic Bi₁₀Cr₂O₂₁, Bi₆Cr₂O₁₅, and BiMnO₃ phases, which has been reported earlier [5, 6].

Selected area electron diffraction (SAED) of appropriate interaction volume through systematic tilting facilitates us to validate the structure and commensurate modulation in Bi₁₀Cr₂O₂₁, Bi₆Cr₂O₁₅, and BiMnO₃ phases, which has been reported earlier [5, 6].

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Figure 1. (a) Diffraction pattern decorated with clear signature of basic and modulated unit (b) [011] ZA of basic unit is oriented parallel to [012] M ZA of modulated unit represents a clear case of commensurate modulation. (c) The simulated model defining the orientation relationship between basic and modulated unit have been approximately verified.
Figure 2. (a) Stripe contrast comprised of 20 fringes with alternate bright/dark contrast, thickness of each stripe equals 9.9 nm while inspecting along [001] zone axis. (b) Magnified image of stripes (c) Commensurately modulated unit comprised of four distinct units separated by 180° Inversion domain boundary parallel to (020)M (d) corresponding Fast Fourier transformed image.

References
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