Elucidation of Crystal Structure of $BiCrO_3$ Structural Derivatives with Transmission Electron Microscopy

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Recently Bismuth transition metal based oxide systems (Bi-M-O system, M = Fe, Cr & Mn) gained immense importance as functional materials due to their multiferroic properties. Many studies were carried out on $BiFeO_3$ and $BiMnO_3$ whereas, $BiCrO_3$ is the least investigated compound of the series. In Bi-Cr-O phase diagram $BiCrO_3$ was reported to be high pressure compound which is unstable at ambient pressure as the oxygen partial pressure changes, the compound undergoes structural modification (in terms of its chemistry and defects), which in turn leads to significant change in the electrical properties hence, enabled this system to be applicable as good oxygen sensor materials. Along with this Bi-Cr-O compound may be used as thin film coating for protection against liquid metal coolant (Na, Pb-Bi eutectic) in nuclear reactors. Due to the multiple oxidation state of chromium, several nonstoichiometric phases have been reported around $BiCrO_3$ compound, the crystal structure of which is not understood. However, in depth understanding of structure of such phases is essential in order to exploit this material in technological applications.

4:1 molar ratio of high purity Bi_2O_3 (99.9% purity) & Cr_2O_3 (99.9% purity) powder mixture was heated from ambient temperature to 500^0 C inside muffle furnace, at this temperature it was held for 14 hours, then it was heated from 500^0 C to 800^0 C & it was held for 24 hours finally, the sample was furnace cooled to ambient temperature. The prepared sample was then characterized with the help of X-Ray Diffraction (XRD) technique. Most of the XRD peaks match with that of the compound $Bi_7CrO_{12.5}$ which was reported earlier to be cubic phase by Popel et al., during 1990. Excessive peak splitting is observed in the XRD pattern.

The structure of the phase was further investigated by electron diffraction in transmission electron microscope (TEM). The electron diffraction patterns were complicated and systematic modulation of intensity of the spots was observed. Selected Area Diffraction pattern (SADP) obtained by systematic tilting from different zones validated existence of cubic phase in our prepared sample. The relationship and the modulation in the intensity distribution of the spot patterns clearly represent a case of commensurately modulated structure. There was a modulating unit cell which repeats itself on every sixth modulating unit cell and each of these modulating structures was different in terms of defects and its chemistry. These modulating structures serve as part of modulated structure whose orientation relationship with respect to the modulated unit cell was well studied by overlaying the stereogram's corresponding to both the structures. Space group, point group of this phase were studied along with symmetry breaking transition with the help of Convergent Beam Electron Diffraction (CBED). Finally, it can be concluded that the phase which we characterized through different techniques of TEM in our prepared sample are structural derivative of $BiCrO_3$.

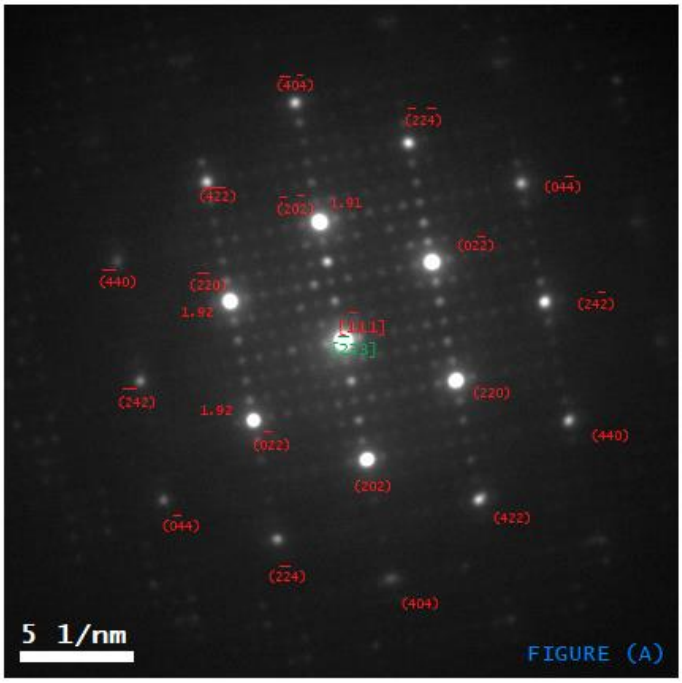

Figure (A). Indexed SADP clearly represents a case of commensurate modulation. Where [-111] zone axis corresponds to modulating structure which is oriented parallel to [-233] zone axis of modulated structure.