

## Structure and Chemistry of La Doped BiFeO<sub>3</sub> Multiferroic Thin Film

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Materials with coupled electric, magnetic and structural order parameters, which result in simultaneous ferroelectricity, ferromagnetism and ferroelasticity are known as multiferroic materials [1]. These materials are the potential candidates for applications in spintronics, memories and sensors. Many of these potential materials contain lead. It has been a major challenge in the scientific community to discover lead free ferroelectric materials due to the environmental concern. In the recent past BiFeO<sub>3</sub> has attracted research interest as it has promising properties and it is lead free [2-3]. The properties can be improved further by suitable replacements of the cations in the BiFeO<sub>3</sub> parent lattice.

Structure and properties of bulk single crystal BiFeO<sub>3</sub> has been studied extensively. This material at the room temperature has a distorted rhombohedral structure. The material has found limited application till date as the transport properties are hampered by leakage problem in the bulk, which might be attributed to the presence of defects and nonstoichiometry. A plausible solution to this problem is to dope the material, which will result in the substitution in the cationic site. Apart from that in thin films and in heterostructures generation of interfacial stress, change in crystal structure may also play a role in altering the properties of pure or doped BiFeO<sub>3</sub>.

In the present work La doped (0.1-0.3 at%) BiFeO<sub>3</sub> thin film has been synthesized by solution based technique. In this technique nitrate salts of Bi, Fe and La dissolved in glacial acetic acid and methanol were mixed together and spin coated onto an ITO substrate. After several spin coating process, the coating was dried at 400 °C in air and annealed at 650 °C in nitrogen to obtain the thin film. In order to characterize the films, they were FIB sectioned with a FEI Strata 400s Dual Beam FIB and observed in JEOL 2010 FasTEM. The chemical nature of the films and the interfaces were characterized by FEI Tecnai T12 TEM equipped with STEM and EDS.

It has been observed from the study that the film is ~600 nm thick with a clearly defined interface with the ITO (Figure 1). A number of pores, which might have been generated during annealing due to the change in volume have been observed. The pores are ~100-300 nm in size. The films appear to be almost fully crystalline at all doping levels of La. Small amorphous regions around the grain body could be observed (Figure 2). The films are polycrystalline with randomly oriented BiFeO<sub>3</sub> grains. A structural change with the change in doping level could be observed. High-resolution diffraction contrast indicates that the grain boundary region may be strained, but it is not possible to quantify the strain at this stage. STEM-EDS chemical mapping indicates that the interfaces are chemically sharp; no elemental segregation or formation of a second phase could be observed (Figure 4). The chemistry of the film is uniform across the thickness of the film (Figure 3). The fluctuation in the elemental line profile that has been observed across the depth of the film falls within the error limit of EDS line profile analysis.

It can be concluded from the study that homogeneous phase-pure and La-doped  $\text{BiFeO}_3$  thin film can be deposited onto ITO substrate by solution based technique. The film is often porous which might be attributed to the volume change, taking place during annealing. This might affect the functional properties of the film considerably. The interfaces are chemically and structurally sharp. No reaction, interdiffusion or second-phase formation could be observed. The chemistry of the film is uniform across the depth of the film. These observations indicate that these microstructural attributes also should be considered while characterizing the functional properties of pure and doped  $\text{BiFeO}_3$ .

#### References

- [1] V. R. Singh et al., Appl. Phys. Lett. 92 (2008) 152905
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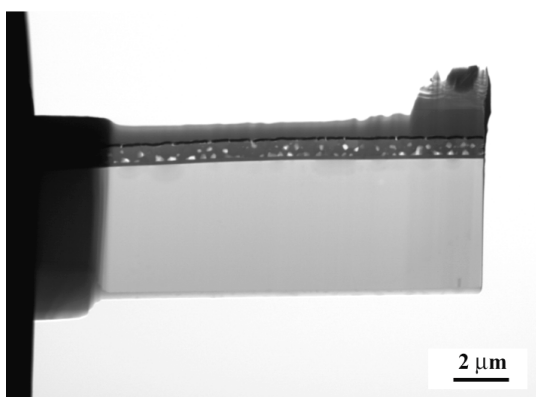


Figure 1: STEM image of the FIB section of the pure  $\text{BiFeO}_3$  thin film on ITO. The interface is structurally sharp and the film is porous.

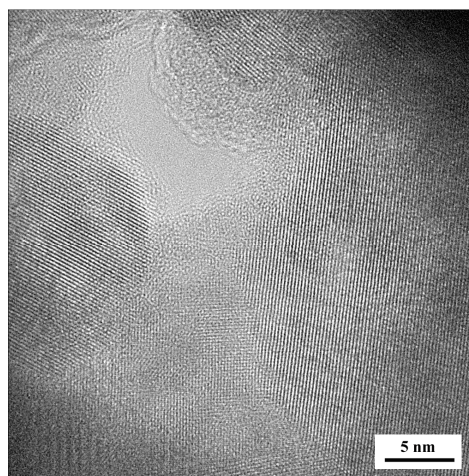


Figure 2: HRTEM image of 0.2 at% La doped  $\text{BiFeO}_3$  film. The film is polycrystalline. A thin amorphous layer is seen at the grain boundary.

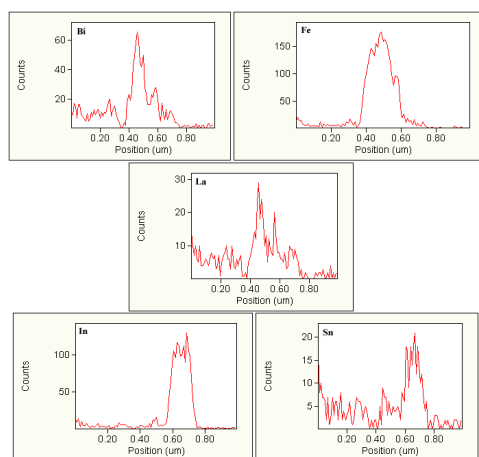


Figure 3: STEM-EDS line profile of 0.1 at% La doped  $\text{BiFeO}_3$  thin film. The elemental distribution across the depth of the film is uniform.

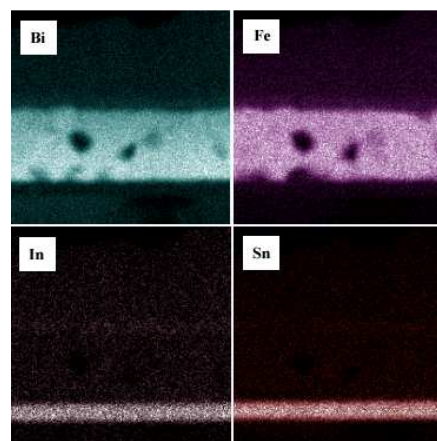


Figure 4: STEM-EDS map of pure  $\text{BiFeO}_3$  film on ITO. The interface is chemically sharp and porous structure is clearly visible.