Electronic Structure studies on Ca-doped $BiFeO_3$ Multiferroic films using X-ray Absorption Spectroscopy

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Introduction

Multiferroic materials exhibit coexisting polar and magnetic orders have unique and interesting properties useful for various applications involving spintronic devices, storage devices, sensors, high-density memory and multi-state electronic devices, etc. [1]. Amongst various multiferroics studied till date, $BiFeO_3$ (BFO) has emerged as the most promising candidate. Pure BFO is characterized by serious leakage problems arising due to the presence of small amount of Fe^{2+} ions and oxygen vacancies [2], which makes it practically unusable. Several methods have been suggested to reduce the leakage current, such as, annealing of BFO films in oxygen environment and doping with rare earth and divalent ion [3]. Substitution on A - site is more important as it reduces the number of Bi^{3+} ions which further reduces the $6s^2$ lone pairs in the system. The present study on, the investigations of the electronic structure, dielectric and magnetic properties of Ca-doped $BiFeO_3$ films is of major importance for understanding electronic structure as well as the effect of doping, role of defects and their interaction with Fe – ions, on the magnetic and electrical properties.

Methods

$Bi_{1-x}Ca_xFeO_3$ (BCFO) (x = 0.05, 0.10, 0.20) films were deposited on single crystalline 1 at % Nb-doped $SrTiO_3$ [$SrTi_{0.99}Nb_{0.01}O_3$] *(100)* oriented substrate using pulsed laser deposition (PLD) technique. KrF excimer laser (λ=248 nm) with an energy of ~ 230 mJ and repetition rate of 5Hz were used to ablate material from the stoichiometric targets of BCFO. During the deposition, oxygen partial pressure was maintained at ~100mTorr and substrate temperature was kept constant at ~650°C. Modification in the dielectric behavior with Ca – doping concentration has been studied using impedance spectroscopy. The electronic structure of all the BCFO films has been studied using Soft X-ray Absorption Spectroscopy (SXAS) measurements in total electron yield (TEY) mode at O K – edge and Fe $L_{3,2}$ – edge.

Result and Discussions

Structural study using XRD shows highly a-axis oriented growth of the films. Shifting of (200) peak towards higher angle indicates relaxation in strain with Ca – doping. Film thickness was estimated to be ~ 53 nm by fitting the X-ray reflectivity data. Fe $L_{3,2}$ – edge spectra of all the films matches well with that of Fe_2O_3 indicating the presence of Fe^{3+} valence state which has been further confirmed through the simulated XAS spectra of $FeL_{3,2}$ – edge. The observed changes in O K-edge XAS spectra have been attributed to modification in the hybridization states between O2p and Fe3d, Bi6s and Ca4s orbitals. The significant changes in temperature dependence of magnetization may be due to magnetic disorder phase induced by divalent Ca.

Conclusion(s)

BCFO films were successfully grown using PLD technique. XRD and ϕ- scan measurements confirm the epitaxial *(100)* oriented growth of the films. XAS spectra at Fe $L_{3,2}$ – edge confirms the presence of Fe^{3+} valence state. Normalized O K-edge XAS spectra of BCFO films show significant change in the O 2p states hybridized with the Fe 3d, Bi 6s, and Ca 4s states. Fitting of the Nyquist plots using R-CPE model indicate the interface and film contribution over the grain and grain boundary relaxation and is to be non – Debye type. Magnetic measurements show magnetization irreversibility with increase in Ca – doping concentration, which is mainly observed due to the magnetic anisotropy and competing magnetic interactions between Fe – O – Fe.

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