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Research articles

Spin-phonon coupling in Mn-Bi co-doped $SmFeO_3$: An experimental study

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ABSTRACT

The intriguing physical properties of $SmFeO_3$ such as spin-phonon coupling and spin reorientation transition (~480 K) make it interesting from fundamental point of view and a suitable candidate for oxide-based spintronic applications. Here, we have studied the temperature dependent structural, vibrational, and magnetic properties of polycrystalline $Sm_{0.9}Bi_{0.1}Fe_{0.9}Mn_{0.1}O_3$ prepared by conventional solid-state reaction method. The compound stabilizes in orthorhombic structure with space group "*Pnma*" and exhibits no structural phase transitions in the investigated temperature range (300–500 K). Magnetic measurements reveal the weak ferromagnetic–paramagnetic transition at 620 K. Thermal evolution of phonon modes investigated using Raman spectroscopy in the temperature range 300–800 K reveal that $A_g(3)$ phonon mode related to FeO_6 vibrations exhibits anomalous behaviour below magnetic transition temperature, which we attribute to spin-phonon coupling. The optical band gap value of ~ 5.17 eV has been estimated from the analysis of UV–Vis diffuse reflectance spectroscopy using the Tauc relation. The value of $\Delta E_{t2u \to t2g}$ is estimated to be ~ 2.6 eV for *p-d* charge transfer transitions in Fe/MnO_6 octahedra. The obtained valence states from X-ray photoelectron spectroscopy analysis of all the elements of the sample are in excellent agreement with the expected values.

1. Introduction

Rare-earth orthoferrites exhibit a wide variety of properties including magnetization reversal [1], magnetic field and/or temperature-induced spin reorientation transition (SRT) [2], spin-phonon coupling [3], multiferroicity [4] and magneto-optic coupling [5]. These fascinating properties make them potential candidates for various technical applications like magnetic sensors and magnetoelastic devices, etc. [6]. Rare-earth orthoferrites ($RFeO_3$) usually crystallize in a distorted orthorhombic structure with Pnma/Pbnm space group [7]. Fascinating magnetic properties of $RFeO_3$ compounds emerge from the independent contribution of 4f electrons of rare-earth ions and 3d electrons of Fe ions and interplay between them [8]. The magnetic response of Fe ions is weakly ferromagnetic, which arises due to the canted Fe spins (canted antiferromagnetism (AFM)) and this behavior usually dominates at relatively higher temperatures (above 140 K) [2,8]. Moreover, rare-earth ions exhibit antiferromagnetic long range ordering at very low temperature (~ 5 K) and the onset temperature of R-Fe interactions is around ~ 100 K (highest for $SmFeO_3$ ~ 140 K) [9,10]. The competing interactions between spin moments of rare-earth and iron cations are the main mechanism leading to temperature-induced magnetic transitions [11]. Physical properties of orthoferrites can be tuned by structural modification such as tilting of FeO_6 octahedra. Octahedral tilting can be estimated by the analysis of X-ray diffraction (XRD) spectra (using ⟨Fe-O-Fe⟩ bond angle) and with Raman spectroscopy (new phonon modes emerge due to tilting of FeO_6 octahedra) [3]. Raman spectroscopy is a powerful technique to probe many interesting properties, i.e., spin-phonon coupling, octahedral distortion, and strain-dependent structural changes in thin films, etc. [12–14]. According to theoretical predictions by Fennie et al. [15], spin-phonon coupling, strain, and optical modes together can induce multiferroicity. Later on, Lee et al. [16] demonstrated these predictions experimentally on $EuTiO_3$ thin films and observed multiferroic behavior by tuning the biaxial strain.

Among all rare-earth orthoferrites, $SmFeO_3$ is found to manifest outstanding characteristics like highest spin reorientation transition

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