Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Temperature dependent Raman scattering and electronic transitions in rare earth $SmFeO_3$

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ARTICLE INFO

Keywords:
Orthoferrite
Reitveld refinement
Raman scattering
Electronic transition
Poling induced magnetic modulation

ABSTRACT

Emerging interdisciplinary fields of multiferroics and spin-optronics demand for new oxide materials that unfolds significant coupling between electric and magnetic order at room temperature, preferably with controlled optical properties. Rare-earth orthoferrites ($RFeO_3$) have received much attention due to their coupled electric, magnetic and optic properties. Here we report structural, optical, temperature-dependent (83–800 K) Raman spectroscopy, electronic transition analysis and electric poling induced magnetic modulation in nanostructured $SmFeO_3$ (SFO). Rietveld refinement of SFO confirmed the orthorhombic phase (space group D_{2h}^{16}, *Pbnm*) with expanded lattice parameters (a_o = 5.3979 Å < b_o = 5.5922 Å < c_o = 7.7104 Å). Microstructural analysis revealed the formation of uniformly distributed spherical grains of 40 ± 2 nm size. First-order 18 Raman active vibrational phonon modes identified using damped harmonic oscillator model suggested the main activity in SFO lies between 100 and 650 cm^{-1}. Above 483 K, clear fading of high frequency mode (~ 632 cm^{-1}) due to spin-reorientation and fusion in low frequency modes (~132 cm^{-1}) around 673 K is considered as direct evidence of possible phase transition from antiferromagnetic to paramagnetic order. Optical response in studied spectral range from 200 to 800 nm is dominated by two (*p-d*) and (*d-d*) charge transfer transitions, which favors strong exchange interaction as well as high magnetic transition temperatures. Large observed bandgap E_g of 5.21 eV, determined from diffuse reflectance Uv–visible spectroscopy in combination with the electric poling induced magnetic modulation establish SFO, a suitable oxide material for future power efficient microelectronic and spin-optoelectronic devices.

1. Introduction

Round the globe, renewed research interests in rare-earth orthoferrites $RFeO_3$ where R stands for rare-earth element is witnessed on account of their profound fundamental characteristics like temperature and/or electric-field controlled magnetic properties modulation [1,2], spin-reorientation [3], magneto-optical effects [4] and all are driven by asymmetric exchange interaction between R-*4f* and Fe-*3d* electrons in such complex compounds. Moreover, recognition of high-frequency magnetization precession [5], stable dielectric as well as charge transport properties over a wide range of frequencies [6,7], and photocatalytic activities [8] make them imperative for wide range of technological applications. Among such various orthoferrites, $SmFeO_3$ (SFO) is one of the most explored rare earth material which undergo for spin reorientation i.e. easy axis rotation transition at temperature of T_{SR} ~ 480 K [9] which is quite high in compare to others. SFO also exhibit exchange bias [10] as well as low magnetic field driven ultrafast magnetization switching [11] at room temperature. In addition to this, a coexistence of both ferroelectric as well as magnetic ordering is also observed in certain reports of SFO, which otherwise considered to be non-ferroelectric in nature [9,12,13]. In particular, spin-orbit-coupling controlled reverse Dzyaloshinskii-Moriya interaction in SFO single crystal [9] and interfacial strain in epitaxial SFO/Nb-$SrTiO_3$ bilayer structure [12] is attributed for improper electric polarization. In addition polarization-electric field (P-E) hysteresis loop is also observed in case of polycrystalline SFO ceramic samples owing to non-centrosymmetric phase $Pna2_1$ formation [13]. However, such experimental evidences of ferroelectric nature in SFO are still highly debated as inspecting from the lattice symmetry, SFO crystallizes in ABO_3-type centrosymmetric orthorhombic perovskite (space group D_{2h}^{16} or *Pbnm*) with four Sm and four Fe ions per unit cell [14] which forbid such behavior. Some researchers have also reported magneto-electric (ME)

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https://doi.org/10.1016/j.ceramint.2017.11.223
Received 22 October 2017; Received in revised form 30 November 2017; Accepted 30 November 2017

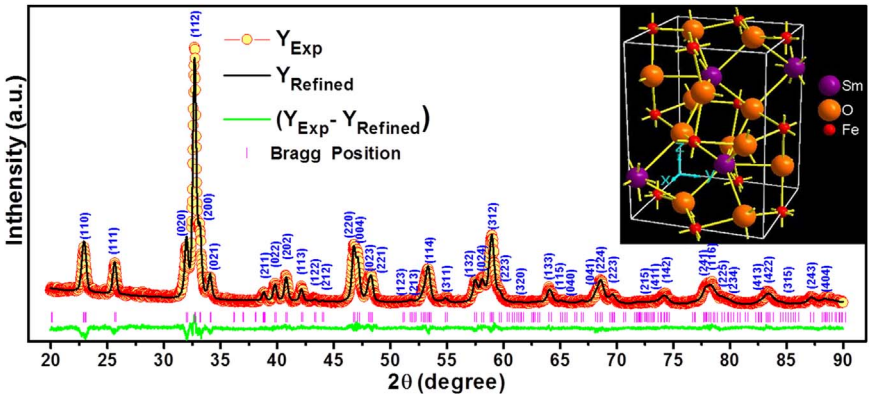

Fig. 1. Experimentally observed and simulated XRD patterns of SFO with Miller indices in *Pbmn* symmetry after final Rietveld least squares minimization. Inset shows 3D unit-cell crystal structure of SFO, projected in x-y plane.

properties for polycrystalline samples with ME voltage coefficient in 2–5 mV cm^{-1} Oe^{-1} range at room temperature [15,16]. Despite the collection of wide literature that exist on various properties of SFO ceramic, temperature dependent vibrational-phonon dynamics, optical properties like energy band gap, charge transfer electronic transitions and also converse ME investigations are still missing. In present paper, a comprehensive effort is paid to understand temperature dependent variations in vibrational phonon modes, optical properties and the possibility of electric field controlled magnetic properties of pure phase SFO electro-ceramics. In-detail Reitveld refinement and scanning electron micrographs concludes high phase purity, distorted orthorhombic structure with stretched lattice constants and nanometer size spherical grains formation throughout the ceramic matrix. Raman scattering spectroscopy over a wide temperature range from 83 to 800 K, excited at 514.5 nm evidently unveils the strong spin-phonon coupling in SFO. Identification of maximum first order phone modes is carried out using damped harmonic oscillator model. Further observation of electric poling induced visible changes in coercive field as well as magnetization of SFO at room temperature explores the potential of orthoferrites as new multifunctional materials, desirable for power-efficient memory storage, ultra-fast photo-magnetic detectors, microelectronic devices etc.

2. Material, experimental and characterization details

Polycrystalline SFO ceramic is synthesized using low temperature co-precipitation technique. Stoichiometric mixture (1:1 M ratio) of Sm $(NO_3)\cdot 6H_2O$ and $Fe(NO_3)\cdot 9H_2O$ (High purity > 99.95%) is dissolved first in 2-methoxy ethanol with continuous stirring, followed by the addition of optimal amount of both glacial acetic acid and N,N dimethyl formamide at room temperature tin order to stabilize the precursor solution. Afterwards, concentrated ammonia is added till pH of the solution approached to 11 and thus obtained precipitate is washed several times with distilled water so that pH value turned to 6.5–7.0. Later powder is calcined at 1000 K for 2 h using programmable furnace with heating/cooling rate of 5 K/min. After thorough mixing of calcined powder with 5 wt% polyvinyl alcohol binder, the dry powder is pressed into circular pellets (diameter ~ 13 mm) by applying an uniaxial pressure of 6 t/in^2. Thereby obtained pellets were heated at 670 K to evaporate the binding agent and sintered at 1025 K for 5 h. Crystallographic structure and phase purity was examined by Rigaku Ultima III X-ray diffractometer equipped with CuKα radiation (λ = 1.5405 Å) source operating at default parameters of 40 kV and 40 mA. X-ray diffraction (XRD) pattern of the SFO pellet is recorded in 20–90° range with scan speed of 0.2°/min. The grain size distribution and surface topography is taken in 25,000× and 130,000× magnifications using field emission scanning electron microscope (SEM, JEOL) in vacuum, operating at 15 kV. Temperature dependent (83–800 K) Raman spectroscopy is carried out using a Jobin Yvon T64000 Raman spectrometer equipped with a triple-grating monochromator. The power of monochromatic green radiation at 514.5 nm emitted by air cooled Coherent Innova 90 C Ar^+ ion laser is kept 10 mW at polished sample surface to avoid sample heating. SFO sample is mounted on cooling–heating stage, placed in vacuum and temperature is varied in temperature window of 83–800 K with a heating rate of 10 K/min using Linkam TP93 and TMS94 temperature controllers and LN_2 cooling module. All micro-Raman scattered light signals are detected in back-scattering geometry with subtractive mode using LN_2-cooled charge-coupled device through an 80× objective. The spectral data is collected with increment of 1 cm^{-1} and an integration time of 10 s to obtain high signal-to-noise ratio. To complete the optical and electronic transition analysis, room temperature diffuse reflectance (R) spectra is recorded in wavelength range of 190–800 nm using Varian Cary UV–Vis spectrophotometer having a wavelength accuracy of ± 1 nm resolution. In addition, electric-poling induced magnetic modulation is probed which highlights its intriguing magnetic properties with extra degrees of control. Thereby, to fabricate metal-insulator-metal (MIM) capacitor structure, 100 nm thick Pt is sputtered (DC power: 20 W, Argon pressure: 20 mTorr) on opposite surfaces of polished 0.46 mm thick SFO pellet at room temperature. Afterward the fabricated Pt/SFO/Pt (MIM) capacitor structure was dried at 500 K to ensure better Pt adhesion. An external poling field (E_P) in steps of 0, 15 and 30 kV/cm is applied before performing room temperature magnetic hysteresis measurement up to maximum applied field of ± 17 kOe using vibrating sample magnetometer (Lakeshore).

3. Results and discussion

3.1. Crystallography analysis using X-ray diffraction

Fig. 1 depicts the RT-XRD pattern of polycrystalline SFO sample in 20° ≤ 2θ ≤ 90° range and confirms the single phase and highly crystalline nature of grown SFO sample with no phase segregation and formation of any other stoichiometry (like $Sm_3Fe_5O_{12}$) within the instrument sensitivity. Observed Bragg reflections are Miller indexed and found to be matching perfectly with the Powder Diffraction Standards (JCPDS) Card No. #74-1474 described by *Pbnm* space group (D_{2h}^{16}, No. 62) [17]. The crystallographic structure simulations including refinement of lattice constants, atomic position coordinates is further performed using Rietveld refinement based on FullProf Suite software package in Young's strategy [18]. Considering atomic site symmetries of space group *Pbnm* in structural model, 5 out of 12 atomic coordinates were kept fixed as Sm at 4c (C_s^{xz} symmetry) (−0.01213 0.05567 1/4), Fe at 4b (C_i symmetry) (1/2 0 0), O(1) at 8d (C_s^{xz} symmetry) (0.10398 0.46987 1/4) and O(2) at 8d (C_1 symmetry) (−0.29247 0.29810 0.04256) [19]. This allowed us to reproduce all the observed reflections of same intensities having a close agreement of fitting (χ^2 ~ 1.9) between simulated and experimental XRD pattern as shown in Fig. 1. Here red solid circles are the experimental data points (Y_{Exp}), the black solid line is the refined pattern ($Y_{Refined}$) and bottom green curve reflects the