Characterization and thermal expansion of Sr$_2$Fe$_{1-x}$In$_x$MoO$_6$ (x=0.0, 0.1 and 0.4 wt. %) double perovskites

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Abstract. Double perovskite oxides of Sr$_2$Fe$_{1-x}$In$_x$MoO$_6$ (x = 0.0, 0.1 and 0.4 wt. %) were prepared by sol-gel growth followed by annealing under reducing atmosphere conditions of 10% H$_2$/Ar flow. These samples were characterized by X-ray diffraction, Scanning Electron Microscopy and Electron Spin Resonance studies. High temperature thermal expansion studies were carried out using Netzsch 402PC dilatometer in the temperature range from 40 to 400°C. The coefficient of thermal expansion (α) was calculated at different temperature for all the samples. The value of α was found to increase with increase of temperature while average value of coefficient of thermal expansion found to decrease with indium composition in SFIMO materials.

1. Introduction

The double perovskite oxides of the type A$_2$BBꞌO$_6$ (where A is divalent cations such as Sr, Ca and Ba; B is tri/divalent cations such as Fe, Cr, Ga, Mg and Mn; Bꞌ is penta/hexa valent cations such as Mo, Re and W;) have been extensively studied for the past several years due to their substantial Low Field Magneto Resistance (LFMR) at room temperature that lead to potential applications of these materials as magnetic field sensors, read heads for magnetic hard disk drives and nonvolatile magnetic computer memory[1–6]. Several investigations were carried out in order to understand the magnetic structure and magnetoresistance of Sr$_2$FeMoO$_6$ by doping with different elements such as Ga, Ni, Mg and Cr, at Fe site [3–6]. However, there are no studies done so far on thermal expansion of double perovskites except on stoichiometric Sr$_2$FeMoO$_6$ [7]. In view of this, the authors have prepared Sr$_2$Fe$_{1-x}$In$_x$MoO$_6$ (x=0.0, 0.1 and 0.4 wt.%). These materials were characterized by various experiments such as X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Electron Spin Resonance (ESR) and thermal expansion studies were made.

2. Experimental

Double perovskite samples of Sr$_2$Fe$_{1-x}$In$_x$MoO$_6$ (x = 0.0, 0.1 and 0.4 wt.%) (SFIMO) were synthesized by sol-gel method using stoichiometric amounts of AR grade Sr(NO$_3$)$_2$, Fe(NO$_3$)$_3$9H$_2$O, In$_2$O$_3$ and H$_2$MoO$_4$ were used and powders of SFIMO are obtained. The details of method of preparation of the materials are given in earlier publication [8]. The powders of SFIMO were pressed into rectangular
pellets of dimensions 25\,mm \times 6\,mm \times 6\,mm using a dies and a hydraulic press by applying a pressure of 5\,ton/m^2. These pellets were sintered at 1200°C for 6 hours and then heated at 1000°C in a stream mixture of 10% \,H_2 / Ar gas for about 3 hours for reducing the \,Mo^6^+ to \,Mo^5^+. These pellets were subjected to XRD studies using Philips PW 1830 generator diffractometer with Cu Kα radiation (40kV×25mA) and graphite monochromator in order to confirm the structure. The surface morphology and micro structural studies of the samples were carried out using the SEM with (Model No. Joel JSM-5600) combined micro analyzer. Room temperature ESR spectra were recorded on a JOEL−1X−ESR X-band spectrometer equipped with a 100 kHz field modulation unit and operating at 9.5 GHz. Thermal expansion measurements were performed using Netzsch 402PC dilatometer in air from 40 to 400°C during heating cycle.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of SFIMO samples along with (hkl) values of reflections are shown in Figure. 1. All the XRD profiles of SFIMO were indexed and found to be single phase double perovskite structure [5]. These materials were found to crystallize in tetragonal crystal structure with space group I4/mmm. The lattice parameters a and c of SFIMO compounds were evaluated using 2θ and (hkl) values of XRD profiles shown in Figure 1. These values are given in Table 1. The unit cell volume of SFIMO compounds were also calculated using the relation V=a^2\,c and included in Table 1. It is found from Table 1 that the values of unit cell parameters of indium doped samples (x=0.1 and 0.4 wt.%) is found to be larger compared to \,Sr_{2}\,Fe_{1-x}\,In_{x}\,MoO_{6}. This may be due to the substitution of the larger \,In^{3+} (0.79Å) ions into the smaller \,Fe^{3+} (0.645Å) ionic sites.

Table 1. The values of lattice parameters (a and c), unit cell volume (V), g-factor, constants A, B, C values of eq.(2) and average coefficient of thermal expansion ($\alpha$) in the temperature range 40-400°C of \,Sr_{2}\,Fe_{1-x}\,In_{x}\,MoO_{6} (x=0.0, 0.1 and 0.4 wt.%) double perovskites.

| Com(x) | 0.0    | 0.1    | 0.4    |
|--------|--------|--------|--------|
| a (Å)  | 5.569  | 5.615  | 5.603  |
| c (Å)  | 7.989  | 7.927  | 7.921  |
| V (Å)^3| 244.982| 249.987| 248.693|
| g-factor| 2.045  | 2.053  | 2.047  |
| A      | -4.31×10^{-4} | -4.00×10^{-4} | -2.99×10^{-4} |
| B      | 8.70×10^{-6}  | 6.10×10^{-6}  | 1.61×10^{-6}  |
| C      | 1.16×10^{-8}  | 1.68×10^{-8}  | 2.61×10^{-8}  |
| $\alpha$ (°C^{-1}) | 13.80×10^{-6} | 13.50×10^{-6} | 13.10×10^{-6} |

3.2. Scanning electron microscopy

The SEM photographs of SFIMO are shown in Figure. 2(a-c). The average grain size of each sample was estimated by taking an average of 10 grains. The estimated average grain sizes of SFIMO are varying between 2 – 3.5 μm for all compositions. It is also found that the value of grain size of
Sr$_2$FeMoO$_6$ is 2.19 against 1–2 reported by Leilei Zhang et al [7] which is slightly higher. This change may be due to different preparation method and sintering conditions.

3.3. Electron spin resonance

Figure 3(a-c) shows the ESR spectrum of SFIMO samples at room temperature. All the figures show a similar spectrum. A peak is resolved at around 310 mT. The $g$-factor of SFIMO samples were calculated using equation $g = \frac{h \nu}{\beta H}$, where $h$ = Planck’s constant, $\nu$ = frequency of magnetic field, $\beta$ = Bohr magneton and $H$ = Applied magnetic field. The calculated $g$-factor are given in Table 1. It is found that the $g$-factor of SFIMO samples vary between 2.045 to 2.053; which is due to the Fe$^{3+}$ ions. The measured $g$-factor, is clearly identified with a spin-only ground state. This resonance corresponds, in the band picture of Ref. [1], to the localized 3d$^5$ Fe cores.

3.4. Thermal expansion

The thermal expansion characteristics ($\Delta L/L_0$) of SFIMO were obtained using dilatometer in the temperature ranging from 40–400°C in air are shown in Figure 4. The thermal expansion depends on the electrostatic forces within the lattice, which depend on the concentration of positive and negative charges and their distances within the lattice [9]. The thermal expansion of a lattice with a certain structure and fixed oxygen to metal stoichiometry is characterized by a steady coefficient of thermal expansion (CTE), $\alpha$, caused by the thermal lattice vibrations. The experimental data of thermal expansion ($\Delta L/L_0$) as a function of temperature (T) of SFIMO in the present study can be fitted to a polynomial of degree 2 as
\[
\Delta L \over L_o = A + BT + CT^2
\]  

(1)

where A, B and C are the constants. The value of A, B and C obtained for different compositions of SFIMO were determined by fitting experimental data on \(\Delta L/ L_o\) with temperature T (°C) using eq.(1) and given in Table 1. The value of \(\alpha\) can be determined using the first derivative of eq.(1) with respect to temperature as

\[
\alpha = \frac{d}{dT} \left( \frac{dL}{L_o} \right) = B + 2CT
\]  

(2)

Eq.(2) shows that the value of \(\alpha\) at any temperature can be obtained using constants B and C. The average value of CTE (\(\overline{\alpha}\)) in the temperature range 40−400°C for all SFIMO materials are calculated and given in Table 1. It is observed from Table 1 that the value \(\overline{\alpha}\) increases with increase of temperature while decreases with increase of indium content. Falcon et al [10] investigated the oxidation profiles of Sr₂FeMoO₆₋ₓoxide. Their results showed that oxygen was relatively easily incorporated into the perovskite structure. With the increase in the oxygen vacancy concentration, oxygen permeation and lattice expansion become much more pronounced [11]. Therefore, in the present study the value of \(\overline{\alpha}\) increase with increase of temperature may be attributed to increase of concentration of oxygen vacancy. The \(\overline{\alpha}\) decreases with increase of indium composition may be due to decreases of covalent nature (increase of ionic nature) of SFIMO samples.

4. Conclusions

It has been found that the lattice parameters and unit cell volume increases with increase of indium content in SFIMO samples. The g-factor of SFIMO samples is about 2.04, which confirm the iron is in Fe³⁺ state. The value of \(\overline{\alpha}\) increases with temperature and decreases with indium content in SFIMO.

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Figure 4. The thermal expansion versus temperature of Sr₂Fe₁₋ₓInₓMoO₆ (x = 0.0, 0.1 and 0.4 wt.%) samples.