Preparation and Characterization of non-stoichiometric SrBaFe\textsubscript{x}Mo\textsubscript{2-x}O\textsubscript{6} (1.0 ≤ x ≤ 1.5) double perovskite

G Rajender\textsuperscript{1*}, Y Markandeya\textsuperscript{2}, A K Singh\textsuperscript{3} and G Bhikshamaiah\textsuperscript{1}

\textsuperscript{1}Department of Physics, \textsuperscript{2}Nizam College, Osmania University, Hyderabad-500007, India.
\textsuperscript{3}Defence Metallurgical Research Laboratory (DMRL), Hyderabad-500058, India.

*Corresponding author E-mail: grphyou@gmail.com,

Abstract

A series of non-stoichiometric amounts of SrBaFe\textsubscript{x}Mo\textsubscript{2-x}O\textsubscript{6} (x = 1.0, 1.2, 1.3, 1.4 and 1.5) (SBFMO) double perovskite samples have been prepared by conventional sol-gel method. The samples were subjected to X-ray diffraction studies and are found to crystallize in cubic structure with a space group \textit{Fm\bar{3}m}. Using X-ray diffraction data, the lattice parameters and the unit cell volume were determined and found to decrease with increase in content of Fe. Porous nature of materials has been studied using Scanning Electron Microscopy technique (SEM). Energy Dispersive X-ray Spectroscopy (EDS) of the present samples showed that Sr, Ba, Fe, Mo and O elements are present in the samples and non-existence of other impurities elements. The absorption bands observed in the range 400-1000 \textit{cm}^{-1} of Fourier Transform Infrared (FTIR) spectra indicates the presence of FeO\textsubscript{6} and MoO\textsubscript{6} octahedra and also confirms the formation of the double perovskite phase.

1. Introduction

Double perovskite oxide A\textsubscript{2}FeMoO\textsubscript{6} (A=Sr and Ba) doped with various elements at Fe site were extensively studied for low field magneto resistance (LFMR) and magnetization [1-17]. These materials find potential applications in devices used for magnetic sensors, magnetic storage, fuel cells as anodes and magneto-electronics. The A\textsubscript{2}FeMoO\textsubscript{6} compounds crystalize in tetragonal lattice with space group I4/mmm for Sr\textsubscript{2}FeMoO\textsubscript{6} and in cubic with space group \textit{Fm\bar{3}m} for Ba\textsubscript{2}FeMoO\textsubscript{6} [1, 7]. The structure of A\textsubscript{2}FeMoO\textsubscript{6} compound can be viewed as a continuous, regular arrangement of corner sharing MoO\textsubscript{6} and FeO\textsubscript{6} octahedra, alternating along the three directions of the crystal, with the ‘A’ cations occupying the voids in between the octahedra [1,3,13]. Double perovskite oxides Sr\textsubscript{2}FeMoO\textsubscript{6} and Ba\textsubscript{2}FeMoO\textsubscript{6} have attracted researchers due to their curie temperature 426 K and 367 K respectively[7, 8] which are above room temperature. In addition, their materials exhibit LFMR at and above room temperature making them good candidates for magnetoresistance applications. Substitution of cation of different radii at ‘A’ site bring changes in the properties of double perovskite including curie temperature and magnetic ordering that has impact on magnetoresistance properties. Therefore, in the present study SrBaFe\textsubscript{x}Mo\textsubscript{2-x}O\textsubscript{6} of various compositions have been synthesized by sol-gel method and caracterized using different experiments techniques namely, X-ray diffraction, SEM, EDS and FTIR. The studies on magnetoresistance of these materials are in progress.

2. Experimentation

Various composition of SrBaFe\textsubscript{x}Mo\textsubscript{2-x}O\textsubscript{6} (x = 1.0, 1.2, 1.3, 1.4 and 1.5) (SBFMO) materials were synthesized by conventional sol-gel method[6] using stoichiometric amounts of AR grade Sr(NO\textsubscript{3})\textsubscript{2}(Strontium nitrate), Ba(NO\textsubscript{3})\textsubscript{2}(Barium nitrite), Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O (Ferric nitrate), and H\textsubscript{2}MoO\textsubscript{4}
(Molybdic acid) are separately taken in beakers. Corresponding solutions are formed in the beaker while adding about 100 ml distilled water to Barium nitrite and Ferric nitrate. Ammonium was added to Molybdic acid for converting ammonium heptamolybdate \[ (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \] latter about 100 ml distilled water is added to get ammonia molybdic solution. The mixture solution was obtained by adding all the three solutions in a single beaker. Citric acid is added to the mixture maintaining the mole ratio of citric acid to metal ions as 2:1. The pH of the mixture solution is adjusted to 7 by adding dilute ammonia solution. After that the beaker containing mixture solution is heated on hot-plate at around 80 °C using magnetic stirrer for 24h. Ethylene glycol is added to this solution such that metal ion to ethylene glycol ratio is 1:1.2 and heated until a dark gel is formed. The gel is transformed into precursors in the continuing heating at the same temperature. These precursors are combusted at 250 °C using Bunsen burner to get dried loose powders. The loosely powder are ground using Agate Motor. Later the powder are taken into a crucible and heated at 500 °C for 6hrs, 700 °C for 6hrs, 900 °C for 6 hrs and 1100 °C for 6 hrs in a furnace with intermittent grinding. Thus obtained powders are then pressed into pellets of 1 cm diameter and about 2 mm thickness using a die, with hydraulic press by applying a pressure of 1 ton. The pellets were then sintered at 1200°C for 6hrs and then heated at ~1000 °C in a mixture stream of gases (10% H₂+90% Ar) for 3hrs for reducing Mo⁶⁺ into Mo⁵⁺. These pellets were subjected to X-ray diffraction using Philips PW 1830 diffractometer with Cu-Kα radiation (40 kV × 25 mA) to confirm the crystal structure. Surface morphology of the samples was found using the Scanning Electron Microscope (Model No. Evo 18 Carl Zeiss Germany) with combined micro analyzer. Elements present in the materials understudy were found using Energy Dispersive X-ray Spectrometer. Fourier transform infrared spectra of the pellets were recorded on Bruker Tensor 27 DTGS TEC detector spectrophotometer in the wave number region 400-1000 cm⁻¹ by using KBr pellet method.

3. Result and Discussion

3.1 X-ray diffraction

X-ray diffractograms of various compositions of SBFMO samples are presented in Fig. 1.

![Fig. 1. X-ray diffraction patterns along with (hkl) values of SrBaFeₓMo₂ₓO₆ samples for x=1.0, 1.2, 1.3, 1.4 and 1.5.](image)

These diffractogram patterns reveal that the profiles belong to double perovskite structure of SrBaFeₓMo₂ₓO₆ [7, 17]. All the profiles of SBFMO are indexed and found to be in single phase. The lattice parameters of SBFMO were evaluated by POWD method using intensity and Bragg’s angles with a suitable software program. It is observed that SrBaFeₓMo₂ₓO₆ crystallizes in cubic lattice with space group \( Fm\bar{3}m \) for all compositions. The values of lattice parameters ‘\( a \)’ of SBFMO are listed in Table
The unit cell volume \((V = a^3)\) of the present samples were calculated using lattice parameter and are tabulated in Table 1. The values of ‘\(a\)’ and ‘\(V\)’ found to decrease with increase of Fe content in SBFMO materials. Since the ionic radius of \(\text{Fe}^{3+}\) (0.645 Å) is larger than that of \(\text{Mo}^{5+}\) (0.61 Å), the decrease in ‘\(a\)’ and ‘\(V\)’ might be attributed to cation or oxygen vacancies or valence disproportion as observed in double perovskites [16].

Table 1. The values of \(a\), \(V\), \(t\), \(m_1\), \(m_2\), \(d_{(\text{exp})}\), \(d_{(\text{th})}\), \(P(\%)\) and \(d(\%)\) of SBFMO samples.

| Com(x) | 1.0     | 1.2     | 1.3     | 1.4     | 1.5     |
|--------|---------|---------|---------|---------|---------|
| \(a\) [Å] | 7.9766  | 7.9761  | 7.9757  | 7.9753  | 7.9749  |
| \(V\) [Å\(^3\)] | 507.52  | 507.43  | 507.35  | 507.27  | 507.19  |
| \(t\) | 1.0185  | 1.0167  | 1.0158  | 1.0150  | 1.0141  |
| \(m_1\) [g] | 1.5653  | 1.1981  | 1.2423  | 1.0330  | 1.5845  |
| \(m_2\) [g] | 1.3111  | 1.0098  | 1.0465  | 0.8670  | 1.3309  |
| \(d_{(\text{exp})}\) [g/cm\(^3\)] | 5.3264  | 5.5038  | 5.4882  | 5.3828  | 5.4029  |
| \(d_{(\text{th})}\) [g/cm\(^3\)] | 5.9236  | 6.0821  | 6.0305  | 5.9790  | 5.9274  |
| \(P(\%)\) | 10.0814 | 9.509   | 8.994   | 9.972   | 8.849   |
| \(d(\%)\) | 89.918  | 90.491  | 90.005  | 90.027  | 91.150  |

3.2 Tolerance factor

The tolerance factor \((t)\) is described as a semi quantitative estimate of how close an ABO\(_3\) perovskite is to the ideal cubic structure, and further the tolerance factor indicates stability of the perovskite structure, that is, the higher is the deviation of tolerance factor \((t)\) from unity, lesser is the stability of perovskite structure. The tolerance factor for ABO\(_3\) perovskite structure is given by

\[
t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}
\]

Eq. 1

Where \(r_A\), \(r_B\) and \(r_O\) are the ionic radii of A, B and oxygen atoms respectively and \(t = 1\) corresponds to an ideal cubic perovskite structure. The concept of tolerance factor \((t)\) has been adopted to \(A_2B_xB'_2\) \(_2\), \(_6\)O\(_6\) double perovskite by Lu et al [18] and it is given by

\[
t = \frac{r_A + r_O}{\sqrt{2}\left(\frac{r_B x}{2} + \frac{r_{B'} (2 - x)}{2} + r_O\right)}
\]

Eq. 2

The tolerance factor for the present material of interest \(\text{Sr BaFe}_x\text{Mo}_{2-x}\)O\(_6\) can be expressed by [18]

\[
t = \frac{\frac{r_{\text{Sr}}}{2} + \frac{r_{\text{Ba}}}{2} + r_O}{\sqrt{2}\left(\frac{r_{\text{Fe}(x)}}{2} + \frac{r_{\text{Mo}(2-x)}}{2} + r_O\right)}
\]

Eq. 3
where \( r_{\text{Sr}}, r_{\text{Ba}}, r_{\text{Fe}}, r_{\text{Mo}} \) and \( r_{\text{O}} \) are ionic radii of Sr, Ba, Fe, Mo and O ions respectively. The values of ionic radii of elements have been taken from R.D. Shannon and C.T. Prwitt [19]. The tolerance factor \((t)\) of SBFMO compounds was calculated employing Eq.(3) and the values are included in Table 1. It is found from Table 1 that the deviation of tolerance factor from unity in SBFMO samples was found to decrease with increase of Fe content indicates that the decrease of distortion from ideal double perovskite structure with Fe content.

3.3. Density measurements

The experimental density \((d_{\text{exp}})\) of the SBFMO samples was measured by Archimedes principle using the relation:

\[
d_{\text{exp}} = \frac{m_1}{m_1 - m_2} \times d_x
\]

where, \(m_1\) is mass of the sample in air, \(m_2\) corresponds mass of the sample when immersed in xylene liquid and \(d_x\) is density of xylene \((d_x = 0.865 \text{ g/cm}^3)\). These measurements were done using single pan balance. The theoretical density \((d_{\text{th}})\) of the SBFMO samples from XRD is calculated using following expression:

\[
d_{\text{th}} = \frac{zM}{NV}
\]

where, \(Z\) is the number of molecules in unit cell of the crystal \((Z = 4\) for cubic), \(M\) is mass per formula unit \((\text{gm})\), \(N\) is Avogadro number \((N = 6.023 \times 10^{23} \text{ mol}^{-1})\), \(V\) is the volume of the unit cell \((\text{cm}^3)\) as determined by XRD. The density is in terms of \(\text{g/cm}^3\). From the values of density evaluated experimentally and calculated theoretically using X-ray data, one can estimate the percentage of porosity \((P\%)\) and percentage of density \((d\%)\) of the sample which is calculated by the following equation:

\[
P(\%) = \frac{d_{\text{th}} - d_{\text{exp}}}{d_{\text{th}}} \times 100 \quad \text{Eq. 6}
\]

\[
d(\%) = 100 - P(\%) \quad \text{Eq. 7}
\]

The values of \(m_1, m_2, d_{\text{exp}}, d_{\text{th}}, d(\%)\) and \(P(\%)\) of SBFMO samples are included in Table 1. It is noticed from Table 1 that high density and low porosity material is found for composition for \(x=1.5\) in SBFMO materials.

3.4. Scanning Electron Microscopy

The microstructure of the sintered samples was studied using Scanning Electron Microscopy (SEM). SEM is an extremely versatile technique capable of providing morphology information over a wide range of magnification. The average grain size and surface morphology of the samples is determined using this technique.

The SEM photos of SBFMO sample were shown in Fig. 2(a-e). It is observed from figures that slight porosity is present in composition \(x=1.0\) and \(1.4\) of these materials. The size of the pores is very small and material is closely packed with less voids for composition \(x=1.2, 1.3\) and \(1.5\). The grain size of the sample are found to be non-varying as notice from SEM photo graphs for composition \(x=1.2, 1.3, 1.4\) and \(1.5\), and for composition \(x=1.0\) the grain size was small compared to all composition of these materials.
Energy Dispersive X-ray Spectroscopy

Energy Dispersive X-ray Spectroscopy (EDS) is used to find the elements present in the given samples. In the present study, EDS of SrBaFe$_x$Mo$_{2-x}$O$_6$ (x = 1.0, 1.2, 1.3, 1.4 and 1.5) samples are shown in Fig. 3(a-e). The results from EDS analysis showed that only the elements Sr, Ba, Fe, Mo and O are present in the samples without the presence of any other elemental impurities.

Fig. 3(a-e). Energy dispersive X-ray absorption spectrograph of SrBaFe$_x$Mo$_{2-x}$O$_6$ samples for (a) x = 1.0, (b) x = 1.2, (c) x = 1.3, (d) x = 1.4 and (e) x = 1.5.
3.6 Fourier Transform Infrared Spectroscopy

Fig. 4 shows FTIR spectra of SrBaFe$_{x}$Mo$_{2-x}$O$_{6}$ (x=1.0, 1.2, 1.3, 1.4 and 1.5) samples in the spectral wave number range 400-1000 cm$^{-1}$. Between 400-865 cm$^{-1}$ two characteristic absorption bands are observed which are usually used to identify the perovskite phase formation. In the present study, FTIR spectra of the SBFMO samples show two absorption bands corresponding to Fe-O and Mo-O vibrations. The first band in the high-wave number region (~ 824 cm$^{-1}$ to 861 cm$^{-1}$) corresponds to the Mo-O symmetric stretching mode of MoO$_{6}$ octahedra due to the higher charge of this cation [10, 20]. The second weak absorption band observed at 422 cm$^{-1}$ is ascribed to Fe-O vibration absorption of FeO$_{6}$-octahedra. In SBFMO double perovskite samples, the highly charged Mo cation octahedra (MoO$_{6}$) acts as independent group, the vibration spectrum therefore arises from such MoO$_{6}$-octahedra. Further, Mo-O symmetric stretching mode of MoO$_{6}$ octahedra between 824 cm$^{-1}$ to 861 cm$^{-1}$ is usually an infrared inactive vibration, but in a double perovskite, both Fe and Mo ions exist in Fe and Mo sites and it becomes partially allowed due to lowering of site symmetry [10]. The bands observed in the present spectra confirm the formation of perovskite phase.

![Fig.4. FTIR spectra of SrBaFe$_{x}$Mo$_{2-x}$O$_{6}$ (x =1.0, 1.2, 1.3, 1.4 and 1.5) samples.](image)

4. Conclusions

1) It is observed that both the lattice parameters and the unit cell volume decrease with increase of Fe content in SBFMO materials.
2) Cubic structure has been confirmed for SBFMO materials from XRD data.
3) SEM photograph of SBFMO materials showed fewer voids for compositions x=1.2, 1.3 and 1.5 with closely packed criteria.
4) Results of EDS showed the presence of Sr, Fe, Mo, O elements and non-existence of elemental impurities in SBFMO materials.
5) The FTIR spectra of SBFMO showed the existence of three characteristic absorption bands between 865-400 cm$^{-1}$ indicating the formation of perovskite structure.

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