PHYSICA B
CONDENSED MATTER

Synthesis of the off-stoichiometric oxide system $Sr_2Fe_{1+x}Mo_{1-x}O_6$ with $-1 \leq x \leq 0.25$

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ABSTRACT

The half-metallic ferromagnetic oxide compounds are extensively studied in view of their spintronic applications. In this work, we have synthesized and characterized the off-stoichiometric double perovskite $Sr_2Fe_{1+x}Mo_{1-x}O_6$ with x being in the range $-1 \leq x \leq 0.25$, the composition $x=0$ corresponding to the well-known ferromagnetic system Sr_2FeMoO_6. The double perovskite has been prepared in a polycrystalline form by the solid-state reaction method and ball milling, calcination in air and reduction in a mixture of He and H_2 atmosphere in a thermogravimetric analyzer. Characterization has been done by X-ray diffraction and scanning electron microscopy techniques. Our results show that mechanochemical activation prior to the reaction synthesis helps to reduce the synthesis temperature and avoid the sublimation of MoO_3 at high temperatures. The Curie temperature has also been obtained.

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1. Introduction

Half-metallic materials, in which only one-spin direction is present at the Fermi energy, have been investigated in view of their attractive properties for spintronics applications [1] and as potential candidates for memory devices by virtue of their large magnetoresistance. The double perovskite Sr_2FeMoO_6 combines half-metallic ferromagnetic character with a high Curie temperature $T_C = 400$ K and substantial low-field magnetoresistance [2].

Structurally, the perfectly ordered lattice Sr_2FeMoO_6 consists of alternating Fe and Mo atoms which are surrounded by six oxygen atoms, forming MoO_6 and FeO_6 octahedra all along the three cubic axes, while Sr lies on the dodecahedral sites. However, in the synthesis of the above compound mis-sites are created, it means Fe and Mo atoms exchange positions modifying the properties of the system, so it is necessary for a detailed investigation of the off-stoichiometric $Sr_2Fe_{(1+x)}Mo_{(1-x)}O_6$ compound, where x takes values from -1 to 0.25 together with the mis-site disorder effects [3,4].

The ferromagnetic and half-metallicity in the Sr_2FeMoO_6 have been understood [5–7] on the basis of a strongly correlated picture, where the Fe^{3+} ($3d^5$) localized ions with a high-spin $S=5/2$, together with Mo^{5+} ($4d^1$) cores and one conduction electron (one per Mo-atom) can hop to Fe sites only with an antiparallel orientation to the localized spin (Hund's coupling). The Fe–Mo hoppings stabilize a ferromagnetic arrangement of the local spins and also leads to the opposite spin polarization of the conduction electrons, this being consistent with ab initio calculations [2,8].

In this work we synthesized $Sr_2Fe_{1+x}Mo_{1-x}O_6$ over a wide range of compositions $-1 \leq x \leq 0.25$. $x=0$ has the same amount of Fe and Mo atoms in the ordered double perovskite; for $x \geq 0$ there is an excess of Fe and bonds prevailing are Fe–O–Fe; for $x \leq 0$ we have an excess of Mo and the bonds prevailing are Mo–O–Mo.
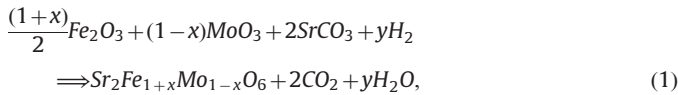
2. Experimental methodology

Polycrystalline samples of the double perovskite $Sr_2Fe_{1+x}Mo_{1-x}O_6$ in the range $-1 \leq x \leq 0.25$ were synthesized following

the stoichiometric reaction:

$$\frac{(1+x)}{2}Fe_2O_3 + (1-x)MoO_3 + 2SrCO_3 + yH_2$$

$$\Longrightarrow Sr_2Fe_{1+x}Mo_{1-x}O_6 + 2CO_2 + yH_2O, \qquad (1)$$

where y is a parameter that fixes the H_2 requirements in the reaction.

Stoichiometric proportions of Fe_2O_3 (Aldrich, 99.98%), $SrCO_3$ (Aldrich, 99.99%) and MoO_3 (Aldrich, 99.9%) were preheated 4 h at 100 °C for dehydration and placed in a high energy reactor at 1725 rpm (8000 M Spex Mixer Mill) for 5 h. In the mechanical grinding process the mixture of high purity reagents were homogenized and particle size reduced during formation of the first precursor phase, $SrMoO_4$. After mechanical grinding, the powders were calcined for 3 h at 900 °C, the unreacted specie Fe_2O_3 is energy activated and mixed thoroughly. The calcination has the purpose of forming the second precursor phase, $Sr_4Fe_4O_{11}$. Fig. 1 shows the X-ray diffractograms for the two precursor phases discussed above. Reduction experiments were carried out non-isothermally using a thermogravimetric analyzer (SETARAM, Setsys Evolution), which has a precision of 0.01 μg. The balance was controlled by a computer through an interface. The weight change during experiments was recorded by the computer at 2 s intervals. The reaction chamber was evacuated to less than 10 Pa for 10 min after introducing the samples previously calcined. Then, the reaction chamber was filled with He∕3% H_2 using a constant flow of 20 ml/min. Thereafter two heating rates were used: 15 °C/min up to 650 °C and 5 °C/min up to 1100 °C, with an isotherm of 1100 °C for 30 min. The experiment was finished by cooling down the furnace at the highest cooling rate (50 °C/min), and the flow of the reducing gas mixture was maintained until the furnace reached room temperature in order to avoid the oxidation of the reduced samples during the cooling.

3. Results and discussion

Fig. 2 shows the reduction curve under a constant heating rate for a wide range of $Sr_2Fe_{1+x}Mo_{1-x}O_6$ compositions. The reduction path seems to be dependent upon the temperature and occurs in two main stages. Under the well-controlled reduction experimental conditions, e.g., steady heating rate and both constant concentration of H_2 and low flow rate ensure an optimal removal of oxygen atoms in excess following Eq. (1).

Scanning electron microscopy (SEM) was made to prove that the obtained results of the homogenizing step by mechanical grinding were consistent with the reagent. The resulting images are shown in Fig. 3(a) and (b) for $x=0.2$ and $x=-0.2$ respectively, where the samples' morphology is made up of agglomerates formed by small homogeneous particles of $Sr_2Fe_{1+x}Mo_{1-x}O_6$.

We obtained an EDS line scan analysis using SEM for part of the sample shown in Fig. 4. As it is well known this technique consists of scanning part of material, so Fig. 4 shows the intensity of the peaks as a function of the material concentration along the scanned line, it can be observed that the main components are Sr, Fe, Mo and O.

Crystal structure and identification of different phases in our samples were done using a RIGAKU X-ray diffractometer with CuK_α radiations. Fig. 5 shows the powder X-ray diffraction patterns for various compositions of $Sr_2Fe_{1+x}Mo_{1-x}O_6$. These patterns suggest that Fe preferentially occupies one sublattice of the double perovskite and Mo occupies the other one. Fig. 6 shows the variation of the lattice parameter c as obtained from Rietveld refinements (Table 1) as a function of composition x, where a
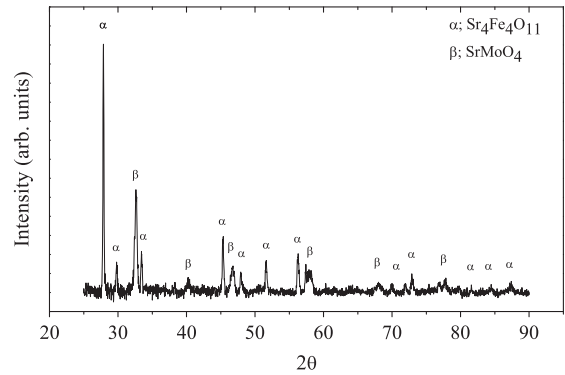

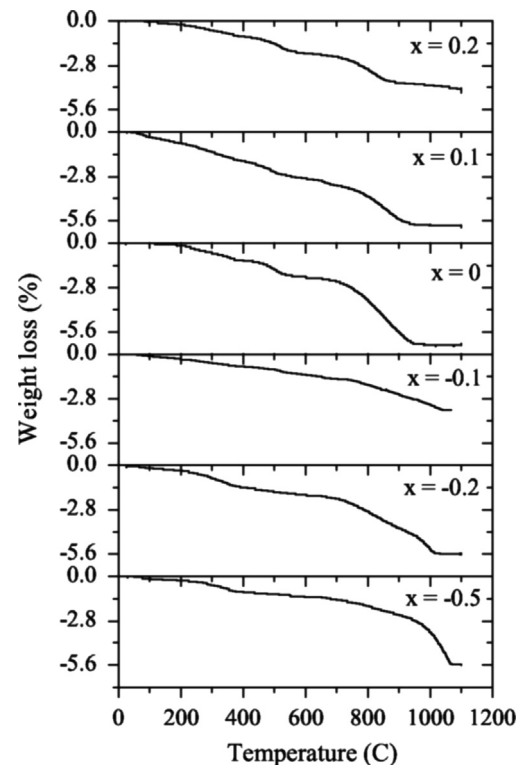**Fig. 1.** X-ray patterns of powders ball milled for 5 h and calcined for 3 h.

Fig. 2. Thermogravimetric curves for different compositions of the system $Sr_2Fe_{1+x}Mo_{1-x}O_6$
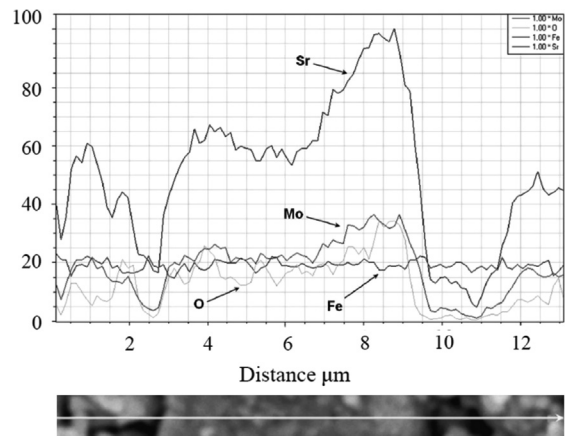

Fig. 3. Scanning electron microscopy images obtained for different compositions of $Sr_2Fe_{1+x}Mo_{1-x}O_6$
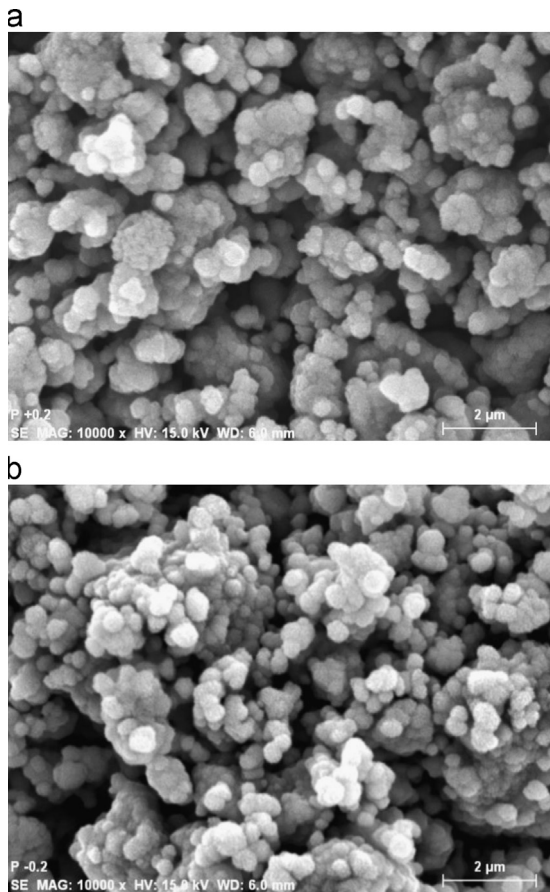
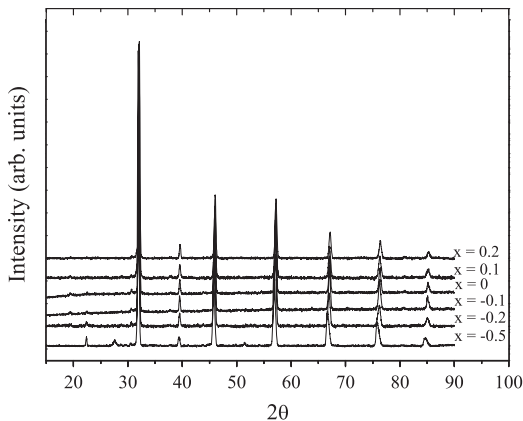**Fig. 4.** Quantitative scan line analysis by EDS-SEM technique of the sample $Sr_2Fe_{1.2}Mo_{0.8}O_6$.

Fig. 5. The X-ray diffraction patterns of $Sr_2Fe_{1+x}Mo_{1-x}O_6$ using CuK_α radiation show the difference among all compositions

systematic reduction in the unit cell parameters is established which is in good agreement with those results by Topwal [3].

Fig. 7 shows the Curie temperature (T_C) for all synthesized $Sr_2Fe_{1+x}Mo_{1-x}O_6$ compositions. The Curie temperature values for each concentration are 418 K for $x=0.2$, 398 K for $x=0.1$, 393 K for $x=0$, 383 K for $x=-0.1$ and 373 K for $x=-0.2$.

4. Conclusion

We have presented the synthesis and characterization of double perovskite $Sr_2Fe_{1+x}Mo_{1-x}O_6$ over a wide range of
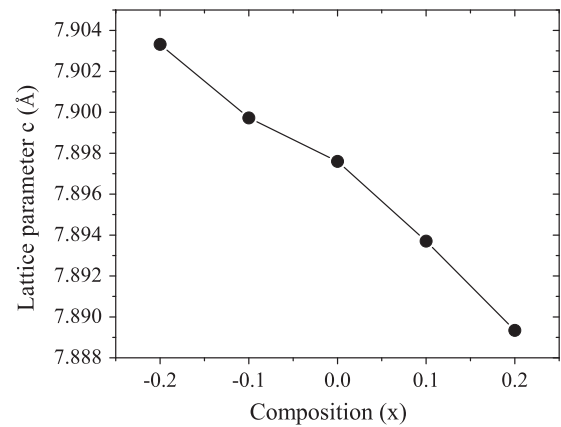

Fig. 6. Lattice parameter c for different compositions.

Table 1
Lattice parameters obtained by Rietveld refinements using GSAS software.

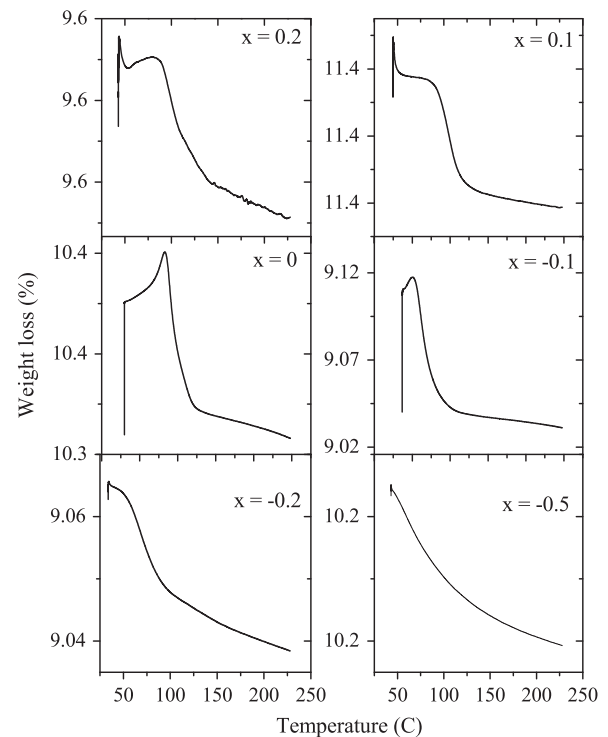| Compound	Lattice parameter		
	a (Å)	b (Å)	c (Å)
$Sr_2Fe_{0.8}Mo_{1.2}O_6$	5.5831	5.5831	7.9033
$Sr_2Fe_{0.9}Mo_{1.1}O_6$	5.5841	5.5841	7.8997
Sr_2FeMoO_6	5.5707	5.5707	7.8976
$Sr_2Fe_{1.1}Mo_{0.9}O_6$	5.5677	5.5677	7.8957
$Sr_2Fe_{1.2}Mo_{0.8}O_6$	5.5697	5.5697	7.8893

Fig. 7. Curie temperature for different compositions of $Sr_2Fe_{1+x}Mo_{1-x}O_6$.

composition. X-ray diffraction results and Rietveld refinements establish a systematic reduction of the unit cell. Experimental observation of the Curie temperature shows that T_C is higher as the Fe composition increases strengthening the ferromagnetic behavior.

Acknowledgments

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