

Structural phase transition and variation of magnetoresistance in the stoichiometric double perovskite Sr 2–x Nd x Fe 1+y Mo 1–y O 6 (0.05 \leq x \leq 0.45 and y = x/2)

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Structural phase transition and variation of magnetoresistance in the stoichiometric double perovskite $Sr_{2-x}Nd_xFe_{1+y}Mo_{1-y}O_6$ (0.05 $\leq x \leq 0.45$ and y = x/2)

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The interplay between magnetic, megneto-transport and structural properties of Nd-doped double perovskite $Sr_{2-x}Nd_xFe_{1+y}Mo_{1-y}O_6$, in the range 0.05 < x < 0.45 for y = x/2 and synthesized by solid state reaction, has been investigated. Specifically, it has been shown that the observed tetragonal to monoclinic crystallographic phase transition at the Nd composition in the range x =0.10 to x = 0.15 is in close relationship with its magnetic and magnetoresistive behavior. The observed crystallographic transition, confirmed by X-ray diffraction experiments, is consistent with the decrease of the unit cell volume when the Nd doping content increases. Besides, the Curie temperature determined by thermogravimetric experiments increases with the Nd content just after the structural transition. Furthermore, the increase of Nd doping up to x = 0.45 in the double perovskite structure leads to a magnetization loss about 98% as a result of the increase of both, anti-site defects and the number of charge carriers. The progressive magnetization loss with Nd doping is also responsible for the observed monotonic decrease of the magnetoresistance ratio due to the predominance of the antiferromagnetic order. Particularly, the electrical behavior in the vicinity of the crystallographic transition is characterized by a very slight increase followed by a rapid drop of the magnetoresistance ratio, which is originated by the corresponding fluctuations of the saturation magnetization.

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I. INTRODUCTION

Double perovskites with general formula A₂BB'O₆ are well known compounds for their potential and versatility of technological applications, for example, the double perovskite Ba₂NiMnO₆ is very important in multiferroic applications, La₂NiMnO₆ as magnetodielectric materials, Sr_2CrOsO_6 in magneto-optic devices and Sr_2FeReO_6 or Sr_2FeMoO_6 compounds in spintronics devices [1–5]. The double perovskite Sr_2FeMoO_6 (SFMO) is also fundamental to understand the electronic and magnetic properties of half-metallic systems. A perfect structural order between the Fe and Mo atoms in the crystalline network of SFMO lends to a full spin polarization, high Curie temperature ($T_C = 410-450$ K) and low field magnetoresistance (MR). The experimental spin polarization and the magnetic moment are 0.85 and $3.7\mu_B$ per formula [6], respectively, in contrast with theoretical values of 1 and $4\mu_B$. This substantial reduction is due to anti-site defects caused by the antiferromagetic arrangement between Fe and Mo [7-10]. The ordered arrangement of Fe and Mo, is responsible for the half-metallic ferromagnetic state and the MR behavior via spin-dependent carrier scattering processes [11–14].

The T_C associated to the double perovskite SFMO can

be increased when this compound is doped with trivalent atoms, such as La^{3+} [15, 16] or Nd³⁺ [17]. However, anti-site defects induced by the above doping reduce the spin polarization, the saturation magnetization and the magnetoresistance [15–17]. The influence of Nd doping on the electronic and magnetic properties of the off-stoichiometric SFMO double perovskite was previously reported [17–19]. The experimental behavior of the Curie temperature with Nd doping in SFMO is still controversial in the off-stoichiometric case [17, 19, 20]. Also, this Nd doping leads to a higher structural disorder and a decrease of the magneto-transport properties. Therefore, further studies are needed to elucidate the detailed interplay between the observed structural transitions due to rare-earth doping and some of their physical properties like the T_C . In this work, we studied experimentally a series of the stoichiometric system $\mathrm{Sr}_{2-x}\mathrm{Nd}_x\mathrm{Fe}_{1+y}\mathrm{Mo}_{1-y}\mathrm{O}_6$ in the range $0.05 \leq x \leq 0.45$ and y = x/2, by taking into account the charge neutrality. In our previous work on the magnetic properties of Nd doping [21], the emphasis was paid on the offstoichiometric case and only few results were given for the stoichiometric system. For instance, the structural phase transition and the Curie temperature were not analyzed in detail and the magnetoresistance study was not included at all, therefore a full study of the stoichiometric case is fundamental in order to understand the Nd doping in SFMO.

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II. EXPERIMENTAL DETAILS

Our experimental analysis include the charge neutrality for Nd doping, it means, Fe atoms partially replace Mo atoms when doping is carried out and the compound becomes stoichiometric $Sr_{2-x}Nd_xFe_{1+y}Mo_{1-y}O_6$ (SNFMO). In our experimental study, a series of polycrystalline samples of the double perovskite $\operatorname{Sr}_{2-x}\operatorname{Nd}_x\operatorname{Fe}_{1+y}\operatorname{Mo}_{1-y}O_6$ in the range $0.05 \leq x \leq 0.45$ and with y = x/2 were synthesized following the stoichiometric reaction:

$$(2-x)SrCO_3 + \frac{1+y}{2}Fe_2O_3 + (1-y)MoO_3 + \frac{x}{2}Nd_2O_3 + zH_2 \longrightarrow Sr_{2-x}Nd_xFe_{1+y}Mo_{1-y}O_6 + CO_2 + zH_2O.$$
(1)

Stoichiometric amounts of Fe_2O_3 (Aldrich, 99.98%), SrCO₃ (Aldrich, 99.99%), MoO₃ (Aldrich, 99.9%) and Nd₂O₃ were preheated for 4 hours at 100 °C for dehydration and placed in a high energy reactor at 1725 rpm (8000 M Spex Mixer Mill) for five hours. After mechanical grinding, the powders were calcined (Nabertherm B180) for 3 hours at 900 °C. The precursors obtained were reduced at 1200 °C (Carbolite High Temperature) under a controlled atmosphere of 1% to 3% of H₂/Ar followed by a 3 h isotherm to obtain the double perovskite SNFMO.

Crystal structure and phases identification were carried out by X-ray diffraction (XRD), using a Bruker X-ray diffractometer with CuK_{α} radiation. Hysteresis loops, in a maximum field of 1T, have been obtained using a Vibrating Sample Magnetometer from Lakeshore, which is part of the mineral magnetism analysis platforms situated at IPGP-IMPMC. Room temperature magnetotransport measurements were carried out by using a 7265 DSP lock-In amplifier from Signal Recovery to inject an AC electric current (I) while sweeping the applied magnetic field (H) between ± 1 T to 1 mm thick pellets made by compressing the double perovskite powders. Both, the AC electric current and magnetic field were applied in the same direction. Electrical contacts to the samples with 2 mm of separation between them were made by using a liquid metal alloy of eutectic gallium-indium (EGaIn). Measurements obtained by four- and two-probe setups were the same because the typical resistance values for all measurable samples were less than 10Ω , thus much larger than those of the leads and contacts to the samples. The electric resistance was recorded using a Keithley 2000 digital multimeter connected in parallel configuration. The input power to the samples was kept below 0.1μ W to avoid self-heating and to keep the resistance within its ohmic regime.

III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns for different compositions of the stoichiometric system $\mathrm{Sr}_{2-x}\mathrm{Nd}_x\mathrm{Fe}_{1+y}\mathrm{Mo}_{1-y}\mathrm{O}_6$ in the range $0.05 \leq x \leq 0.45$ and with y = x/2, the ordered case (x = 0 and y = 0)is also included in this figure as a reference. The high intensity of the diffraction peaks at the superstructure reflections (011) and (121) corresponding to Fe/Mo ordering, indicates the high degree of ordering for x = 0and y = 0. The intensity of those peaks decreases as x increases showing the presence of anti-sites and so the disorder of the compound, this behavior is shown in the inset of Figure 1. In a Rietveld analysis of Nd concentration, from x = 0 to x = 0.15, the diffraction peaks were successfully refined in the tetragonal phase and space group I4/m without secondary phases, while from x = 0.15 to x = 0.45 the crystal structure was well refined with a monoclinic lattice and space group $P2_1/c1$. This structural phase transition is more evident with the splitting of the reflection peaks shown in Fig. 2, it means, the reflection (240) T splits into the two reflections (24-2) M and (33-5) M.

Figure 3 shows the lattice parameters a = b and c, together with the unit cell volume obtained through Rietveld refinements in a tetragonal crystalline structure for x compositions from 0 to 0.15. The space group used for the refinement was I4/m. Increments of x values were very small in order to give a good identification of the Nd doping effects in the crystallographic phase transition. This transition occurs between x = 0.10 and x = 0.15due to the lattice deformation coming from the increase of Nd atoms in the system. From x = 0.15 to x = 0.45, Rietveld refinements were carried out using a monoclinic crystalline structure with space group $P2_1/c1$. For the latter composition, the lattice parameters and the unit cell volume are shown in Fig. 4. The effect of Nd systematic substitution, with a smaller ionic radius than Sr, can be observed by the decrease of the unit cell volume shown in Fig. 4.

The magnetic characterization of the compound $\operatorname{Sr}_{2-x}\operatorname{Nd}_x\operatorname{Fe}_{1+y}\operatorname{Mo}_{1-y}\operatorname{O}_6$ is shown in Figure 5. The hysteresis loops for samples with x = 0.05 to x < 0.2, exhibit a clear ferromagnetic response. The magnetization loss for x > 0.2 is about 98%, which means that the increase of Nd atoms leads to almost non-magnetic compounds.



FIG. 1: XRD patterns of the double perovskite $\text{Sr}_{2-x}\text{Nd}_x\text{Fe}_{1+y}\text{Mo}_{1-y}O_6$ in the range $0 \le x \le 0.45$. In our experimental analysis the charge neutrality for Nd doping has been included, therefore y should be y = x/2 and also $y \le 1/3$.

Composition x	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	Volume $(Å^3)$	Spacial group	Wt Fraction	% Ordering
0	5.5743	5.5743	7.9062	245.672	I4/m	-	100
0.05	5.5713	5.5713	7.9051	245.373	I_4/m	-	48.5
0.1	5.5683	5.5683	7.9074	245.183	I_4/m	-	29.8
0.15	5.5692	5.5692	7.9047	245.179	I_4/m	0.98625	29.8
	5.5635	5.5798	9.6676	246.130	$P2_{1}/c1$	$0.1375 {\rm x} 10^{-1}$	-
0.2	5.5678	5.5678	7.9120	245.285	I_4/m	0.22244	12.6
	5.5717	5.5604	9.6495	244.513	$P2_{1}/c1$	0.77756	-
0.25	5.5658	5.5646	9.6598	244.771	$P2_{1}/c1$	-	-
0.35	5.5584	5.5624	9.6444	243.891	$P2_{1}/c1$	-	-
0.45	5.5693	5.5527	9.6423	243.682	$P2_{1}/c1$	-	-

TABLE I: Atomic parameters after the Rietveld refinement for the double perovskite $Sr_{2-x}Nd_xFe_{1+y}Mo_{1-y}O_6$ in the tetragonal and monoclinic phases

This is also attributed to the number of anti-site defects in the crystal lattice and the increase in the number of charge carriers due to doping [22]. In the close view for compositions from x = 0 to x = 0.2 (see the inset in Fig. 5), it can be observed the variations of coercive field.

It is important to mention that, in the stoichiometric Nd doping, the number of itinerant electrons on Mo sites decreases as n = 1 + x - 3y = 1 - x/2 with y = x/2, so y should be $y \leq 1/3$ in order to Fe retain its trivalent

state and Mo must be in an oxidation state less than 6+. Figure 6(a) shows a minimum in the Curie temperature T_C at the beginning of the series, around x = 0.15, since the itinerant electrons diminishes and the electronic effects prevail over the structural distortion. However, for high Nd doping (x > 0.15) T_C increases since a structural transition occurs indicating that the structural distortion prevails over the electronic effects. It is noting the difference in T_C behavior between the off-stoichiometric



FIG. 2: XRD reflection peaks corresponding to the structural phase transition from tetragonal lattice to monoclinic lattices of the double perovskite $Sr_{2-x}Nd_xFe_{1+y}Mo_{1-y}O_6$.

[17, 19, 20] and the stoichiometric cases [21]. Here our results for the Curie temperature clarify this difference and shows a shift of the minimum of T_C associated with the structural transition. That is, since the structural transition shifts to small doping values due to the charge neutrality considering in the stoichiometric case, the T_C has the same behavior. Figure 6(b) shows the variation of the saturation magnetization (Ms) with increasing Nd doping, the abrupt increase of Ms for x = 0.15 is associated with the crystallographic transition occurred in this value.

Magnetoresistance (MR) is the most interesting property in double perovskites, for instance, in the low-field it is mostly determined by the level of the anti-site disorder. Figure 7(*a*) shows room temperature MR curves recorded in the range ± 1.5 T for representative samples with different Nd doping compositions. These curves were obtained using the well known relation for the MR ratio given by [7]:

$$MR(H) = \frac{R(H=0) - R(H)}{R(H)},$$
(2)

where R(H) and R(H = 0) are the resistance values at a fixed applied field and zero field values, respectively. As



FIG. 3: Lattice parameters and unit cell volume obtained from Rietveld refinements for the double perovskite $\operatorname{Sr}_{2-x}\operatorname{Nd}_x\operatorname{Fe}_{1+y}\operatorname{Mo}_{1-y}\operatorname{O}_6$ with compositions from x = 0 to x = 0.15 (tetragonal crystalline structure).

seen in Fig. 7(a), the abrupt decrease in resistance in low fields for diluted compounds (x < 0.15) is consistent with their abrupt decrease of ordering and magnetization in the vicinity of zero field and with previous results for the double perovskite [7, 17]. For these samples, an interesting feature observed from the MR branches recorded by sweeping the field from the positive to the negative and from the negative to the positive saturation states is the distinct position of the resistance maxima observed at low field values (see the inset). This effect is directly related to the magnetic hysteresis by virtue of the low coercive field for most of the samples, as shown in 7(a). However, this behavior is not clearly seen for Nd rich compounds for which a more flat variation of MR with the magnetic field is observed. As mentioned above, increasing the Nd doping favours the presence of anti-site defects, then promoting the antiferromagnetic order and leading to a reduction of Hc when the structural transition takes place. Besides, 7(b) shows the variation of MR at ± 1.5 T as a function of the Nd doping composition. The MR for the compound with x = 0.10 and x = 0.15is in good agreement with the structural transition observed by XRD patterns. This behavior is also consistent



FIG. 4: Lattice parameters and unit cell volume obtained from Rietveld refinements for the double perovskite $Sr_{2-x}Nd_xFe_{1+y}Mo_{1-y}O_6$ using a monoclinic crystalline structure.



FIG. 5: Magnetic hysteresis loops for all $Sr_{2-x}Nd_xFe_{1+y}Mo_{1-y}O_6$ compositions.



FIG. 6: (a) Coercive field and (b) Curie temperature behavior of the double perovskite system $\mathrm{Sr}_{2-x}\mathrm{Nd}_x\mathrm{Fe}_{1+y}\mathrm{Mo}_{1-y}\mathrm{O}_6$, The minimum in T_C agrees with the structural transition

with the increase of antiferromagnetism as confirmed by 7(b), which is a consequence of the increase of the Fe interatomic distance due to Nd substitution. Indeed, this behavior is consistent with previous results on rare-earth-doped SFMO, which have lower saturation magnetization values at high temperatures in comparison with the stoichiometric compound SMFO [23]. In turn, this behavior is opposite to what has been reported for SFMO double perovskites doped with an element with lower ionic radius like Co, for which an increase of both the magnetization and magnetoresistance with doping ($x \le 0.15$) have been observed in the low field regime (< 1T) [24]. Such a behavior in doped compounds with transition metals can be ascribed to a reinforcement of the ferromagnetic order between Fe ions.

IV. CONCLUSIONS

Summarizing, we have observed by XRD patterns a tetragonal to monoclinic structural phase transition in the stoichiometric $\text{Sr}_{2-x}\text{Nd}_x\text{Fe}_{1+y}\text{Mo}_{1-y}\text{O}_6$ compound for Nd doping in the range x = 0.10 to x = 0.15 in good agreement with its magnetic and magnetoresistive properties. When the number of itinerant electrons on Mo sites decreases due to Nd doping x < 0.15, the Curie temperature diminishes indicating that the electronic ef-



FIG. 7: (a) Magnetoresistance curves for different representative composition values. The inset shows a close view of the MR curve for x = 0.05 where the arrows indicate the field sweep direction. (b) Magnetoresistance ratio as a function of the composition in the range x = 0.0 to x = 0.45

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fects prevail over the structural distortion, while for Nd doping x > 0.15 the Curie temperature increases indicating that structural distortion prevails over the electronic effects. Finally, the difference in T_C behavior between the off-stoichiometric and the stoichiometric cases is observed as a shift in the minimum of T_C .

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HIGHLIGHTS

"The Nd doping in Sr₂FeMoO₆ double perovskite causes a crystallographic phase transition from tetragonal to monoclinic"

"Important differences in magnetic and electronic behavior are noticed between stoichiometric and off-stoichiometric cases of Nd doped double perovskite"

"At low Nd doping (x ≤ 0.15) the electronic effects prevail over structural distortion in Sr_{2-x}Nd_xFe_{1+y}Mo_{1-y}O₆ double perovskite"

"Magnetoresistance is clearly affected by crystallographic phase transition because of magnetization fluctuations"



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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

⊠The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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