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Crystalline structure, transport and magnetic properties of $Sr_2Fe_xNi_{1-x}MoO_6$ compounds

M.–L. CRAUS[a,b], L. BÎLTEANU[a,c], C. NECULIŢĂ[d], M. LOZOVAN[b,*]
[a]*LNF – JINR, Dubna Russia, Joliot-Curie 6, 141980 Dubna, Mosk.Obl, Russia*
[b]*National Institute of R & D for Technical Physics, 47 D. Mangeron Blvd., 700050 Iasi, Romania*
[c]*Faculty of Physics, University of Bucharest, 405 Fizicienilor Street, RO 077125 Bucharest-Măgurele, Romania*
[d]*Faculty of Physics, "Al. I. Cuza" University, 11 Carol I Blvd., RO 700506 Iasi, Romania*

We sintered $Sr_2Fe_xNi_{1-x}MoO_6$ perovskites by means of improved ceramic technology, adding a specific reduction agent, between 1100 ÷ 1200°C in air. Some test treatments were performed in O_2 or vacuum. The sintered/treated samples were investigated by means of XRD by using a DRON 2.0 diffractometer, with an acquisition data system. The magnetic measurements were performed between 77 and 600 K by using a Foner-type magnetometer. In the same range of temperatures we made the transport measurements. The XRD data were handled with DICVOL©/Check Cell©/Powder© programs. The structure of the sintered sample in the presence of the reduction agent is different relatively to those treated in H_2 + Ar atmosphere samples with the same chemical composition. The test performed by means of FullProf© program indicated a smaller oxygen concentration, as comparing with the stoechiometric double perovskites, which leads to a change of the compounds crystalline symmetry. All sintered phases have the same structure characterized by the GS 117 (P4b2). The volume of the unit cell and the lattice constants increases with the Fe concentration in the sample. Large values of magnetoresistance were observed near room temperature.

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1. Introduction

$A_2BB'O_6$ double perovskites, where A is an alkaline earth cation, B=Cr, Fe and B'=Mo, W, Re are ferromagnetic, with Curie temperature near room temperature [1]. Kobayashi et al showed that Sr_2FeMoO_6 ($T_C \approx 415$ K) is a CMR-type half-metallic ferromagnet, with a magnetoresistance significantly higher as those corresponding to the manganites with perovskite structure [2]. These double perovskites exhibit ferromagnetism, with a high spin polarization at the Fermi level. The ideal structure consists in a regular BO_6 – $B'O_6$ alternating octaedra lattice, the voids between them being occupied by the A cations. The real structure, derived from the ideal Fm3m structure and reported as tetragonal, hexagonal or monoclinic, depends on the chemical composition ant thermal treatment. The order of the B, B' cations in pseudo cubic/orthorhombic structure can cause the localization of the electrons and renders the double perovskites insulating/semiconducting [3]. The substitution of the B/B' cations with other transition cations/W or Ta cations modify the crystalline order and influences the magnetic/electronic structure of the perovskites. We present the results of the structure, magnetic and transport investigations of $Sr_2Fe_xNi_{1-x}MoO_6$ (SFNMO) double perovskites.

2. Experimental

The SFNMO samples were sintered by an improved ceramics technology, in air. The precursors ($SrCO_3$, Fe_2O_3, Ni_2O_3 and MoO_3) were mixed in corresponding stoichiometric ratio in a bill mill and pressed as small flat cylinders. The crude samples were heated at temperatures between 400 and 700 °C. The treated samples were mixed with a specific deoxidizing agent, milled and pressed. In agreement with the data published in the last 20 years (s. SCOPUS, SCIRUS and ISI) this procedure was for the first time applied by the authors of the present paper. The sintered/treated samples were investigated by means of XRD by using a DRON 2.0 diffractometer, with an acquisition data system. The XRD data were handled with DICVOL@/CheckCell@/Powder@ programs; the foreign phases were identified with the corresponding data from literature. The space group was selected by means of the FullProf@ program. The samples contain about 10% foreign phase. The magnetic and transport measurements were performed between 77 and 600 K by using a Foner-type magnetometer and, respectively, by means of four probe method.

3. Results and discussion

For all sintered samples the main phase has the same structure, characterized by the SG 117 ($P\bar{4}b2$) (Fig. 1 (a and b)). The volume of the unit cell and the lattice constants increases with the increase of the Fe concentration in the sample. The structure of the sintered sample in the presence of the reduction agent is different relatively to those treated in H_2 + Ar atmosphere samples with the same chemical composition. We supposed, in agreement with sintering procedure, the data concerning $A_2B_2O_{5+\delta}$ compounds [4,5], and FullProf tests that actual $Sr_2Fe_xNi_{1-x}MoO_6$ (nominal composition) double perovskites have an oxygen deficit as comparing with the stoechiometric double perovskites.

The lattice constants were determined by means of CellRef@ programme, while to determine the average size of the crystalline blocks and the microstrains we use the fitting of the main maximums by using a modified pseudo-Voigt function (Table 1). This function allows us to introduce a correction for the maximum anisotropy.

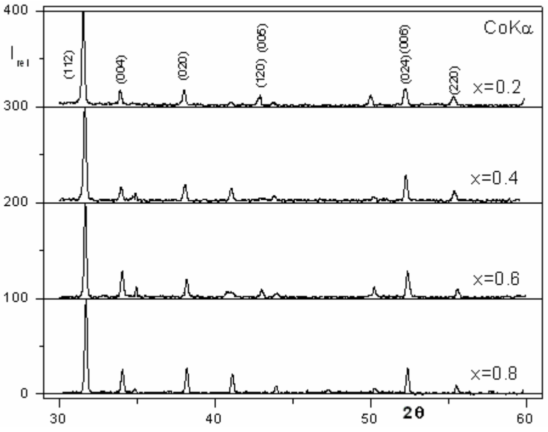

Fig. 1a. The difractograms of the $Sr_2Fe_xNi_{1-x}MoO_6$ double perovskites.

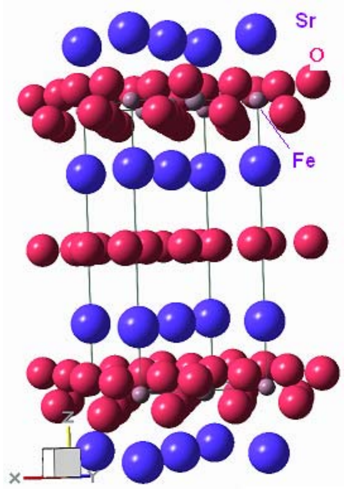

Fig. 1b. The structure ($P\bar{4}b2$) of the main phase in the $Sr_2Fe_xNi_{1-x}MoO_6$.

Table 1. The cell constants (a, b, c), the volume (V), average size of the crystallites (D) and the microstrains (ε) for the $Sr_2Fe_xNi_{1-x}MoO_6$ perovskites.

Nominal composition	a=b (Å)	c (Å)	V (Å^3)	D (Å)	ε (x10^{-3})
$Sr_2Fe_{0.2}Ni_{0.8}MoO6$	5.357_7	11.941_0	342.77	1970	2.850
$Sr_2Fe_{0.4}Ni_{0.6}MoO6$	5.363_2	11.953_0	343.82	1358	2.836
$Sr_2Fe_{0.6}Ni_{0.4}MoO6$	5.369_9	12.002_5	346.10	1158	0.535
$Sr_2Fe_{0.8}Ni_{0.2}MoO6$	5.375_3	12.002_5	346.80	1171	1.233

The increase of the Ni concentration (r_{Ni2+}=0.69 Å), cation with a smaller radius as those corresponding to Fe^{2+} (r_{Fe2+}=0.78 Å) (Shannon ionic radii) leads to a decrease of the lattice constants and of the unit cell volume, that is in agreement with the results from Table 1. The substitution of Fe with Ni improves the average size of the crystalline blocks (D), which increases monotonously with the increase of Ni concentration. The microstrains (ε) have a minimum for x=0.4, which is connected with two processes with takes places at substitution of Fe with Ni: 1) a better accommodation of cations on B places, which means a diminish of the microstrains, on a hand, and 2) the increase of Ni^{3+} concentration, which contributes to the increase of the microstrains, on other hand.

The magnetic behavior of the actually investigated $Sr_2Fe_xNi_{1-x}MoO_6$ compounds is typical for a ferromagnet, with Curie's temperature between 325 and 370 K. A comparison between the calculated (p_{cal}), without Ni contribution, and the experimental molecular magnetization (p_{exp}) (Table 2) indicates a complex behavior of the samples. For a small amount of Fe in the samples, the superexchange interaction Fe-O-Mo, which produces the alignment of the elementary magnetic moment of Fe and Mo, does not take places (Table 2). We suppose that the presence of Ni on the B places favors the disorder of Fe and Mo on B and B' places and the disappearance of Fe-O-Mo-O-… bonds. The formation of the Fe/Ni-O-Fe/Ni-O-Mo... bonds lead to the appearance of the antiferromagnetic zones, implicitly, to the decrease of the magnetic moment. On other hand, the increase of the Fe concentration in the samples should lead to an increase of the magnetic moment of the samples.

Table 2. The Curie temperature (T_C), specific (σ) and molecular (p) magnetization for $Sr_2Fe_xNi_{1-x}MoO_6$ double perovskites.

Chemical composition	T_C (K)	σ(ému/g)	$p_{exp}(\mu_B)$	$p_{cal}(\mu_B)$
$Sr_2Fe_{0.2}Ni_{0.8}MoO_6$	-	0.00	0.000	1.118
$Sr_2Fe_{0.4}Ni_{0.6}MoO_6$	370.0	21.57	1.641	2.236
$Sr_2Fe_{0.6}Ni_{0.4}MoO_6$	325.0	46.35	3.521	3.354
$Sr_2Fe_{0.8}Ni_{0.2}MoO_6$	370.0	14.11	1.071	4.472

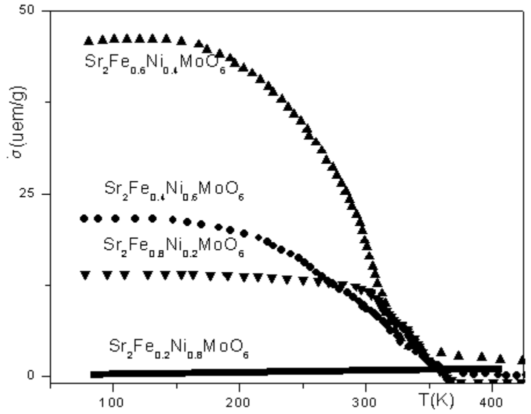

Fig. 2. The dependence of the specific magnetization vs. temperature and chemical composition in the $Sr_2Fe_xNi_{1-x}MoO_6$ system.

The corroboration of these processes explains the observed behavior of specific magnetization vs temperature and the concentration of Fe/Ni in the samples. For small Fe concentration, the Fe cations do not behave any superexchange interaction, implicitly no alignment of the magnetic moments could be observed at the samples which contain less iron as corresponding to $x \leq 0.2$. It is possible that a small amount of Ni cations to participate to the superexchenge interaction and to the magnetic moment of the samples (Table 2), if we take account of the differences between the experimental and calculated molecular magnetic moment of $Sr_2Fe_{0.6}Ni_{0.4}MoO_6$ perovskite. The lengths of Fe-O and Mo-O bonds have a smaller influence on the Curie temperature as the presence of an increase number of Ni/Fe cations in the neighborhood of Fe cations.

The substitution of Ni has an indirect effect on the transport properties of the $Sr_2Fe_xNi_{1-x}MoO_6$ complex oxides by means of changes of the microstrains level and the average size of the coherent crystalline blocks. When Ni^{2+}/ Ni^{3+} cations concentrations increase, takes places a change of the semiconductor component of the samples, due to the difference between the activation energy associated with electron hopping corresponding to $Fe^{2+} \rightarrow Fe^{3+}$ and $Ni^{2+} \rightarrow Ni^{3+}$ processes.

The general behavior of the magnetoresistence is due to the contribution of the extrinsic component. We suppose that the magnetoresistance is manly formed by two components: (1) an intrinsic component, which is due to the ordered crystalline core, and (2) an extrinsic component, due to the boundary layer of the crystallite, which is disordered. The intrinsic component depends on the chemical composition of the samples, while the extrinsic component is strong influenced by the sintering conditions. Near room temperature, where the extrinsic behavior predominates, there is a good correlation between the microdistortions (ε) degree and the average size of the mosaic blocks (D), on the side, and the magnetoresistance for the samples with ferromagnetic behavior, on other side (Table 1 and Fig. 3).

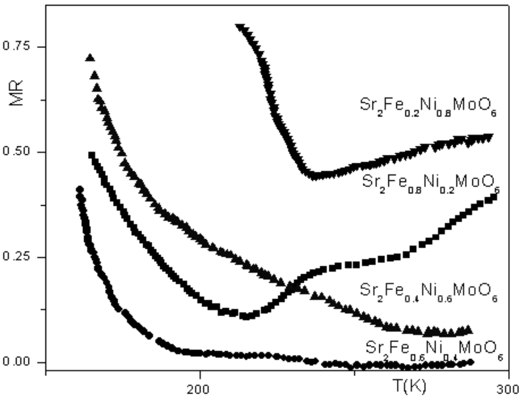

Fig. 3. The dependence of the magnetoresistance vs temperature and chemical composition in $Sr_2Fe_xNi_{1-x}MoO_6$ system.

The largest values of the magnetoresistance were obtained for $Sr_2Fe_{0.2}Ni_{0.8}MoO_6$, which is non-magnetic in the investigated range of temperatures. Because the magnetoresistance have the largest value for this sample (Fig. 3), the applied magnetic field is more effective concerning the spin transfer between two different crystallites.

4. Conclusions

$Sr_2Fe_xNi_{1-x}MoO_6$ double perovskites with tetragonal structure were obtained by an improved ceramic technology, using a specific reductor agent. The unit cell volume and the average size of the mosaic blocks monotonously decrease with the Ni concentration. Compounds with $x \geq 0.4$ are ferromagnetic, with an increase of the disorder of Fe/Ni and Mo cations on B and, respectively, B' places, when the Fe concentration increases. A very small amount of Ni cations could takes part to the magnetic moment of the samples. The substitution of Fe with Ni leads to a no monotonous variation of the Curie temperature. Because no maxim of the magnetoresistance was observed near Curie temperature, we consider that it dominates the extrinsic behavior. $Sr_2Fe_xNi_{1-x}MoO_6$ compounds exhibit very large magnetoresistance at relatively low applied magnetic field (about 2 T), nearly room temperature. In this temperature range, a good agreement was observed between the magnetoresistance and the microdistortions and average size of coherent blocks.

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[*] Corresponding author: loz@phys-iasi.ro