

Influence of the microstructure on extrinsic magnetoresistance in $\text{Sr}_2\text{Fe}_{0.9}\text{Gd}_{0.1}\text{Mo}_{1-x}\text{W}_x\text{O}_6$ double perovskites

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We have prepared by an improved standard ceramic technology $\text{Sr}_2\text{Fe}_{0.9}\text{Gd}_{0.1}\text{Mo}_{1-x}\text{W}_x\text{O}_6$ double perovskites. As precursors were used oxides and carbonates, mixed in stoichiometric ratios, corresponding to the expected chemical composition. The final treatment was performed in vacuum at 1190°C. The sintered/treated samples were investigated by means of XRD by using a DRON 2.0 diffractometer, with an acquisition data system. Transport measurements were performed between room temperature and 700 K. The samples contain small quantities of foreign phases as $\text{Sr}_2\text{Fe}_2\text{O}_5$, SrFeO_{3-x} , SrMoO_3 or similar. The crystalline structure of the main phase can be identified as Fm3m (GS 225) or a cubic phase with a low tetragonal distortion, identified by FullProf® tests as having an I4/mmm structure. The lattice constant, volume unit and the microstrains level have a minimum value for $x = 0.4$. We attributed this minimum to corroboration of two processed: (1) a general increase of the concentration of B' cations in the low valence state, and (2) an increase of the W concentration in the samples. The Mott mechanism seems to dominate around room temperature, while at higher temperature the transport is similar to that of the semiconductors.

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1. Introduction

The magnetoresistance of $\text{A}_2\text{BB}'\text{O}_6$ double perovskites is due to the intergrain tunneling (ITM=intergrain tunneling magnetoresistance) of the charge carriers, the interfacial magnetism and or the presence of the domain walls [1]. The effect is present also in the polycrystalline manganites or CrO_2 , some pyrochlores etc and can be caused by the dependence of the boundary layer resistivity of the relative orientation of the atomic magnetic moments. Recent theoretical investigation on the ITM of the ferromagnetic semiconductors showed that a strong correlation exists between the extrinsic magnetoresistance, on one hand, and the itinerant-carriers and magnetic-ion densities, on other hand [2]. We intend to investigate the magnetoresistance behavior of the $\text{A}_2\text{BB}'\text{O}_6$ ($\text{A}=\text{Sr}$; $\text{B}=\text{Fe}$, Gd ; $\text{B}'=\text{Mo}$, W) double perovskites, where Fe and Mo cations, which contribute to the magnetic structure, are substituted by rare-earth cations (Gd) or, respectively, with W.

2. Experimental

The samples were obtained by means of standard ceramic technology. We used as precursors some oxides and carbonates, mixed in stoichiometric ratios, which corresponds to the expected chemical composition. The final treatment was performed in vacuum at 1190°C. The

details concerning the XRD and electrical measurements are the same with those already communicated [3]. All the samples were also investigated at temperatures higher than room temperature. The XRD data were handled with DICVOL[®], CELLREF[®] and FULLPROF[®]. To obtain a better fitting between the observed and calculated XRD data we use a modified pseudo-Voigt function.

3. Results and discussion

$\text{Sr}_2\text{FeMoO}_6$ parent compound of the investigated samples have an $\text{Fm}\bar{3}\text{m}$ structure at high temperature. Under 400 K it undergoes a transition to a lower symmetry structure (tetragonal). Some authors obtained a good fit between the experimental and observed data by using a $\text{P4}_2/\text{m}$ SG [4]. The introduction on B places of rare earth, including Gd, leads to an increase of the antiferromagnetic interaction and the appearing, under Néel temperature, of antiferromagnetic regions [5]. On other hand the substitution of Fe with Gd on B places could changes the local microstrain state ($r_{\text{Fe}^{3+}}=0.645 \text{ \AA}$; $r_{\text{Gd}^{3+}}=0.938 \text{ \AA}$ (radii on Shannon)) and the magnetic interaction ($p_{\text{Fe}^{3+}}=5\mu_{\text{B}}$; $p_{\text{Gd}^{3+}}=7.9\mu_{\text{B}}$; $p_{\text{Mo}^{5+}}\approx 1.7\mu_{\text{B}}$, where p is the magnetic moment of the ion). It is known that by the substitution of Mo with W one can obtain: (1) a supplemental local microstrain due to the small difference between ionic radii

and (2) a modification of the magnetic properties due to the difference between the atomic magnetic moments. A large variation of the itinerant electrons takes place with the substitution of the Mo with W, when the sintering takes places in air. On other hand the modifications of the sintering atmosphere strong influences the ratio between the low/high valence cation concentrations [6].

We observed a small number of maximums in our diffractograms and the tests performed with CheckCell[®] program indicated the $Fm\bar{3}m$ structure as most probable. XRD data were handled supposing an fcc unit cell (SG 225, $Fm\bar{3}m$), with Sr cations on (8c), Fe (Gd) cations on (4a), Mo (W) on (4b) and O on (24e) Wyckoff positions. Rammeh et al prepared by [8] by ceramic technology similar compounds, $Ba_2(Fe, W_{1-x}Mo_x)O_6$, by ceramic technology[8]. They founded that the structure can be characterized with GS $Fm\bar{3}m$, the lattice constants increasing with the increase of the W concentration in the samples.

The samples contain small quantities of foreign phases as $Sr_2Fe_2O_5$, $SrFeO_{3-x}$, $SrMoO_3$ or similar. The crystalline structure of the main phase can be identified as $Fm\bar{3}m$ with a low tetragonal distortion (Fig. 1). The tests with FullProf[®]/CheckCell[®] programs indicated the $I4/mmm$ as most probable distorted tetragonal unit cell. Because in the both lattice (cubic and tetragonal structures) the positions of the cations and anions are practically the same, we cannot exclude at this stage the possibility that the main phase could be a mixture from a cubic and a tetragonal phase. The results concerning the secondary phases (less than 10% in the actual samples) and thus concerning the tetragonal/cubic ratio concentrations will be published elsewhere. The unit cell of main phase of $Sr_2Fe_{0.9}Gd_{0.1}Mo_{1-x}W_xO_6$ compounds is formed by Fe (Gd) O_6 and Mo(W) O_6 chains (Fig. 2). Only FeO_6 octahedrons are marked in the sketch of the unit cell (Fig. 2).

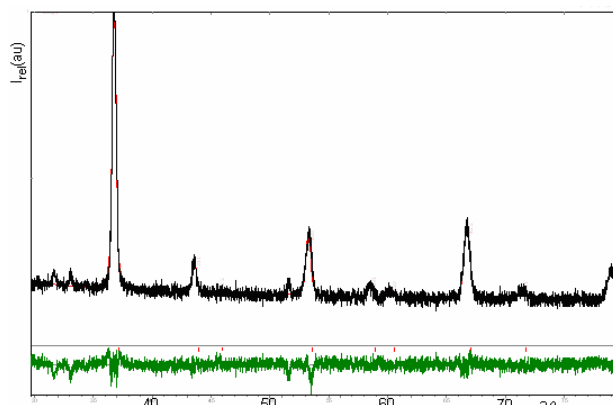


Fig.1. Observed (black) and calculated (red) diffractograms for $Sr_2Fe_{0.9}Gd_{0.1}WO_6$. The difference is represented with green.

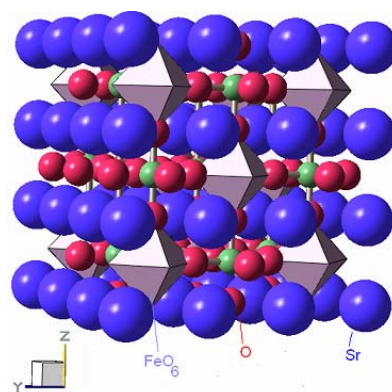


Fig. 2. Unit cell ($Fm\bar{3}m$) of main phase in the $Sr_2Fe_{0.9}Gd_{0.1}Mo_{1-x}W_xO_6$ system.

Table 1. The lattice constant (a), unit cell volume (V), average size of the mosaic blocks (D), the microstrains (ϵ), the Fe-O and Mo-O distances in the $Sr_2Fe_{0.9}Gd_{0.1}Mo_{1-x}W_xO_6$ system.

Chemical composition	a (Å)	V (Å ³)	D (Å)	ϵ ($\times 10^{-3}$)	d_{Fe-O} (Å)	d_{Mo-O} (Å)
$Sr_2Fe_{0.9}Gd_{0.1}Mo_{0.8}W_{0.2}O_6$	7.890 ₁	491.19	289.3	1.023	2.0514	1.8936
$Sr_2Fe_{0.9}Gd_{0.1}Mo_{0.6}W_{0.4}O_6$	7.891 ₄	491.43	320.5	0.652	2.0526	1.8947
$Sr_2Fe_{0.9}Gd_{0.1}Mo_{0.4}W_{0.6}O_6$	7.898 ₈	492.81	383.3	0.287	2.0537	1.8957
$Sr_2Fe_{0.9}Gd_{0.1}Mo_{0.2}W_{0.8}O_6$	7.945 ₅	501.61	294.5	1.038	2.0658	1.9069
$Sr_2Fe_{0.9}Gd_{0.1}WO_6$	7.922 ₂	497.21	308.6	1.080	2.0598	1.9013

Sr cations (blue color) are sitting into the space between the Fe(Gd) O_6 and Mo(W) O_6 octahedrons. Our data, concerning the lattice constant, the distances Fe - O and Mo - O (s.Tab.1) and the position of O in the unit cell, are in agreement with the data from the literature [4,7,8]. Kobayashi et al. have obtained tetragonal (at room temperature) $Sr_2FeMo_xW_{1-x}O_6$ double perovskites by standard ceramic technology and a final treatment in a 0.1% H_2 /Ar at 1400°C [9]. The lattice constants and the volume of the tetragonal unit cell decrease with the increase of the Mo concentration [9]. At room temperature

Kobayashi et al. have observed a variation of the resistivity of about 15%/7 T and explained the results in the terms of percolation model.

The lattice constant, the unit cell volume and average size of the mosaic blocks attain a maximum, while the microstrains have a minimum for $0.8 < x < 0.6$ when concentration increases in the $Sr_2Fe_{0.9}Gd_{0.1}Mo_{1-x}W_xO_6$ system (Table 1). The variation of the Fe-O and Mo-O distances, which are in a good agreement with the corresponding ionic radii, follows the same dependence vs Mo/W concentration in the samples (Table 1). Supposing

that the W cations preserve the valence state of the Mo, the substitution of Mo cations ($r_{\text{Mo}^{6+}}=73$ pm) with W cations ($r_{\text{W}^{6+}}=74$ pm) (cations radii after Shannon) should leads to an increase of the lattice constant with the increase of the W concentration. We observed a non-monotonous dependence of lattice constant vs Mo/W concentration, which corresponds to a relative decrease of the Mo^{5+} ($r_{\text{Mo}^{5+}}=75$ pm) and, respectively, an increase of W^{6+} ($r_{\text{W}^{6+}}=74$ pm) concentration. The increase of the B' low valence cations concentration leads to an increase of B' radius ($\langle r_{\text{B}'} \rangle$), while the increase of the W^{6+} concentration diminish $\langle r_{\text{B}'} \rangle$. Taking account the lattice constant values we consider that the samples corresponding to $x=0.8$ and $x=1.0$ contain the highest concentration of low valence state cations. The decrease of the microstrains vs Mo/W concentration, for samples corresponding to $x \leq 0.6$, is due to a better accommodation of the cations on B' places. The high temperature resistivity measurements showed the influence of two mechanisms on the transport properties: (1) the Lorentz effect, which gives a positive contribution to the resistivity, and (2) the negative contribution to the magnetoresistance, due to the relative alignment of the atomic magnetic moments. We observed that the contributions of these mechanisms are strongly dependent on the chemical composition of the samples and of the distortion degree of the boundary layers of the crystallites (Fig. 3).

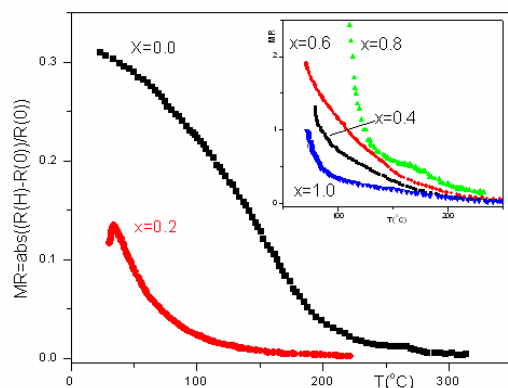


Fig. 3. The dependence of the magnetoresistance vs temperature for the $\text{Sr}_2\text{Fe}_{0.9}\text{Gd}_{0.1}\text{Mo}_{1-x}\text{W}_x\text{O}_6$ double perovskites.

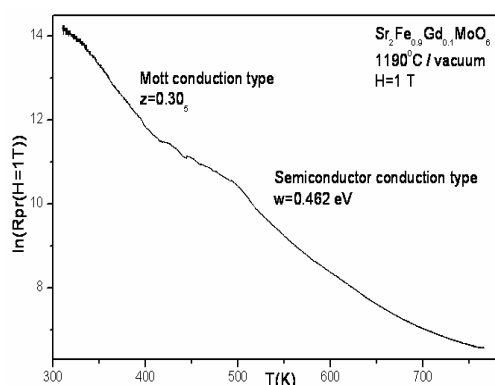


Fig. 4. The dependence of resistance vs temperature for $\text{Sr}_2\text{Fe}_{0.9}\text{Gd}_{0.1}\text{MoO}_6$.

The resistivity decreases rapidly at temperatures near room temperature, following the law: $\ln R = \ln R_0 + (T_0/T)^z$, while at higher temperature the samples exhibit a semiconductor conduction type (s. Fig.4). The value of z (≈ 0.32), corresponds to the VRH (variable range hopping) process. Corroborating the results from the literature concerning the crystalline structure and structural phase transition of $\text{Sr}_2\text{FeMoO}_6$ or similar double perovskites [10-12] with our transport data on $\text{Sr}_2\text{Fe}_{0.9}\text{Gd}_{0.1}\text{Mo}_{1-x}\text{W}_x\text{O}_6$ system, we can conclude that at relatively low temperature, between 50 and 150°C, the samples with $x > 0.2$ undergo a crystallographic transformation (Fig. 3). We suppose that the sudden variation (Fig. 3, inset) of the magnetoresistance takes place because the ordered tetragonal component undergoes a transformation to a disordered cubic structure. The substitutions of the Fe with Gd and Mo with W have as effect the increase, respectively, the decrease of the magnetoresistance, for small values of the W in $\text{Sr}_2\text{Fe}_{0.9}\text{Gd}_{0.1}\text{Mo}_{1-x}\text{W}_x\text{O}_6$ system. For the $x \leq 0.2$, the magnetoresistance decreases with the increase of the W concentration and decrease of the microstrains in the sample (Table 1). The transition from an ordered tetragonal phase to a disordered cubic phase increases the resistivity of the sample and the disorder degree of the samples, which leads to an increase of the probability of the electronic spin transfer between magnetic atoms, implicitly of the magnetoresistance.

4. Conclusions

For the first time new magnetoresistive materials from $\text{Sr}_2\text{Fe}_{0.9}\text{Gd}_{0.1}\text{Mo}_{1-x}\text{W}_x\text{O}_6$ system were obtained by means of improved ceramic technology. Due to the variation of the low valence cations and Mo/W concentration a non-monotonous dependence of lattice constant vs Mo concentration was observed. A crystallographic transition takes place for the samples with $x > 0.2$. Close room temperature the perovskites with $x < 0.2$ have a Mott-like conduction, while at higher temperature dominates semiconductor type conduction. Large values of the magnetoresistance for relatively small applied magnetic field were observed near room temperature, for double perovskites corresponding to $x \leq 0.2$. For $x > 0.2$ a variable amount of tetragonal phase, with the same composition as the cubic phase, is present in the sample. A sudden increase of the magnetoresistance takes place with the increase of the disorder degree of the samples.

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