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Peculiar structural effect of Sr_2FeMoO_6 perovskite type compounds

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Double perovskite Sr_2FeMoO_6 type compounds show special properties, such as magnetoresistance response at relatively small-applied fields and at rather high temperatures (ca. 400 K). Perovskite precursors were obtained unconventionally, in liquid phase, using oxalic acid as complexing agent, in the presence of ethylene glycol as polymerization agent. Ordering control concerning the magnetic properties is predictable to be strongly influenced by the synthesis route. The thermal stability of the precursors and the phase transitions of the oxide samples were analyzed by thermal analysis method, IR spectroscopy, Mossbauer spectroscopy, X-ray diffraction method and magnetic measurements. The experimental data for the perovskite compounds prepared by using oxalic acid as complexing agent revealed a double perovskite structure of analyzed samples, convenient magnetorezistive response (3.51 μ_B/f.u), in good agreement with the Mossbauer spectra. Moreover, Mossbauer spectreoscopy allows the distinction between the ordered and the disordered phases of the perovskite structure and put in evidence the strong dependence of the structural and magnetic characteristics of the double perovskites on the synthesis route.

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1. Introduction

The recent discovery of room temperature magnetoresistance (MR) in Sr_2FeMoO_6 ($T_c \sim 440$ K) has stimulated research on this material and related double perovskite oxides with the general formula $A_2BB'O_6$ [1]. As specified in other papers, Sr_2FeMoO_6 has a *rock salt* ordering of Fe and Mo atoms alternating B sites of ABO_3 type perovskite [1-3].

The structural building blocks ABO_3 are ordered in a three-dimensional network, in such a way, that the B sites are occupied by Fe and Mo ions. The magnetic structure is ferromagnetic due to the antiferromagnetic coupling of Fe and Mo sublattices [2]. The parallel aligned of Fe^{3+} (d^5; S = 5/2) spins in the B sublattice, are antiferromagnetically coupled to Mo^{5+} (d^1; S = 1/2) spins which leads to an expected saturation moment (M_s) per formula unit of $4\mu_B$ 4

Frequently the M_s values for this type of oxides are systematically lower then the predicted value. This effect could be related to antisite defects in the B/B' sublattice, i.e. occupation of Fe (Mo) ions in the Mo(Fe) sites, which proved to be the main cause of a reduced magnetization [3].

As a consequence of the fact that the itinerant $4d^1$ electron of the formally pentavalent Mo transfers part of its charge and spin to the formally trivalent Fe, both ^{57}Fe Mössbauer and Fe K- and L-edge XANES [4-9] data have indicated a mixed-valence state of II/III for Fe in Sr_2FeMoO_6.

From Mössbauer spectra for Sr_2FeMoO_6, the antisite (AS) Fe atoms have been revealed to be trivalent, or Fe^{2+}/Fe^{3+} in right sites [6, 7]. Their concentration is conveniently monitored by means of Mössbauer spectroscopy.

It has been suggested that the tunneling magnetorezistive effect is related to the Fe/Mo ordering such that the higher degree of order yields the larger magnetoresistance [9]. Thus, ways to increase the degree of order in the B-cation sublattice of Sr_2FeMoO_6 are needed for both technological and fundamental considerations. Consequently, we have tried to adapt the "soft chemistry" method to perovskite oxide precursor synthesis, which should improve resulted perovskite oxides structure and properties of the resulted perovskites

2. Experimental

The perovskite precursors were obtained unconventionally, by soft chemistry, using a mixture of $SrCO_3$, $Fe_2(NO_3)_3 \cdot 4H_2O$ and $MoO_3 \cdot H_2O$ in oxalic acid ($C_2O_4H_2$) solution as complexion agent. The oxalic acid was precipitated through the etherification reaction with ethyl-glycol.

The precursor was heated up to 1200 ^{0}C, in the air to obtain oxide powder.

The compacts obtained from precursor powder were reduced in (5%H_2/Ar) atmosphere, 4 hours to reduce Mo^{6+} to Mo^{5+} and Fe^{3+} to Fe^{2+}.

The thermal stability of perovskite precursors was checked by ATD method, using a Perkin Elmer Thermal analyzer, and the structure and phase purity of the samples were performed at room temperature by X-ray diffraction (XRD) using a PANalytical/Phillips (Cu Kα radiation) diffractometer.

The ^{57}Fe Mössbauer spectra were acquired at room temperature, in transmission geometry. A standard set-up with symmetrical wave form and working in constant acceleration mode was used. The gamma radiation was provided by a ^{57}Co(Rh) source. The isomer shifts are reported relative to α-Fe at room temperature.

3. Results and discussion

IR spectroscopy of precursors (400 - 4000 cm^{-1}) revealed the presence of characteristic vibration for the carboxyl group (ν_{COO^-}) which indicated the presence of poly-nuclear oxalates of Fe and Mo.

The thermal analysis shows the formation of double perovskite structure (Fig. 1). The first exothermic peak (232 °C) is attributed to water evaporation and the two peaks, at 498 °C and 571 °C, correspond to the thermal decompositions process of organic acid. Finally, the last peak, at 815 °C represents the temperature where the perovskite structure is formed.

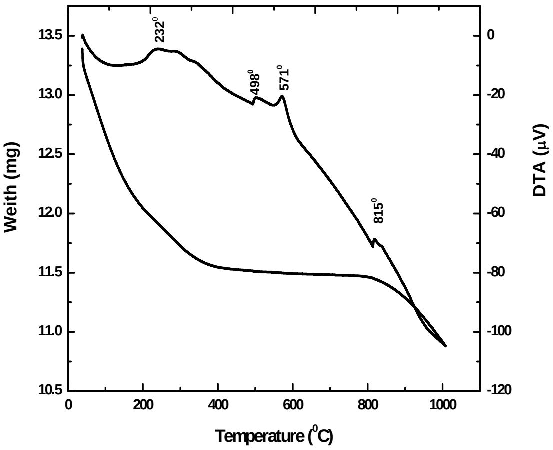

Fig. 1. The thermal analysis of Sr_2FeMoO_6 precursor.

The X-ray diffraction revealed the formation of Sr_2FeMoO_6 as a majority phase in the final product (Fig. 2). No superstructure was observed. The saturation magnetization measured at 5 K on the sample S_1 (Sr_2FeMoO_6 with oxalic acid sintered 4 hours at 1200 °C in 5%H_2/Ar) was 3.51 μ_B/f.u and the magnetoresistance coefficient in 0.5T was negative and about 12% in magnitude [10].

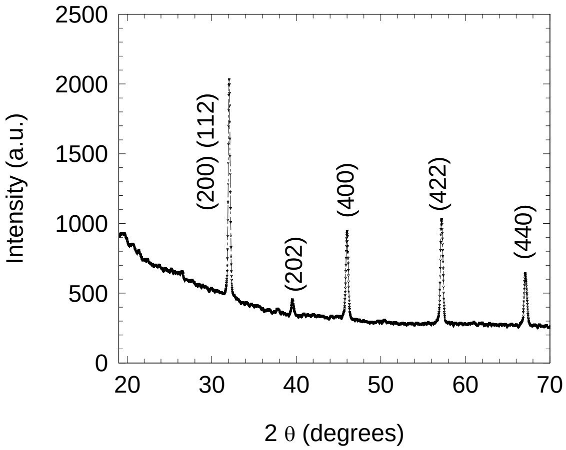

Fig. 2. X-ray diffraction pattern for Sr_2FeMoO_6 sample.

The Mössbauer spectra of samples S1 and S2 (Sr_2FeMoO_6 with oxalic acid sintered 8 hours at 1200^{0}C in 5%H_2/Ar) are collected at room temperature (RT) are presented in Fig. 3.

Both spectra consist mainly of a six-line absorption pattern, showing the presence of the magnetic order at this temperature. The splitting of the involved sextet offer information about the hyperfine magnetic field, which in turn is proportional with the Fe magnetic moment. The broad absorption lines suggest not only a unique hyperfine field but rather a distribution of hyperfine fields. Hence, the fit of the spectra was mainly based on such a distribution.

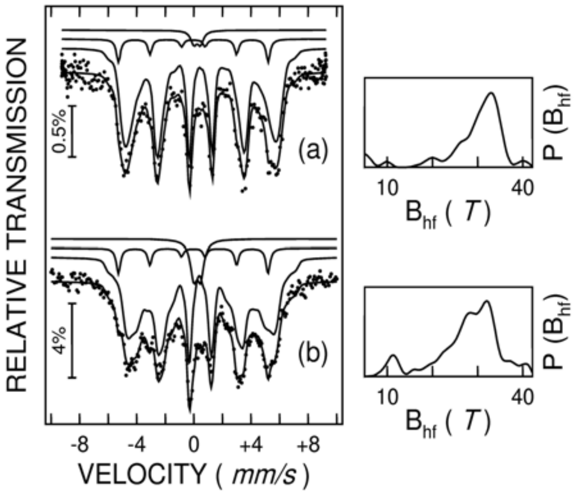

Fig. 3. Mössbauer spectra collected at room temperature for the two analyzed samples: S1 (a) and S2 (b). The central doublet corresponds to an insignificant paramagnetic component, the weak narrow sextet to α-Fe and the main broad sextet to the double perovskite structure. The probability distribution of hyperfine field assigned to the last component is shown on the right side of each spectrum.

Additionally, the increased absorption in the central part of the spectra required the presence of a weak paramagnetic doublet, whereas the presence of small shoulders at about -5.3 mm/s and +5.3 mm/s inferred the presence of a weak sextet belonging to the metallic body center cubic α-Fe phase. All these three spectral components, namely the weak central doublet, the weak narrow sextet and the main large sextet involving distributed hyperfine fields are shown in Fig. 3 for each of the analyzed spectrum. It is worth mentioning that the spectral area of the main broad sextet is 92(1) % for sample S1 and 88(1) % for sample S2. So, this will be the spectral component responsible for the main information in respect to structural aspects and local interactions in the analyzed samples. The hyperfine field distribution resulted from this component is presented on the right side of Fig. 3, for each spectrum. It might be observed that on average, both distributions are centered on a field of about 30 T.

Mössbauer spectra obtained previously on Sr_2FeMoO_6 double perovskites [1,2-4,5] have evidenced sextets with hyperfine fields of about 50 T at 4.2 K and of about 30 T at room temperature. Moreover, at room temperature the spectral lines became much broader, similar to our case. That is not unexpectedly, because the decreasing of the field is quite significant over the mentioned interval of temperature, meaning that at room temperature the magnetic relaxation is enough enhanced in order to induce the significant broadening of the absorption lines. Hence, we may consider that the main component of present spectra (the broad sextet with an average hyperfine field of about 30 T) is assign to the octahedral Fe position in the double perovskite Sr_2FeMoO_6. The difference between the two analyzed samples should be examined starting from the two hyperfine field distributions presented in Fig. 3. Before proceeding to such an examination we should mention that the presence of about 6% of α-Fe in the samples (resulted from relative spectral area of the corresponding sextet) shows a certain inhomogeneity, accompanied with a deviation from stoichiometry of the main double perovskite phase, in the sense that this one is slightly enriched in Mo. However, the relative amount of α-Fe is identical in the both samples (6%) and can not be the reason for eventually different behaviour in respect to electron transport phenomena.

The main difference in the hyperfine field distributions presented in Fig. 3 consists of the presence of a main peak centered at about 32 T for samples S1 and of two comparable peaks centered at about 28 T and 32 T respectively, for sample S2. The average isomer shift of the broad sextet is about 0.55 mm/s, which is a relatively high value for Fe^{3+} in high spin state, suggesting a relative enhanced charge density at the Fe sites. This behaviour is expected in the double perovskite Sr_2FeMoO_6 and has its origin in the delocalization of the $4d^1$ electrons of Mo over the more localized $3d^5$ electrons of Fe. Two cases may be considered here: (i) a maximal delocalization of the Mo electrons which may happened in the perfectly ordered double perovskite structure with its regular alternate FeO_6 and MoO_6 octahedra and (ii) a decreased delocalization of the Mo electrons in a disordered structure when Fe and Mo may mutually replace each other, decreasing so the local number of Mo next neighbors around a considered central Fe. Due to the antiferromagnetic type of coupling between Fe and Mo ions, the spin polarization of the $4d^1$ electron of Mo has to be opposite to the spin polarization of the $3d^5$ electrons of Fe in its high spin state. So, an enhanced delocalization of the Mo electrons, means an increased charge density and a decreased spin density of the hybrid $4d^1$(Mo)/ $3d^5$(Fe) electrons around Fe. Because the Fe hyperfine field is proportional with the spin density of 3d-like electrons of Fe, it results a lower hyperfine field for an increased delocalization of the Mo electrons, as compared with the case of a decreased delocalization. Hence, the two peaks in the hyperfine field distribution corresponding to sample S2 may be interpreted as follows: the peak centered at about 28 T belongs to Fe positions in an ordered double perovskite structure, involving a high delocalization of Mo electrons, whereas the peak centered at 32 T belongs to Fe positions in the disordered perovskite structure with Mo and Fe anti-site occupation and a reduced delocalization of the Mo electrons. Both phases coexist in each sample, but in sample S2 they are comparable, with a relative amount of about 50% for the ordered phase. For sample S1, the weak shoulder around 28 T in the corresponding probability distribution is consistent with a relative content of less than 20% for the ordered perovskite phase. It is well known that the literature stands for a maximal CMR effect in ordered double perovskite structures and in these respect the Mössbauer results would infers an enhanced MR effect in sample S2 with its 50% content of the ordered phase. However, the effect should be not significant either in this sample, due to the enhanced relative content (the rest of about 50%) of disordered phase.

4. Conclusions

The double perovskite was obtained by unconventional method, using oxalic acid as complexion agent. The Mössbauer spectra allow the distinction between ordered and disordered Sr_2FeMoO_6 structures, via electron delocalization processes with influence on the Mossbauer hyperfine parameters. It was clearly observed that ordering control concerning the magnetic properties are strongly influenced by the synthesis route.

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