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Effect of preparation procedure on the magnetic and transport properties of double perovskite Sr_2FeMoO_6*

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Ordered and disordered double perovskite Sr_2FeMoO_6 ceramics have been investigated by powder x-ray diffraction, magnetic and transport measurements, as well as Mössbauer spectroscopy. The heavily disordered sample can be acquired by annealing the ordered samples in argon. The annealing procedure affects not only the nature of grain boundaries but also the grain itself. The evidence of Mössbauer spectra performed at 77 and 300 K indicates that there exist small oxygen deficient clusters of $SrFeO_{3-y}$ in the disordered sample. The paramagnetic Fe^{4+} and Fe^{3+} ions in the compound subsist down to 77 K and the ratio of Fe^{4+}/Fe^{3+} increases with decreasing temperature.

Keywords: double perovskite, magnetoresistance, Mössbauer spectra
PACC: 7220M, 7680, 8140

1. Introduction

Recently, the double perovskite $A_2BB'O_6$ (A is rare-earth or alkaline-earth ion, B and B' are different transition-metal ions) has received renewed interest since the large low-field magnetoresistance (LFMR) at room temperature observed in the ferromagnetic double perovskite Sr_2FeMoO_6 (SFMO).[1] Partly due to a large difference in charge and ionic radii of Fe^{3+} ($3d^5$, S=5/2) and Mo^{5+} ($4d^1$, S=1) ions, this compound exhibits an ordered rock-salt structure, i.e. Fe and Mo ions alternately occupy octahedral sites.[2] For fully ordered structure, the LFMR arises from the high degree spin-polarized carriers tunnelling across grain boundaries. The inherent half-metallic character of SFMO compound has been confirmed by band structure calculations.[1,3,4]

However, unfortunately, all the papers in the literature so far have revealed that none of the SFMO polycrystalline specimens are completely ordered.[5,6] The magnetic state and transport properties of such materials are intimately connected with the antisite disorders and oxygen deficiency according to the theoretical prediction and experimental results.[7,8] The local chemical disorders in these compounds have been characterized by the broadening of the linewidth of the ferromagnetic resonance (FMR) peak.[9]

To date, Mössbauer spectra have been scarcely measured on the disordered SFMO. In this paper, we investigate the effects of the preparation conditions on the properties of SFMO double perovskites and the Mössbauer spectra of heavily disordered samples at 77 and 300 K.

2. Experimental details

The stoichiometric high-purity $SrCO_3$, Fe_2O_3 and MoO_3 powders were well ground using an agate mortar and pestle, pelletized and calcined at 1223 K for 3 h in evacuated silica capsules, then pulverized, pelletized again, finally sintered at 1423 K for 2 h in evacuated silica capsules and denoted as sample A. Part of sample A were annealed at 1423 K for 3 h in high-purified argon atmosphere and designated as sample B.

The crystal phases and lattice structure for all samples were checked by powder x-ray diffraction

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(XRD) with Cu$K\alpha$ radiation. The resistivity (ρ) measurements were carried out using the standard four-probe technique in a cryostat equipped with a superconducting magnet which had a maximum field of 8 T. The magnetic properties were obtained by commercial vibrating sample magnetometer (Lakeshore, VSM system). The ac susceptibility (χ) was measured at a low field (<159 A/m) to determine the magnetic transition temperature T_C. The Mössbauer spectra measurements were carried out using a ^{57}Co/Pd source on a constant-acceleration spectrometer at 77 and 300 K. The spectrometer was calibrated with a standard α-Fe foil and the reported isomer shifts (δ) are relative to the centre of the α-Fe spectrum at room temperature. The MOSFUN program was used to determine the Mössbauer parameters.

3. Results and discussion

The room-temperature XRD patterns for samples A and B indicate that all the peaks can be ascribed to SFMO phase with a tetragonal symmetry. The lattice constants are a_0=0.5619(4) nm, c_0=0.7943(2) nm for sample A and a_0=0.5615(0) nm, c_0=0.7937(4) nm for sample B.

The first derivatives of susceptibility as a function of temperature dχ/dT for samples A and B are plotted in the respective insets of Fig.1, and the T_C are determined to be 386 and 376 K, respectively. The isothermal magnetization versus applied field curves at room temperature for the two samples are also shown in Fig.1. It can be seen that the magnetization has not attained saturation under a field up to 7.96×10^5 A/m. The magnetization at a field of 7.96×10^5 A/m and coercive force for samples A and B are 27.2 Am^2/kg, 2.78×10^3 A/m and 10.4 Am^2/kg, 2.38×10^3 A/m, respectively.

The resistivity ρ as a function of temperature for samples A and B is indicated in the insets of Fig.2. Obviously, the resistivity exhibits different temperature dependence under zero field. For sample A, the ρ reduces linearly with decreasing temperature down to 50 K, and then reaches a nearly saturated value around $1.07\times10^{-4}\Omega$cm. In contrast, sample B has a much greater resistivity and apparently displays a semiconducting behaviour. The ρ for sample B increases moderately with decreasing temperature and tends to a finite value about $1.1\times10^1\Omega$cm.

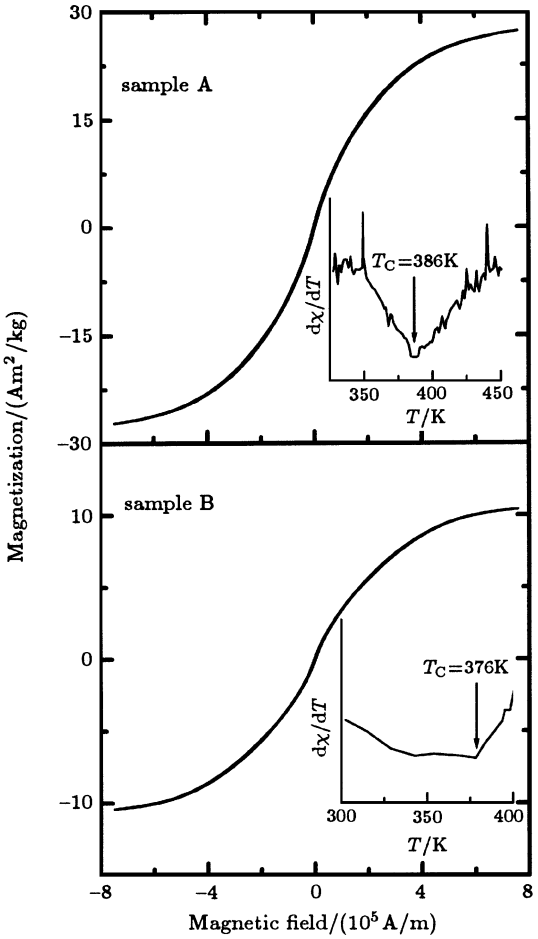


Fig.1. Magnetization of samples A and B as a function of magnetic field at room temperature. The temperature dependence of the first derivative of susceptibility of the samples is shown in respective panels to determine the Curie temperature.

Figure 2 also displays that the ρ for both samples, taken at 6 K, gradually decreases with increasing applied field. However, in the case of sample A, one can find that the ρ decreases steeply in the field region below 7.96×10^5A/m, implying the presence of LFMR. This observation is in good agreement with previous reports.[1,5] The LFMR has been interpreted in terms of tunnelling magnetoresistance (MR) at the grain boundaries and is closely related to the domain rotations. In contrast, the ρ for sample B decreases linearly with increasing applied field without low-field response. In the higher field region, the two MR-H curves are approximately parallel with each other with almost the same slope (10^{-2}/(10^6A/m)); here, the MR(H) is defined as $(\rho(H)-\rho(0))/\rho(0)$. The reduction of resistance in high field for the two samples may be ascribed to the same mechanism, i.e. the suppression of the spin fluctuations with the application of an external field.

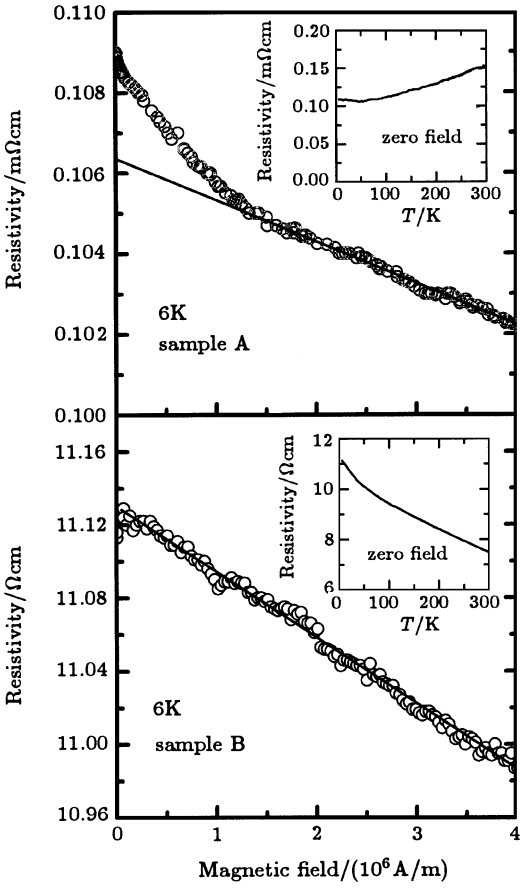


Fig.2. Isothermal resistivity for samples A and B as a function of magnetic field at 6 K. The straight lines are guides to the eye. The insets display the temperature dependence of resistivity for respective samples.

Sample B exhibits a lower value of magnetization, larger resistivity and absence of LFMR response with respect to sample A; thus, it can be identified to be disordered SFMO double perovskite. The absence of LFMR observed in the heavily disordered SFMO samples is probably due to the fact that the antisite disorders are detrimental to half-metallic nature.[5]

It is well known that Mössbauer spectra can provide information about the electronic configuration of iron and its local crystallographic environment,[10] and the investigations of Mössbauer spectra of ordered SFMO have been in more detail than those of disordered samples. In order to gain a better understanding of the structural and magnetic properties of the disordered sample B, the Mössbauer spectra were measured at 77 and 300 K and the results are shown in Fig.3.

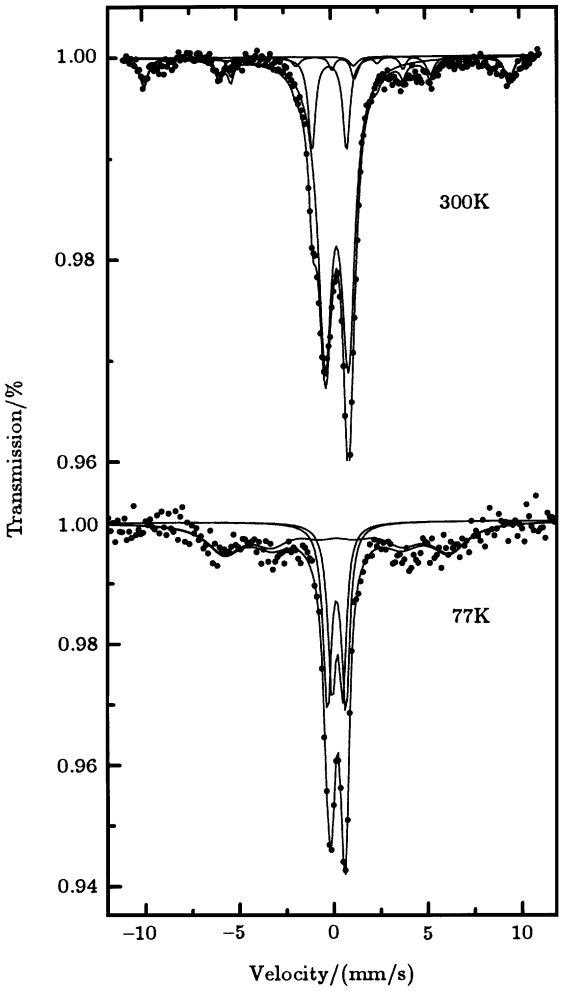


Fig.3. Mössbauer spectra of sample B recorded at 300 and 77 K, respectively.

Both spectra consist of main doublets and a small amount of sextet absorption lines. The spectra were fitted using two paramagnetic doublets (D_1, D_2) and one or two magnetically splitting sextets (H_1, H_2). The obtained hyperfine parameters are shown in Table 1.

Table 1. Mössbauer data for sample B. The hyperfine parameters, δ (isomer shift), Δ (quadrupole splitting), $B_{\rm hf}$ (hyperfine field), I (relative intensity), and Γ (linewidth) are obtained at 77 and 300 K.

Temperature/K	Component	δ/(mm/s)	Δ/(mm/s)	$B_{\rm hf}$/T	I/%	Γ/(mm/s)
300	D_1	0.087	1.830		12.3	0.435
	D_2	0.432	1.236		75.1	0.870
	H_1	–0.053		59.78	8.5	0.500
	H_2	0.147		23.10	4.1	0.346
77	D_1	0.155	1.171		31.2	0.260
	D_2	0.571	0.710		25.7	0.266
	H_1	0.360		36.80	43.1	2.120

The isomer shifts δ for D_1 are 0.155 and 0.087 mm/s at 77 and 300 K, respectively. These values are somewhat smaller than the low end of the range expected for high-spin Fe^{3+} and Fe^{2+} ions,[11] but in good agreement with that of high-spin Fe^{4+} ions in oxygen deficient compound $SrFeO_{3-y}$.[12,13] Moreover, the quadrupole splittings Δ of D_1 within 1.171 mm/s at 77 K and 1.830 mm/s at 300 K support that this component could be ascribed to the contribution of paramagnetic Fe^{4+} ions. The values of another paramagnetic component D_2 with Δ=1.236 mm/s, δ=0.432 mm/s at 300 K and Δ= 0.710 mm/s, δ=0.571 mm/s at 77 K agree with the reported values,[14] and can be assumed to come from paramagnetic high-spin Fe^{3+} ions. The large value of Δ at room temperature implies the heavy local distortion of iron nuclei than that at 77 K. The distortion environment in iron sites of doublets at room temperature is also proved by the broad linewidths (0.870 and 0.435 mm/s) of both doublets, whose linewidths become sharp as the temperature lowers. The relative intensity (I) of D_1 increases from 12.3% to 31.2% as the temperature decreases from 300 to 77 K, while the intensity of D_2 reduces from 75.1% to 25.7%. The intensities of magnetic components H_1 and H_2 are about 8.5% and 4.1%, respectively, at 300 K, but then overlap and form a significantly broad magnetic relaxation sextet (linewidth >2 mm/s) at 77 K, whose average hyperfine field $B_{\rm hf}$ is around 36.8T. This phenomenon has also been observed by Venkatesan and his coworkers,[15] but our lower $T_{\rm C}$ of the compound gives rise to the broad relaxation sextets appearing at lower temperatures. However, Sarma [5] claimed that, for disordered samples, the Mössbauer spectra exhibit a magnetic hyperfine splitting with a relatively large linewidth and have no paramagnetic contribution below $T_{\rm C}$. This is probably due to the fact that sample B displays a greater degree of disorder to induce two short scale paramagnetic iron sites according to the two doublets.

In disordered samples, some Mo^{5+} ions occupy the sites of Fe^{3+} cations and vice versa, which may lead to small clusters with antiferromagnetic Fe–O–Fe configuration.[16] Such clusters have been observed in pulsed-laser-deposited epitaxial SFMO thin films by virtue of transmission electron microscopy.[6] Asano and his colleagues suggested that the clusters had chemical composition close to $SrFeO_3$, thus exhibiting low Nèel temperature $T_{\rm N}$ =134 K. Sánchez [17] agreed with the local chemical composition in the clusters near $SrFeO_3$ but thought that the Fe–O–Fe antiferromagnetic interactions seemed more similar to $LaFeO_3$ with Fe^{3+} high spin state. According to our Mössbauer studies, the presence of paramagnetic Fe^{4+} ions in sample B clearly favours the former scenario. In addition, the doublets corresponding to the paramagnetic Fe^{4+} ions survive down to 77 K, far lower than the $T_{\rm N}$ of $SrFeO_3$, implying that oxygen deficiency occurs in the clusters. The reason is that the $T_{\rm N}$ decreases with the increase of oxygen deficiency.[18] That is to say, the clusters remain paramagnetic down to 77 K. Furthermore, Mössbauer spectra studies for oxygen deficient oxide $SrFeO_{3-y}$ display that Fe ions can be assigned to different valences according to $Sr(Fe^{3+}_x Fe^{4+}_{1-x})O_{3-y}$.[19] The Fe^{4+}/Fe^{3+} ratio is closely connected with temperature.[10] The intensities corresponding to Fe^{4+} and Fe^{3+} paramagnetic ions increase and decrease with reducing temperature from 300 to 77 K, respectively, giving rise to an increase of Fe^{4+}/Fe^{3+} ratio.

The comparative investigation of samples A and B shows that the argon-annealing procedure promotes the degree of antisite disorder and thereby causes the difference of physical properties. This procedure not only affects the nature of the grain boundaries as reported in Ref.[3], but also modifies the properties of grain bulk such as magnetization, Curie temperature, lattice parameters; in addition, it even leads to paramagnetic $SrFeO_{3-y}$ clusters. The size of the $SrFeO_{3-y}$ clusters is intimately related to the annealing procedure and strongly affects the magnetoresistance of SFMO.

4. Conclusions

The disordered Sr_2FeMoO_6 double perovskite ceramic displays lower magnetization and larger resistivity than that of the ordered sample. The annealing procedure can lead to modification of both grain boundary nature and intragrain properties. Mössbauer spectra for the disordered sample show that there exist small clusters of oxygen deficient compound $SrFeO_{3-y}$ in the disordered sample. This clearly indicates that the properties of the double perovskite Sr_2FeMoO_6 depend strongly upon the preparation conditions, and in the heavily disordered samples the paramagnetic clusters of $SrFeO_{3-y}$ will emerge.

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