Simple and Efficient Route to Prepare Homogeneous Samples of Sr_2FeMoO_6 with a High Degree of Fe/Mo Order

Y. H. Huang,[†,‡] J. Lindén,[§] H. Yamauchi,[†] and M. Karppinen*[,†]

Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, and Physics Department, Åbo Akademi, FIN-20500 Turku, Finland

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Polycrystalline Sr_2FeMoO_6 samples are synthesized by an encapsulation technique under very low oxygen partial pressures utilizing the Fe/FeO redox couple as an oxygen getter. A route based on thermal decomposition of metal complexes, using ethylenediaminetetraacetic acid as the complexant, is developed to prepare a precursor powder. Single-phase samples are readily obtained even at temperatures as low as 900 °C. The degree of Fe/Mo ordering and the grain size are well-controlled by sintering temperature and time. Homogeneous morphology of the samples is confirmed from scanning electron microscopy images. Rietveld refinements of X-ray diffraction patterns indicate that the degree of order (S) at the Fe/Mo sites is higher than 0.95 for samples sintered at 1150 °C for 100 h. For the same sample a record-high saturation magnetization of 3.96 μ_B, which is very close to the theoretical value of 4 μ_B, is obtained. It is considered that the high degree of order stems from the uniform mixing of starting reactants in an atomic scale and also from the stability of overall cation stoichiometry during sample sintering in an encapsulated ampule. It is found that the Curie temperature exhibits a nonmonotonic dependence on S, with the maximum at $S \approx 0.84$. Additionally, evidence for super-paramagnetic-type behavior in the present solution-derived samples is obtained from the Mössbauer data.

Introduction

Due to its remarkable tunneling-type magnetoresistance (TMR) effect achieved even at room temperature and low applied magnetic fields, the $A_2BB'O_6$-type double-perovskite, Sr_2FeMoO_6, has drawn a great deal of attention.[1] It is considered that in Sr_2FeMoO_6 a long-range magnetic interaction between the spins of the B-site cation constituents, Fe^{III} ($S = 5/2$) and Mo^{V} ($S = 1/2$), can induce a ferrimagnetic half-metallic state with a large saturation magnetization (M_S) of 4 μ_B *per* formula unit. 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[2] and Fe K- and L-edge XANES[3] data have indicated a mixed-valence state of II/III for Fe in Sr_2FeMoO_6. In line with the II/III valence state of Fe, an NMR study suggested a mixed-valence state of V/VI for Mo.[4] Even though 4 μ_B is expected for the M_S value, experimentally observed values typically remain below 3.7 μ_B,[5,6] and values exceeding 3.9 μ_B[7] have not been reported yet. (Note that the magnitude of M_S should not depend on the degree of valence mixing between $Fe^{II/III}$ and $Mo^{V/VI}$.) It is well-documented that the lower-than-predicted M_S value is due to partial disorder within the B-cation sublattice, i.e., antisite (AS) defects.[5,8] From Mössbauer spectra for Sr_2FeMoO_6, the AS Fe atoms have been revealed to be trivalent. Their concentration is conveniently monitored by means of Mössbauer spectroscopy.

It has been suggested that the TMR 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. Thermodynamically the lower the synthesis temperature is, the higher the degree of order should be.[7] However, at low temperatures cation diffusion is extremely slow such that the

* Corresponding author. Phone: +81-45-924-5333. Fax: +81-45-924-5365. E-mail: karppinen@msl.titech.ac.jp.
† Tokyo Institute of Technology.
‡ Permanent address: Institute of Advanced Materials, Fudan University, Shanghai 200433, China.
§ Åbo Akademi.

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degree of order is rather limited by kinetics.[7] The most commonly employed synthesis route for the Sr_2FeMoO_6 phase involves firing of mechanically mixed powder precursors in flowing H_2/Ar or H_2/N_2 gas at 900−1200 °C.[1,5] The drawback of this method is that once one aims at samples with a high degree of Fe/Mo order the very long heating periods that are required to complete the cation diffusion are likely to yield cation-nonstoichiometric samples due to partial evaporation of some of the constituent metals. Impurity phases of $SrMoO_4$ and $SrFeO_{3-\delta}$ commonly appear in such samples. Moreover, application of H_2-containing gas flow brings about the need to pay extra attention to experimental safety. Some efforts to shorten the required heating periods by employing sol−gel routes to obtain homogeneous precursors have been reported.[10,11] In these studies sintering was carried out under H_2/N_2 gas flow, and thus impurities such as $SrMoO_4$ were still observed. We recently introduced an encapsulation technique utilizing iron as an oxygen getter to prepare high-quality Sr_2FeMoO_6 samples.[7,12] This technique not only makes the preparation procedure safe and simple but also efficiently prevents the volatilization of the constituent metals during the (long) sintering period. Here we further improved this encapsulation technique by using a wet-chemistry route for preparing a homogeneous precursor powder, such that the formation of the Sr_2FeMoO_6 phase and the ordering of cations are facilitated more efficiently. Using a solution-homogenized powder as the precursor, an almost completely ordered sample with a record-high M_S value of 3.96 μ_B was obtained.

Experimental Section

The precursor powder for Sr_2FeMoO_6 was prepared by thermal decomposition of a complex gel obtained using ethylenediaminetetraacetic acid (EDTA) as a complexant. Stoichiometric amounts of $SrCO_3$, $Fe(NO_3)_3 \cdot 9H_2O$, and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were dissolved in a diluted nitric acid aqueous solution. The molar ratio between the total amount of metal ions and the amount of EDTA was 1:1.5. The acidic solution containing the metal ions was added in drops into an NH_4−EDTA solution, while being stirred at ambient temperature. Ammonia and nitric acid were used to adjust the pH value to ~9 to achieve a clear deep-purple solution. After heating this solution at ~200 °C, an amorphous gel was formed. The gel ignited spontaneously to turn into a raw ash when the excess free water evaporated. The ash was calcined in air at 900 °C for 15 h to obtain the precursor powder for the encapsulation synthesis. The precursor powder was pelletized and subsequently encapsulated into an evacuated fused-quartz ampule containing Fe grains (≥99.9%, under 10 mesh) to act as a getter for oxygen, as described in our previous works.[7,12] The sample ampule was fired at different temperatures (T_s) ranging from 900 to 1150 °C. Also the sintering period (t_s) was varied. In the employed temperature range the oxygen partial pressure inside the ampule in the presence of the Fe/FeO redox couple is estimated at 10^{-13}−10^{-17} atm.[13]

The phase purity and the lattice parameters were checked by X-ray powder diffraction (XRD; Cu Kα radiation). The diffraction profiles were analyzed using a Rietveld refinement program, RIETAN 2000.[14] All the patterns were refined in tetragonal space group, $I4/m$.[15,16] The degree of B-cation order was calculated as $S = 2(g_{Fe} - 0.5)$ from the refined occupancy of Fe at its correct site (g_{Fe}). Micrographs were taken for the samples by a scanning electron microscope (SEM; Hitachi: S4500). Magnetic measurements were performed using a superconducting quantum interference device (SQUID; Quantum Design: MPMS-XL5) and a vibrating sample magnetometer (VSM; Lakeshore VSM 7300).

For the ^{57}Fe Mössbauer measurement an absorber was made of the sample sintered at 1150 °C for 100 h by spreading a portion of the sample powder, mixed with an epoxy resin, on an Al foil. The absorber thickness was ~20 mg/cm^2. For the second measurement under a magnetic field the sample was cut into rectangular shape of 6 mm × 20 mm and inserted between the poles of two permanent Nd−Fe−B magnets. The direction of the field was parallel to the shorter edge of the rectangle, and the field strength was approximately 600 mT. The field was homogenized using an external "horseshoe" of soft iron. Both spectra were recorded in a transmission geometry using the maximum Doppler velocity of 11.15 mm/s. The absorber temperature was set at 77 K. A Cyclotron Co. ^{57}Co:Rh (25 mCi, Jan. 2002) source was used. The direction of the γ-rays was perpendicular to the external magnetic field. The full Hamiltonian of combined electric and magnetic interactions was used to fit the spectra, with the total magnetic field experienced by the Fe nucleus (B), the chemical isomer shift relative to α-Fe at 300 K (δ), the quadrupole coupling constant (eQV_{zz}), the resonance line widths (Γ), and the relative intensities of the components (I) as fit parameters. For each component a certain variation in the parameter B was allowed in order to simulate the fact that the internal fields have a certain spread: a Gaussian distribution was assumed, and its width (ΔB) was also introduced as a fit parameter.

Results and Discussion

High-quality precursor powders were readily obtained by the EDTA-based complexing method. Since EDTA is a strong complexing agent, it quickly reacts with Sr^{2+}, Fe^{3+}, and Mo^{6+} to form a complex at pH ≈ 9. Moreover, EDTA serves as an efficient fuel, producing a large quantity of heat to directly crystallize the oxide phase from the molecular mixture of the precursor solution. Previously it was demonstrated that EDTA is decomposed almost completely when the temperature reaches 500 °C.[17] In Figure 1, shown are XRD patterns for precursor powders which were calcined at 700, 800, and 900 °C. After calcination at 700 °C, the precursor powder consists of two main phases, $SrMoO_4$ (JCPDS No. 80-0842) and $SrFeO_{3-\delta}$ (JCPDS No. 34-0641). The Sr_2FeMoO_6 phase appears in precursors calcined at 800 °C and higher temperatures. For powders calcined at 800 or 900 °C three main phases are seen: $SrMoO_4$, $SrFeO_{3-\delta}$, and Sr_2FeMoO_6. We found that the precursors calcined at 800 and 900 °C more efficiently facilitated the formation of the Sr_2FeMoO_6 phase during the encapsulation synthesis as compared with the 700 °C-calcined precursor. Therefore, for the further experiments all the precursor powders used were calcined at 900 °C.

Figure 2 shows XRD patterns with intensities in logarithmic scale for samples sintered at different

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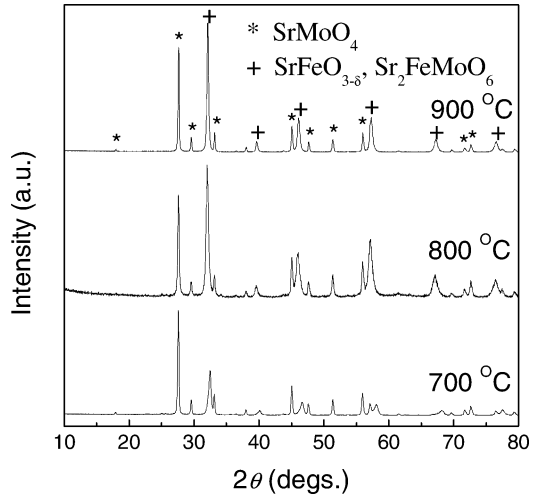

Figure 1. XRD patterns for the precursor powders calcined at different temperatures for 15 h.

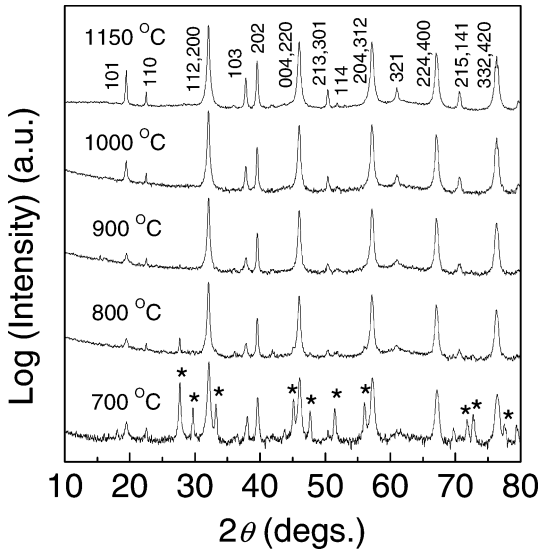

Figure 2. XRD patterns with intensities in logarithmic scale for Sr_2FeMoO_6 samples sintered at different temperatures for 24 h. The asterisks represent the peaks of $SrMoO_4$.

temperatures, T_s, for 24 h. It is seen that only the 700 °C-sintered sample contains larger amounts of $SrMoO_4$ as an impurity. For the $T_s = 800$ °C sample, a very tiny amount of $SrMoO_4$ is observed. When T_s exceeds 900 °C, no peaks due to any impurity are detected. The pure Sr_2FeMoO_6 phase is obtained at 900 °C even with a 4 h sintering period only. Here it seems that the fast phase formation is facilitated because the precursor powder already contains some preformed Sr_2FeMoO_6 that serves as growing centers for further crystallization during the sintering process.

In Figure 3, SEM images for Sr_2FeMoO_6 samples obtained at different sintering temperatures are shown. For T_s = 900 °C (t_s = 24 h), round grains with a diameter of about 0.1 μm are observed. Some of them aggregate with each other. The size of the grains becomes larger and also the shape of them changes when T_s increases. For T_s = 1000 °C (t_s = 50 h), the grains are of cubic shape with a size of ~0.5 μm. When $T_s = 1150$ °C, polyhedral grains with an average size of about 3 μm are achieved for t_s = 50 h, but the grain size increases very slowly with a further increase in t_s.

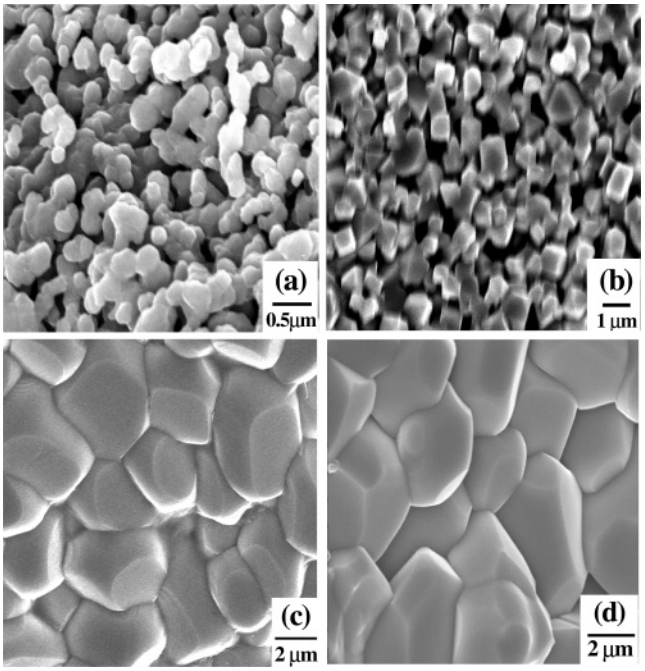

Figure 3. SEM images for Sr_2FeMoO_6 samples obtained under different conditions: (a) 900 °C for 24 h, (b) 1000 °C for 50 h, (c) 1150 °C for 50 h, and (d) 1150 °C for 100 h.

From the sample morphology, all the present samples look highly homogeneous. The shape of the grains depends mainly on T_s. The gradual change in grain shape from the round one to a polyhedron indicates that sintering of the grains/crystallization becomes enhanced as T_s increases.

The degree of B-cation order, S, as calculated from Rietveld refinement results is greatly enhanced with increasing T_s within the investigated temperature range of 900−1150 °C (with t_s = 50 h). On the other hand, at each T_s, increasing the sintering time causes S to increase. According to our previous work,[7] the optimum temperature range to achieve high-S samples is about 1150 °C, because at ~1150 °C the equilibrium value of S is close to unity: lowering the T_s below ~1150 °C would not considerably enhance the equilibrium value of S but would make the sintering time required to achieve that value markedly longer. For T_s = 1150 °C, S was found to be higher than 0.90 for the sample sintered for 4 h only, reached 0.94 for a sample sintered for 24 h, and exceeded 0.95 for the one sintered for 100 h. The degree of Fe/Mo order is much higher in the present case as compared with the samples prepared with the same encapsulation technique but using mechanically mixed precursor powders; see Figure 4. In fact, in the wet-chemical route the starting metal ions are mixed in an atomic scale, which enables us to achieve a homogeneous reaction system. In this case, the pure phase is readily formed, and Fe and Mo ions are distributed at the B- and B′-sites more strictly.

For some of the samples the degree of Fe/Mo order was checked on the basis of saturation magnetization as well. The theoretical relationship[8] between M_S and S has been derived as $M_s = 4S$. Figure 5 depicts magnetization (M) as a function of applied field (H) at 5 and 300 K for Sr_2FeMoO_6 samples sintered at 1150 °C for different time periods. The M_S value is obtained

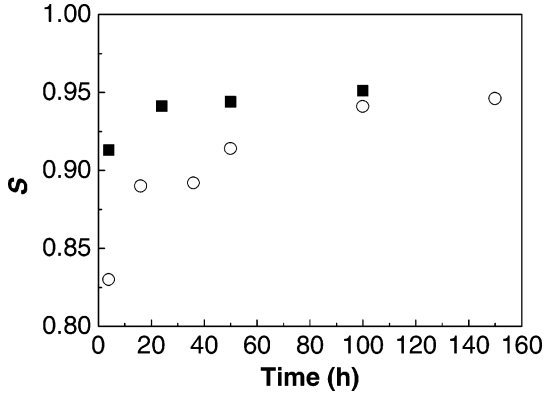

Figure 4. Dependence of sintering time on degree of order (S) for Sr_2FeMoO_6 samples fired at 1150 °C. Solid squares are the data of the present work, and the open circles are for samples synthesized from mechanically mixed precursors in ref 7.

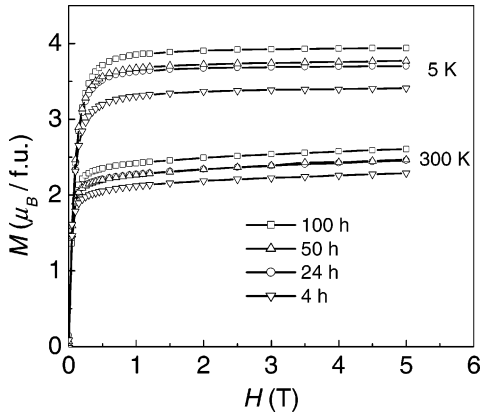

Figure 5. Magnetization as a function of applied field at 5 and 300 K for Sr_2FeMoO_6 samples sintered at 1150 °C for different times.

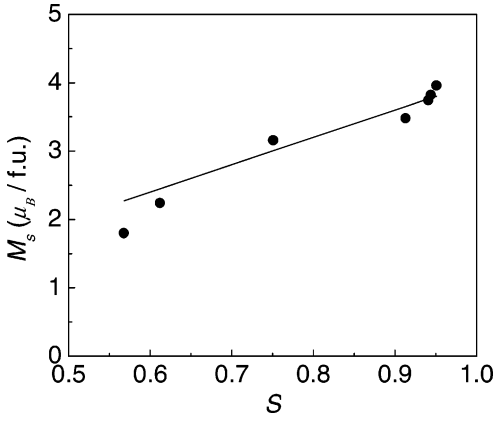

Figure 6. Saturation magnetization (M_s) at 5 K as a function of degree of order (S) for Sr_2FeMoO_6 samples. The line represents the theoretical M_s values calculated by $M_s = 4S$.

from extrapolation of M vs $1/H$ to $1/H = 0$. In Figure 6, we plot M_S as a function of S: it is seen that M_S increases with S roughly according to theory. However, the experimental M_S is lower than the theoretical one when S is small. This is because of the magnetic disorder in grain boundaries caused by incomplete crystallization at low T_s. Here, the striking feature is that a high M_S value can be obtained when $T_s = 1150$ °C even for a short sintering time. For example, $M_S = 3.48\ \mu_B$ for 4 h sintering, and $M_S = 3.74\ \mu_B$ for 24 h

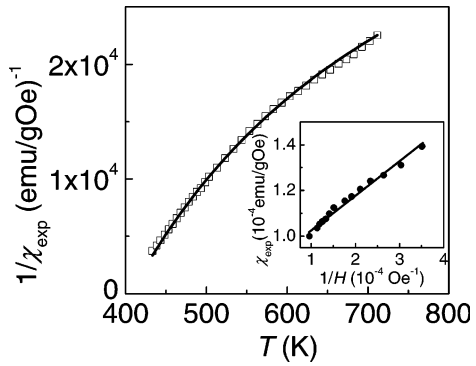

Figure 7. Temperature dependence of magnetic susceptibility (open symbols) at $H = 0.7$ T for the sample sintered at 1150 °C for 100 h. The line shows the fitness using an ordinary Curie−Weiss expression: $\chi = C/(T - \theta_p) + A$. The isothermal field dependence of the measured susceptibility at $T = 500$ K is displayed in the inset.

sintering. Notably, M_S reaches 3.96 μ_B for a sample sintered at 1150 °C for 100 h, which is close to the theoretical maximum. To our knowledge, this is the highest reported value of M_S for Sr_2FeMoO_6.

The record-low concentration of antisite Fe and high M_S value for the sample sintered at 1150 °C for 100 h deserves further studies. To do this, the paramagnetic susceptibility was measured up to 710 K in a field of 0.7 T. As shown in Figure 7, the thus-obtained data can be well-fitted by an ordinary Curie−Weiss expression:

$$\chi_{exp} = C/(T - \theta) + A \qquad (1)$$

where the constant A accounts for the bending of the χ_{exp}^{-1} curve, as explained further in the text. The fitted value of the Curie constant is $C = 7.63 \times 10^{-3}$ Kemu/gOe, and the Weiss temperature $\theta = 406.1$ K. An effective paramagnetic moment μ_{eff} of 5.1 μ_B is obtained from C. This is less than expected for the $3d^5$ (Fe) and $4d^1$ (Mo) high-spin configuration, but slightly larger than that of a pure mixed-valence configuration of $3d^{5.5}$ (Fe) and $4d^{0.5}$ (Mo). In other words a certain degree of valence mixing is still present above T_C. This is in accordance with a Mössbauer study of paramagnetic samples.[18] The bending of the χ_{exp}^{-1} vs T curve has been explained by temperature-induced delocalization of charge carriers.[19] However, the most logical explanation is the presence of tiny amounts of metallic Fe,[20] which is invisible to probing by X-ray diffraction or Mössbauer spectroscopy. The ferromagnetic moment of the Fe impurities is given by $M_S(Fe) = AH$, where A is the constant from expression (1). From the fitting of the data in Figure 7, we get an estimate of 0.13 emu/g for M_S(Fe). On the other hand, we can also obtain the value of M_S(Fe) by a field scan, given in the inset of Figure 7. The field scan was recorded at 500 K in a maximum field of 1.1 T. According to expression (1), the experimental susceptibility is given by $\chi_{exp} = (1-x)\chi(Sr_2FeMoO_6) + xM_S°(Fe)/H$, where x is the fraction of impurity Fe and $M_S°$(Fe) is the saturation magnetiza-

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tion of Fe. Thus, χ_{exp} should be linear to $1/H$, which indeed is the case. From the slope of the χ_{exp} vs $1/H$ line, we extract $M_S(Fe) = 0.14$ emu/g, close to the above estimate of 0.13 emu/g. Assuming this to originate from metallic Fe ($M_S° = 220$ emu/g), we obtain $x \approx 0.1$ wt %. Presence of a ferromagnetic impurity (albeit small) naturally influences the overall magnetic moment obtained at 5 K. After deducting the magnetic contribution of 0.1 wt % impurity Fe, an estimate for the correct M_S value at 5 K for the best-ordered sample with observed M_S of 3.96 μ_B is still as high as 3.94 μ_B assuming no other impurities exist. In case nonmagnetic impurities (e.g. $SrMoO_4$) are present, the actual M_S value is certainly no less than 3.94 μ_B.

We further confirmed the high degree of order by means of ^{57}Fe Mössbauer spectroscopy for the best-ordered sample. In general the Mössbauer spectra of Sr_2FeMoO_6 are completely accounted for using four spectral components.[21,22] The main component, M1, arises from Fe atoms at the correct lattice site. The component originating from Fe atoms occupying the Mo site, i.e. the antisite of Fe, is denoted AS. Furthermore Fe atoms adjacent to the AS atoms, but otherwise at their proper positions, have hyperfine parameters slightly different from those of the M1 atoms and are identified as the third component, denoted M2. The theoretical intensity ratio of 6:1 for the M2 and AS atoms is seen for low concentrations of AS atoms.[22] Finally, Fe atoms residing at antiphase boundaries were recently identified and denoted AP.[21] For component AP very small values of internal field were seen. These four components can be used as starting points also in the analysis of the present spectra.

In Figure 8 the Mössbauer spectra recorded at 77 K for the present sample with $M_S = 3.96$ μ_B are shown. The upper spectrum was recorded at zero applied field, whereas the lower spectrum was obtained in an external field of 600 mT directed perpendicularly to the Mössbauer beam. By visual inspection only two components are resolved from the upper spectrum: M1 and a new (almost) paramagnetic component, denoted SP. In the actual fitting also components M2 and AS were included. Component AS was included in the fit in order to get an estimate of the concentration of antisite Fe based on the Mössbauer data. The possible absence of AS indicates a very low concentration; i.e., only an upper estimate for the concentration of AS Fe can be obtained. The fitted intensity was 1.3%, and judging by the fit curve the concentration is probably smaller. The fitted intensity of M2 was 5%, but this value remains slightly uncertain as the component is located in the outer slopes of component M1. Nevertheless, using the theoretical 6:1 ratio between M2 and AS, an antisite concentration of ~1% for the Fe atoms is obtained. According to the magnetization data and the Rietveld analysis, the concentration of AS Fe is indeed very low in the sample measured by Mössbauer spectroscopy. For component M1 typical hyperfine parameter values of the $Fe^{II/III}$ state were found: 45.7 T for the internal field and 0.703 mm/s for the isomer shift. The component SP could by

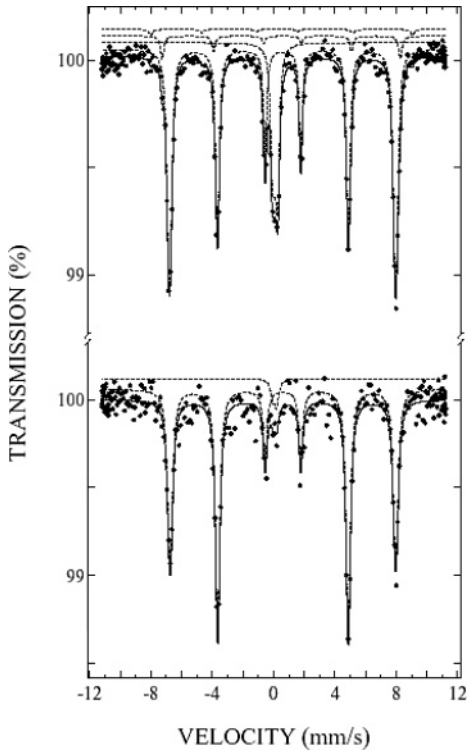

Figure 8. Mössbauer spectra for a Sr_2FeMoO_6 sample sintered at 1150 °C for 100 h recorded at (a) 77 K, 0 T and (b) 77 K, 600 mT. The upper spectrum exhibits the presence of superparamagnetism, which has been suppressed using an applied field in the lower spectrum. The average angle between the domain magnetization and direction of the beam was fitted to 79.7°. The components used in the fitting are displayed above each spectrum. Reading from the top they are AS, M2, SP, M1 and SP, M1 for the upper and lower spectrum, respectively.

the first glance be interpreted to reflect Fe atoms on antiphase boundaries.[21] However, when the sample was remeasured in an applied magnetic field, the paramagnetic component almost completely disappeared and merged with component M1, suggesting that it has the same origin and that the absence of an internal field was possibly due to super-paramagnetic-type behavior in small sample grains. Note that component AP previously detected for some Sr_2FeMoO_6 samples has been found to persist in spectra measured under an applied field of 5 T.[21] To elucidate the origin of component SP, the sample was remeasured in zero applied field at 77 K. Only ~3% of the original intensity remained; i.e., the intensity transfer to component M1 was irreversible. However, by heating the sample in a vacuum furnace to 445 K (above T_C) and again measuring the sample at 77 K and zero applied field, component SP regained a part of its intensity (~7%). By magnetizing the sample, SP could be made to disappear again. At present there is no clear explanation for the presence of component SP. It seems probable that the magnetization of the smallest grains fluctuates easily in the unmagnetized sample, due to the very low coercive force and anisotropy energy. Apparently the magnetization of nearby larger particles does not suffice to pin the magnetization. Upon magnetizing the samples the situation changes as all domains become aligned.

Finally to gain further insight into the magnetic behavior, the temperature dependence of magnetization was measured at 1 T for representative samples having

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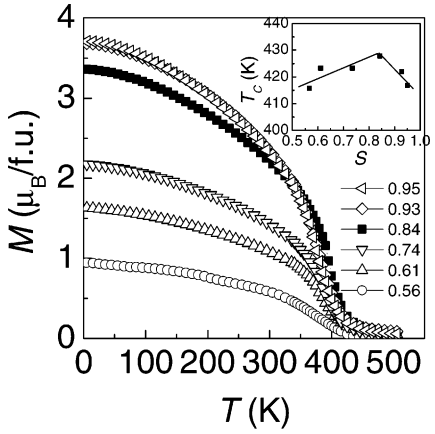

Figure 9. Temperature dependence of magnetization at $H = 1$ T for representative Sr_2FeMoO_6 samples having different degrees of order (S). Inset shows S dependence of Curie temperature T_C.

different S values. Figure 9 depicts these magnetization curves. We determine Curie temperature T_C by linear extrapolation of the transition-range data on the $M-T$ curve to zero magnetization.[6,23] The dependence of T_C on S is displayed in the inset of Figure 9. Interestingly, the sample with $S = 0.84$ exhibits the highest T_C of 428 K. For $S < 0.84$, T_C increases with S along the prediction based on Monte Carlo simulations,[8] whereas T_C decreases with a further increase in S. The value of T_C for the best-ordered sample is 417 K, close to that obtained by the Curie−Weiss law in Figure 7. The effect of Fe/Mo ordering on the Curie temperature has seldom been experimentally investigated, but predictions based on theoretical models have been reported. Monte Carlo simulations assuming superexchange-like interactions between each pair of neighboring cations suggested that T_C linearly increases with S.[8] However, a more recent work using a three-band model Hamiltonian led to an increase in T_C with S only up to $S \approx 0.8$, beyond which the further increase in S decreased the value of T_C.[24] Our T_C data thus are in accordance with the latter prediction. The drop in T_C within the high-S region is believed to have its origin in the decrease in the ferromagnetic interaction due to the next-nearest-neighbor B-cations (experienced only when the intermediate nonmagnetic Mo between two Fe species is replaced by Fe).[6]

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Conclusion

We have developed a simple and efficient route to prepare high-quality samples of the B-site ordered double-perovskite phase, Sr_2FeMoO_6: a wet-chemical process for the precursor preparation and an encapsulation technique for the sintering are simultaneously used to achieve samples with homogeneous morphology and high degree of B-cation order. The high degree of Fe/Mo order was confirmed from X-ray diffraction, magnetization, and Mössbauer data independently. For the sample sintered at 1150 °C for 100 h, the observed saturation magnetization, M_S, was as high as 3.96 μ_B, which is the highest value reported *hitherto*. Application of the wet-chemical process for precursor preparation guarantees that the starting chemicals are mixed in an atomic level and hence makes the precursor powder quite uniform, whereas the encapsulation technique ensures effective reduction by the oxygen getter and keeps the overall cation stoichiometry of the sample stable during the sintering. The combination of these contributions should be responsible for the achieved high degree of order. The present approach can provide a valuable method to synthesize samples of Sr_2FeMoO_6 and other similar double-perovskite oxides with high quality.

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