Effect of Quench Treatment on Fe/Mo Order and Magnetic Properties of Double Perovskite Sr_2FeMoO_6 *

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A quench-treatment technique is used to prepare a high-quality polycrystalline sample of double perovskite Sr_2FeMoO_6 (SFMO). X-ray powder diffraction analysis reveals that the sample has a single phase and exhibits I4/m symmetry. The cation order η of the sample increases to 98.9(2)% from 94.2(3)%, which is prepared by the traditional sol-gel method. The initial magnetization isotherm of the sample is detected at 300 K. Unit-cell magnetization for the current sample is 1.332 μ_B at 300 K, and the one for the traditional sol-gel method sample is 0.946 μ_B. Unit-cell magnetization is enhanced to 40.80% by the quench-treatment technique. Quench treatment is an effective method of enhancing the Fe/Mo order and magnetic properties of double perovskite SFMO.

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Room-temperature low-field magnetoresistance (LFMR) materials have attracted considerable scientific and technological interests.[1] The double perovskite-like compound Sr_2FeMoO_6 (SFMO), with a remarkable magnetoresistance R_{MR} above room temperature, has become one of the most promising magnetic storage materials.[2] The ferromagnetic (FM) property of SFMO has also gained considerable interest due to its high spin polarization and high Curie temperature T_c.[3−5] Electronic structure calculations show that ordered SFMO is half-metallic and exhibits a tunnelling-type R_{MR} at room temperature.[6,7] Ordered SFMO could be used in room-temperature spintronics and magnetoresistive sensor applications.[8]

The ideal structure of SFMO consists of a regular arrangement of corner-sharing FeO_6 and MoO_6 octahedra, alternating along three directions of the crystal, with the voluminous Sr cations occupying the voids between the octahedrals.[9,10] In reality, the SFMO structure exhibits a certain degree of Fe/Mo disorder, i.e., anti-site (AS) defects. The existence of AS defects greatly influences the magnetic and transport properties of SFMO.[11,12] For device applications, magnetism enhancement and electromagnetic coupling manipulation are desirable.

We prepare an SFMO by standard solid-state reaction[13] and the sol-gel method.[14] Reducing AS defects is one of the most important problems of this material for applications. Quench-treatment is a useful method to improve the micro-structure, the strength and elongation of the product,[15,16] which take the status of high temperature to the room temperature. The rapid quench can effectively affect the structure, anisotropy and coercivity of alloy materials.[17,18] The sample treated by air quenching exhibits the best combination of strength and toughness.[19] This study optimizes the Fe/Mo order and magnetic properties of SFMO by quench treatment. In this study, the crystal structure and magnetic properties of SFMO prepared by the quench-treatment method are reported.

Stoichiometric amounts of high-purity $Sr(NO_3)_2$, $Fe(NO_3)_3{\cdot}9H_2O$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and citric acid monohydrate were dissolved in dilute HNO_3 and mixed in a glass beaker. The gel was dried at 80℃ and then was powdered with an agate mortar to avoid any metallic contamination. The powder was heated at 260℃ in an oven for 10 h. The obtained powder was further powdered by using an agate mortar and preheated at 680℃ for 5 h. The preheated powders were sintered at 1200℃ under a stream of 5% H_2/Ar gas for 15 h. The flow rate of the reducing atmosphere gas mixture was established at 35 ml/min. Samples were heated at a rate of 10℃/min. When the 15 h sinter at 1200℃ was completed, quench treatment was conducted. The sample was removed from the furnace at 1200℃ and then was cooled in Ar atmosphere for 30 min. Samples were labelled with samples 1 and 2 for the sample cooled in the pipe furnace at a rate of 10℃/min under reducing atmosphere and the sample with quench treatment, respectively. The structure of the samples was examined by x-ray powder diffraction (XRD) by using a Rigaku D/max 2500 diffractometer with Cu $K\alpha$ radiation (50 kV, 120 mA). The XRD data were analyzed by using the Rietveld refinement programme general structure analysis system.[20] The M–H curves and R_{MR}–H curves of these samples were measured by using a vibrating sample magnetometer. Scanning electron microscopy (SEM) was used to detect the microstructure of these samples. The valence variation of these samples was examined by x-ray pho-

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toelectron spectroscopy (XPS).

The Rietveld refinements of XRD diffraction patterns are conducted by using $I4/m$. The occupancies of each atom are as follows: Sr, $4d$ (1/2, 0, 1/4); Fe/Mo, $2a$ (0, 0, 0) (denoted as B-site); Mo/Fe, $2b$ (0, 0, 1/2) (denoted as B′-site); O1, $8h$ (x, y, 0); and O_2, $4e$ (0, 0, z). Before refinements, a full occupancy for each site in the unit is assumed. The total occupancies of Fe and Mo at B and B′ are fixed as 1.0. The weak scattering of O on XRD results is due to its small atomic number; thus, O occupancies are assumed to be full. Figure 1 shows the results from the XRD analysis of sample 2, which illustrates the representative pattern for the two samples. Refinement processes are smooth and lead to reasonable R-factors (Table 1). All the samples have tetragonal crystal structures without structure transition. The structure parameters obtained from Rietveld refinements are summarized in Table 1.

Table 1. Structure parameters and cation order η of the two samples of SFMO obtained from Rietveld refinement of the XRD data.

	a (Å)	c (Å)	V (Å^3)	η(%)	Fe–O(1)–Mo(°)	R_{wp}(%)	R_p(%)	R_{exp}(%)
Sample 1	5.57885(2)	7.86458(3)	244.77405(4)	94.2(3)	163.6(1)	5.02	5.13	4.64
Sample 2	5.57867(3)	7.86478(1)	244.76450(9)	98.9(2)	167.2(3)	4.56	3.12	3.29

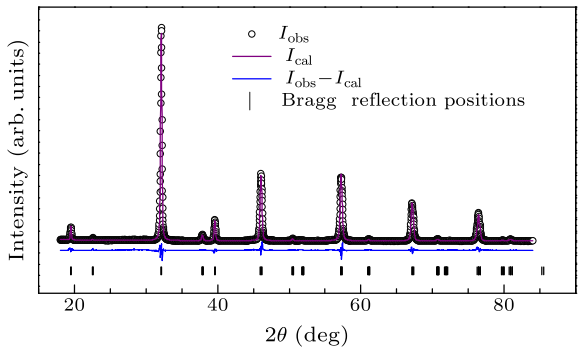

Fig. 1. Observed (cross) and calculated (solid line) XRD patterns for sample 2. The lowest curve is the difference between the measured and calculated XRD patterns. The vertical bars at the bottom indicate the Bragg reflection positions.

As listed in Table 1, the lattice parameters of samples 1 and 2, such as a, c and V are almost similar. The cation order is defined as $\eta = 1 - 2AS$, where AS is the occupancy of Fe at B′-site or Mo at B-site, which is also called the AS occupancy. The value of η is 94.2(3)% for sample 1 and 98.9(2)% for sample 2, which suggest that the quench treatment is an effective method for enhancing the Fe/Mo order. The magnetism of SFMO is mainly caused by the anti-FM array of Fe^{3+} and Mo^{5+}. Enhancement of Fe/Mo order has an important effect on the magnetic property of SFMO.

The magnetization dependence on the applied magnetic field for each sample at 300 K is shown in Fig. 2. On the basis of the magnetization curves, we calculate the unit-cell magnetization at 300 K. The magnetizations are 0.946 and 1.332 μ_B/unit-cell at 300 K for samples 1 and 2, respectively. To evaluate enhancement of the unit-cell magnetization by quench treatment, we define the enhancement percentage as $\frac{M_2-M_1}{M_1}$, where M_1 and M_2 are 0.946 and 1.332 μ_B/unit-cell, respectively. Enhancement percentage is 40.80% at 300 K. This result suggests that the quench treatment is a useful method for enhancing the magnetic property of SFMO. Fe–O(1)–Mo bond-angle and AS defects may have important effects on magnetization. The Fe–O(1)–Mo bond-angle increasing by quench treatment, as listed in Table 1, enhances the double exchange between Fe and Mo. AS defects are decreased by the quench treatment. Annealing temperature and mode in preparation of the SFMO material have a great influence on Fe/Mo order. The high temperature is good for Fe/Mo order. The higher the annealing temperature is, the more ordered the Fe/Mo becomes. Quench treatment can keep the high temperature status to room temperature. The valence state of Fe/Mo may be changed and the Fe/Mo Lattice position may be dislocated in SFMO materials with furnace cooling. The Fe/Mo order enhances the FM-ordering in SFMO compounds.[21] Enhancement of double exchange and the cation order between Fe and Mo enhance the magnetic property of SFMO.

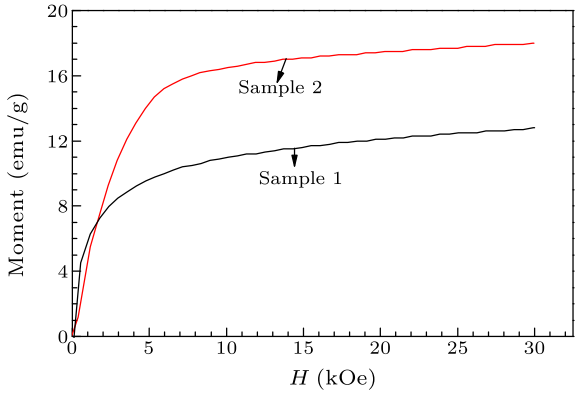

Fig. 2. Initial magnetization isotherms of samples 1 and 2 at 300 K.

Figure 3(a) shows the Fe $2p$ XPS spectra for samples 1 and 2. Fe element has +2 and +3 mixed valence in the SFMO material, confirmed by Hou *et al.*[22] The valence electrons of Fe^{2+} and Fe^{3+} are $3d^6$ and $3d^5$, respectively. The magnetic moment of Fe^{3+} is stronger than Fe^{2+}. Quench treatment makes the ratio of Fe^{3+}/Fe^{2+} have a great change. The asymmetric broad peak at 711.0 eV can be observed for the two samples indicating the coexistence of Fe^{3+} and Fe^{2+}. The valence variation occurs unavoidably during the

high temperature annealing process. The peaks at the binding energies of ∼710.3 and ∼711.8 eV are assigned to Fe^{2+} $2p_{3/2}$ and Fe^{3+} $2p_{3/2}$, respectively, as shown in Fig. 3(b). The ratios of Fe^{3+}/Fe^{2+} for samples 1 and 2 are 0.98 and 1.25, respectively. The percentage of Fe^{3+} would cause a double exchange interaction among Fe^{2+}–O–Fe^{3+} and would result in the enhancement of ferromagnetism.

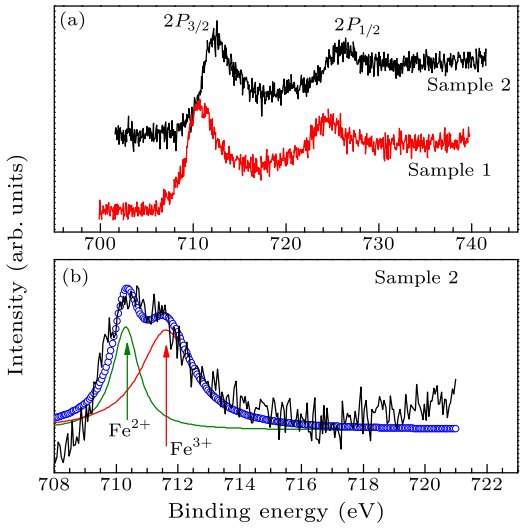

Fig. 3. (a) Fe 2p XPS spectra for samples 1 and 2. (b) Lorentzian dividing of the Fe $2p_{3/2}$ core level for samples 1 and 2.

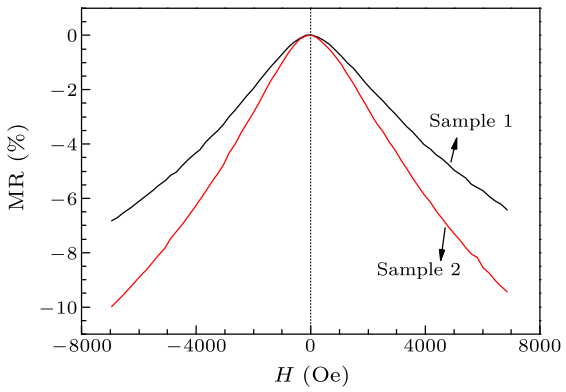

Fig. 4. $R_{\rm MR}$ versus magnetic field for the SFMO samples investigated at 300 K.

For each sample, $R_{\rm MR}$ versus H is measured at 300 K, as shown in Fig. 4. Both samples exhibit negative $R_{\rm MR}$. One of the most remarkable properties of polycrystalline SFMO is its large $R_{\rm MR}$, which is usually explained by the intergrain spin-dependent carrier scattering process.[23] The obtained curves are symmetrical for negative and positive field regions. In the SFMO samples, the LFMR is consistently attributed to the inter-grain tunnelling $R_{\rm MR}$ between strongly spin polarized grains separated by insulating grain boundaries. This statement is supported by the absence of sharp LFMR effect in highly ordered single crystalline bulk[24] and the epitaxial thin film[25] samples of SFMO. Grain boundary resistance can be modulated by an applied magnetic field. $R_{\rm MR}$ is defined as $R_{\rm MR}(T,H) = \frac{\rho(T,H)-\rho(T,0)}{\rho(T,H)}$, where $\rho(T,H)$ and $\rho(T,0)$ are the resistivity under a field of H and a zero field at temperature T, respectively. Transfer integral increases with the bond-angle of Fe–O(1)–Mo.[26] An increase in transfer integral may enhance the $R_{\rm MR}$. Quench treatment also enhances the Fe/Mo order. AS defects may indicate the existence of anti-FM configuration of Fe–O–Fe patches in the system. A decrease in AS defects reduces the anti-FM configuration of Fe–O–Fe patches and enhances the $R_{\rm MR}$ property.

Quench treatment changes the microstructure of SFMO, as shown in Fig. 5. The grain boundary of the sample is clear for sample 1, though there are many blowholes among the crystalline grains. Quench treatment embrittles sample 2 and makes the crystal plate loose. Furnace cooling gives the material enough time to find the equilibrium phase. Quench treatment makes the material keep the high temperature status to room temperature for a short time. The microstructure difference between samples 1 and 2 has an important effect on the physical property of the material.

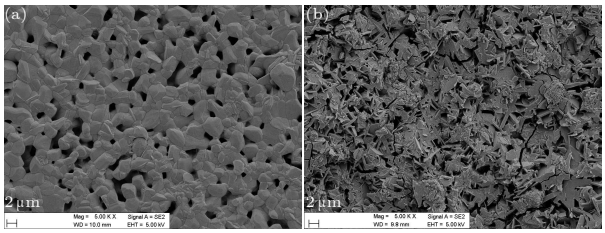

Fig. 5. Microstructures of SFMO: (a) sample 1, (b) sample 2.

In summary, the quench-treatment technique is used to prepare a high-quality polycrystalline sample of double perovskite SFMO. Enhancement of the Fe/Mo order and magnetic properties of the synthesized sample is detected. XRD analysis reveals that both samples have a single phase and exhibit the $I4/m$ symmetry. The cation order η of the sample increases to 98.9(2)% from 94.2(3)%, which is prepared by the traditional sol-gel method. The initial magnetization isotherm of the sample is detected at 300 K. The unit-cell magnetization for the current sample is 1.332 $\mu_{\rm B}$ at 300 K, and that for the traditional sol-gel method sample is 0.946 $\mu_{\rm B}$. Unit-cell magnetization is enhanced to 40.80% by the quench-treatment technique. The LFMR effect is detected and has a great enhancement. The bond angle of Fe–O(1)–Mo, Fe/Mo order and grain boundary are the main reasons for the enhancement of the LFMR effect.

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