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Sintering Effects on Fe/Mo Ordering and Magnetoresistance in Double Perovskite Sr_2FeMoO_6

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We have investigated sintering effects on Fe/Mo ordering and magnetoresistance (MR) in double perovskite -reflection lines due to Sr_2FeMoO_6 (SFMO). Polycrystalline samples have been prepared by the conventional solid-state reaction by sintering in a stream of 5% H_2/Ar gas. All samples are single phase and exhibit a series of superstructurecation ordering at Fe and Mo sites. As sintering temperature increases from 900 to 1300 °C, the degree of Fe/Mo ordering increases from 82 to 92%, magnetization (15 K, 7 kOe) increases from 1.6 to 2.7 μ_B/f.u., and Curie temperature increases at a rate of 4.3 K/% with the increase of Fe/Mo ordering ratio. The magnitude of MR measured at 5 K is 19% for sample prepared at 1000 °C with magnetic fields of 7 kOe. The observed MR is proportional to the square of magnetization indicating that the MR feature in SFMO is explained by the spin-polarized tunneling at grain boundaries.

Key words : Double perovskite, Magnetic ordering, Magnetization, Magnetoresistance

1. Introduction

A great deal of attention has been focused on the colossal magnetoresistance in doped perovskite manganates due to scientific interests and possible technological applications [1]. Since the significant magnetoresistance (MR) effect only occurs with a relatively high magnetic field or at low temperature, it is questionable whether these compounds would be useful for most applications. Recently, the room temperature low-field sensitive MR has been observed in polycrystalline samples of Sr_2FeMoO_6 (SFMO), which exhibits the intrinsic tunneling-type MR due to the spin dependent scattering at the grain or magnetic domain boundaries [2].

SFMO has a double-perovskite structure $A_2B'B''O_6$ with ordering of localized up spin $Fe^{3+}(3d^5;\ t^3_2g\ e^2g)$ and itinerant down spin $Mo^{5+}(4d^1;\ t^1_2g)$ ions arranged alternatively on the B sites in the cubic perovskite ABO_3 [3-5]. The parallel magnetic moments of Fe^{3+}, antiferromagnetically coupled with the spins of Mo^{5+}, induces a ferrimagnetic state with an ideal saturation magnetization (M_s) of 4 μ_B per formula unit (f.u.). However, the reported M_s values are smaller than the expected one [2, 6]. This reduction of M_s can be caused by antisite disorder [2, 7, 8] arising from misplacement of Fe and Mo ions at B'/B'' sublattices in the double-perovskite structure. Monte-Carlo simulations have predicted a reduction of M_s as a function of the antisite disorder [7]. In addition to its ordering structure, this compound displays a metallic behavior with the Curie temperature (T_c) of 410-450 K [3-5]. Because of the high ferromagnetic transition temperature and the half-metallic nature [2], conduction electrons in this compound are expected to be highly spin-polarized even at room temperature and electronic transport across the boundary depends on the relative angle between magnetic moments of the ferromagnetic domains on both sides of the boundary.

2. Experimental

Polycrystalline SFMO samples were prepared by standard solid state reaction. Powders of high purity (99.99% or better) of $SrCO_3$, Fe_2O_3, and MoO_3 were mixed, ground, and fired at 900 °C in air with several intermediate grindings, followed by a final grinding before the powder was pressed into pellets. The pellets were sintered in a stream of 5% H_2 /Ar at various temperatures in the range 900~1300 °C for 2 h. X-ray diffraction (XRD) patterns were taken with a diffractometer using Cu K_α radiation.

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Magnetization was performed on a commercial vibrating sample magnetometer (Lake Shore, model 730). MR was measured by a standard four-probe technique with ac nano-ohm meter (Linear Research, LR700) in magnetic fields of 7 kOe.

3. Results and Discussion

Fig. 1 shows powder XRD patterns for polycrystalline SFMO samples S09 (sintered at 900 °C) and S13 (sintered at 1300 °C). It shows a clean single phase without detectable secondary phases. X-ray data indicate that symmetry is tetragonal, and the data are compatible with the *I4/mmm* space group. The qualitative estimate of B-site ordering is determined by observing the relative intensity of the most intense superstructure (101) reflection. Fig. 2

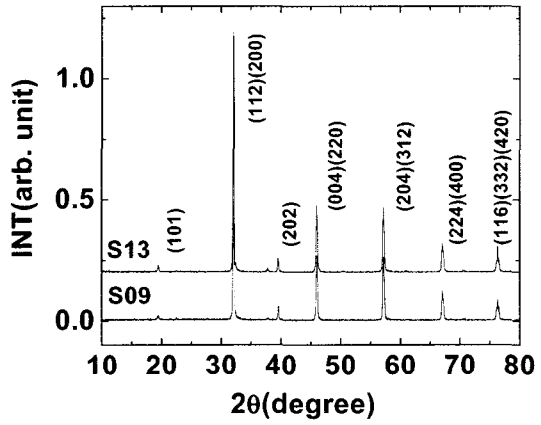

Fig. 1. X-ray diffraction patterns for polycrystalline Sr_2FeMoO_6 prepared at different sintering temperatures. S09 and S13 samples were prepared at 900 and 1300 °C, respectively.

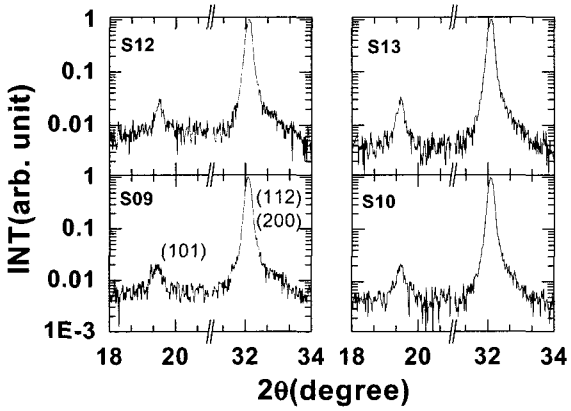

Fig. 2. Portions of the relative diffraction intensity patterns displaying the I(101) and the {I(200)+I(112)} reflections for polycrystalline Sr_2FeMoO_6 prepared at different sintering temperatures. S09, S10, S12, and S13 samples were prepared at 900, 1000, 1200 and 1300 °C, respectively.

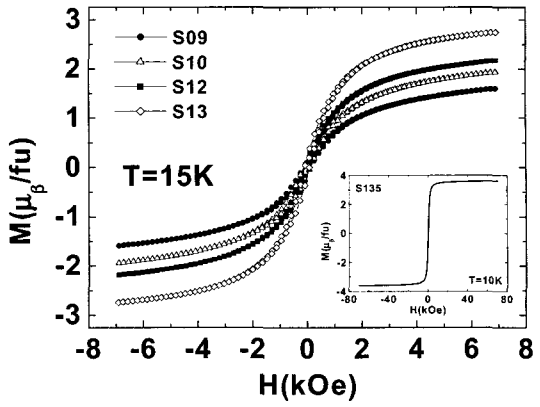

Fig. 3. Magnetization (15 K, 7 kOe) for polycrystalline Sr_2FeMoO_6 prepared at different sintering temperatures. The inset shows the saturation magnetization of S135 sample prepared at 1350 °C for 9 h.

shows portions of the diffraction intensity patterns displaying the I(101) and the {I(200)+I(112)} reflections for SFMO prepared at different sintering temperatures. As sintering temperature increases from 900 to 1300 °C, the relative intensity I(101)/{I(200)+I(112)} increases from 0.7% for sample S09 (sintered at 900 °C) to 2.2% for sample S13 (sintered at 1300 °C). The corresponding value of Fe/Mo ordering is 82% for S09 and 92% for S13 from XRD refinements. This indicates that the cation ordering of Fe and Mo ions at B'/B" sublattices in the double-perovskite structure is improved by high temperature sintering process.

Fig. 3 shows magnetization for SFMO samples prepared at different sintering temperatures. Magnetization (15 K, 7 kOe) increases from 1.6 to 2.7 μ_B/f.u.. The relatively low values of magnetization are attributed to sintering process. As shown in the inset of Fig. 3, saturation magnetization (M_s) of S135 sample which was prepared at 1350 °C for 9 h is 3.6 μ_B/f.u.. According to Ogale *et al.*, the value of M_s = 3.6 μ_B/f.u. is corresponding to the Fe/Mo ordering of 95% at the B'/B" sites in the double-perovskite structure $A_2B'B''O_6$ [2].

Fig. 4 shows the normalized temperature dependence of magnetization $M(T)$ for SFMO samples S10 and S13 measured at 50 Oe. The samples show ferromagnetism at lower temperature, paramagnetism at higher temperature. The magnetic transition temperature T_c is defined as the minimum value of temperature in the dM/dT vs T curve. In SFMO, the T_c increases from 375 K for S10 to 405 K for S13 with the increase of sintering temperature. We cant define the T_c for sample S09 because there is no sudden change in magnetization.

Fig. 5 shows T_c and magnetization (15 K, 7 kOe) as a function of the Fe/Mo ordering ratio. As sintering temper-

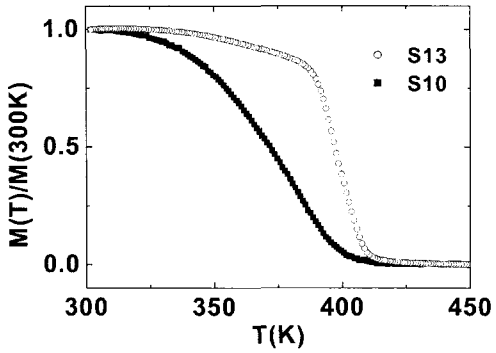

Fig. 4. Normalized magnetization curves for polycrystalline Sr_2FeMoO_6 measured at 50Oe.

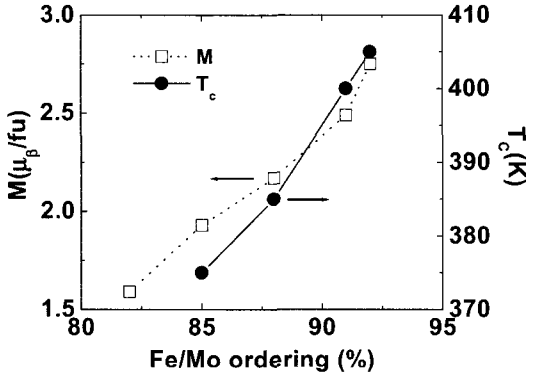

Fig. 5. T_c and magnetization (15 K, 7 kOe) for polycrystalline Sr_2FeMoO_6 as a function of Fe/Mo ordering ratio.

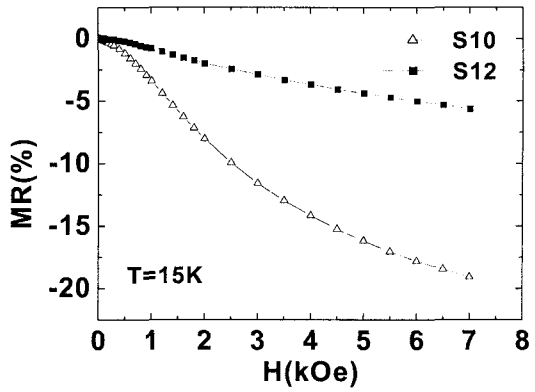

Fig. 6. Magnetoresistance of polycrystalline Sr_2FeMoO_6 for different sintering temperatures.

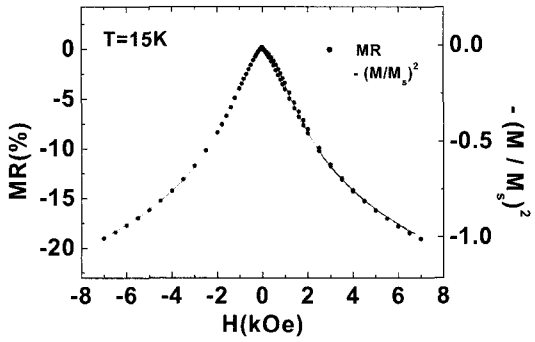

Fig. 7. Relation between MR and $(M/M_s)^2$ for polycrystalline Sr_2FeMoO_6 sample S10 (prepared at 1000) at 15 K.

ature increases from 900 to 1300 °C, the Fe/Mo ordering increases from 82 to 92%. With the increase of Fe/Mo ordering, magnetization (15 K, 7 kOe) increases from 1.6 to 2.7 μ_B/f.u.. The T_c increases at a rate of 4.3 K/% with the increase of Fe/Mo ordering. This indicates that the Fe/Mo ordering controlled by thermal conditions affects the magnetic properties of SFMO.

Application of magnetic field reduces the resistivity for all samples. In particular, the magnitude of MR is appreciable in a low field region. Fig. 6 shows the isothermal MR for S10 and S12 at 15 K with a maximum applied magnetic field of 7 kOe. The resistance decreases with increasing external magnetic field. We define the magnitude of MR as

$$MR = \Delta\rho/\rho(0) = [\rho(H)-\rho(0)]/\rho(0) \quad (1)$$

where $\rho(0)$ is the zero field resistivity and $\rho(H)$ is the resistivity under magnetic field. The MR ratio is considerably high for sample S10. The steep MR curve at low field is associated with magnetic domain rotation motion in the magnetization curve shown in Fig. 3. The magnitude of negative MR for S10 with magnetic fields of 7 kOe at 15 K is 19%. In the case of sample S12, the value of MR (15 K, 7 kOe) is 6%. Even Fe/Mo ordering and magnetization for S12 are higher than those for S10, the magnitude of MR is smaller than that of sample S10. This discrepancy in MR is not merely due to the Fe/Mo ordering. Since the grain size increases with the increase of sintering temperature, sample prepared at higher sintering temperature has less grain boundaries. Therefore the observed lower value of MR in S12 is considered as a consequence of transport across grain boundaries.

The correlation between the MR and magnetization for sample S10 at 15 K is shown in Fig. 7. The sharp drop in resistivity at low fields coincides with the steep magnetization. The relationship reveals that the MR is proportional to the square of (M/M_s), where M_s is the saturation magnetization. Since the MR due to the spin-polarized tunneling at grain boundaries is approximately proportional to the square of (M/M_s) [2, 9], it is likely that the observed MR in SFMO is dominated by the spin-polarized tunneling at grain boundaries.

4. Conclusions

In conclusion, we have examined sintering effects on magnetic properties of SFMO. As sintering temperature increases, the Fe/Mo ordering increases from 82% for sample sintered at 900 °C to 92% for sample sintered at 1300 °C. The magnetization and the T_c increase with increasing Fe/Mo ordering, which indicates that the Fe/Mo ordering is related to the magnetic properties in SFMO. The transport properties are dependent on the sintering temperature that affects the character of grain boundaries in SFMO. The observed MR is proportional to the square of (M/M_s) indicating that the spin-polarized tunneling is responsible for the MR in SFMO.

Acknowledgment

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