Large low-field magnetoresistance effect in Sr_2FeMoO_6 homocomposites

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Homocomposites consisting of two single-phase Sr_2FeMoO_6 components with different grain sizes were prepared by a sol-gel method. Large low-field magnetoresistance (LFMR) effect was achieved for the composites. Experimental results show that the LFMR strongly depends on both the relative amounts of the two components and their grain sizes. The magnetoresistance value is found to be proportional to the square of the relative magnetization (M/M_s). We suggest that the LFMR enhancement in the homocomposites compared with parent Sr_2FeMoO_6 has its origin in the enhanced intergranular effects. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1864241]

Double-perovskite Sr_2FeMoO_6 has been extensively studied due to the half-metallic property and remarkable low-field magnetoresistance (LFMR) caused by spin-polarized tunneling.[1] Two types of barriers are believed to serve for the tunneling magnetoresistance. The first is intragranular two-dimensional defects which are related to the intrinsic behavior, such as antiphase boundaries and some domain boundaries.[2,3] The second is ascribed to grain boundaries and even impurity-phase grain boundaries, which lead to the intergranular tunneling effect.[1,4–7] It should be noted that the influence of antisite disorder at Fe and Mo sites, i.e., point defects, on the MR effect was investigated,[2,8,9] but no obvious MR enhancement has been observed even when the concentration of antisite atoms is varied. However, it has been found that grain boundary effect plays an important role in MR behavior. Yin *et al.*[4] proposed that the LFMR is due to electron spin dependent transfer across grain boundaries. Yuan *et al.*[5] observed an enhancement in LFMR when decreasing the grain size into nanometric scale. Thus, it is likely that among all kinds of tunneling barriers, the grain boundary effect is most significant to yield a high LFMR value. From both scientific and technological points of view it is worthwhile to learn the ways to control the tunneling effects and hence improve the MR property. Here the choice of material synthesis process is believed to be crucially important for controlling the magnetic and magnetotransport properties of double perovskites.[10,11]

In this letter, we report preparation and magnetotransport characterization of Sr_2FeMoO_6 (SFMO) "homocomposites" consisting of larger grains of SFMO with a high degree of Fe/Mo order and smaller grains of less-ordered SFMO. A significant enhancement in LFMR has been achieved for the composites.

The initial precursor powder for the SFMO synthesis was prepared by a sol-gel route starting with $SrCO_3$, $Fe(NO_3)_3 \cdot 9H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and ethylenediaminetetraacetic acid (EDTA) as a complexant, as described elsewhere in detail.[12] The precursor was calcined in air at 900 °C for 15 h (component A). A portion of component A was pressed into pellets which were sintered at 1150 °C for 100 h in an evacuated and sealed fused-quartz ampule in the presence of Fe grains as a getter of oxygen,[13] and the sintered pellets were ground into a coarse powder to obtain component B. Homocomposite samples were then prepared by mixing (with careful grinding) components A and B into various weight ratios. Each mixture was pelletized and encapsulated again into an evacuated ampule together with Fe grains and fired for 8 h at a selected sintering temperature (T_s) in the range of 900–1100 °C. Thus a series of homocomposite samples, each consisting of SFMO grains with two different sizes, was prepared. Component B was taken as the main component, and x is employed to denote the weight fraction of component A in the composite.

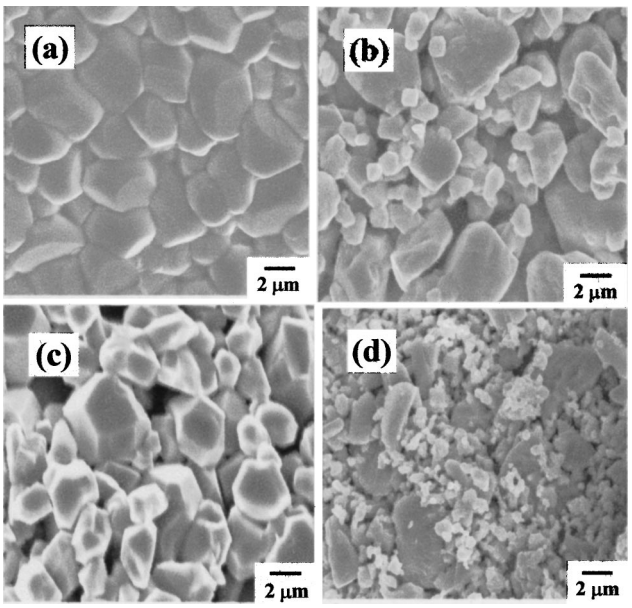

FIG. 1. SEM images for typical Sr_2FeMoO_6 homocomposites: (a) $x=0$, (b) $x=0.2$, $T_s=950$ °C, (c) $x=0.2$, $T_s=1100$ °C, (d) $x=0.5$, $T_s=950$ °C.

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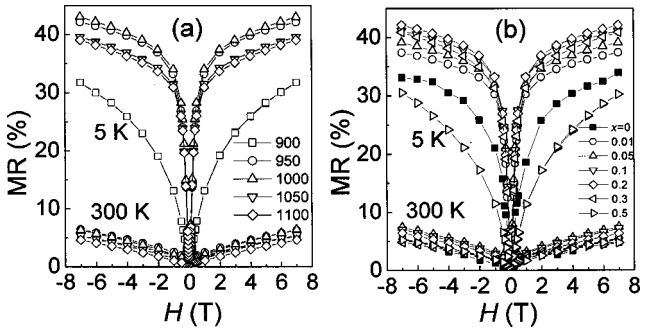

FIG. 2. Magnetoresistance ratio (MR) as a function of applied field for the homocomposites: (a) $x=0.2$ sintered at different temperatures for 8 h; (b) different x from 0 to 0.5 sintered at 950 °C for 8 h.

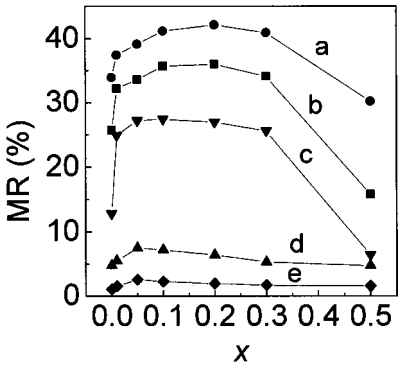

FIG. 3. Dependence of MR on x for homocomposites (sintered at 950 °C for 8 h): (a) 5 K, 7 T; (b) 5 K, LFMR; (c) 5 K, 0.5 T; (d) 300 K, 7 T; (e) 300 K, 0.5 T.

All the samples are phase-pure as confirmed by x-ray powder diffraction. Component B is highly ordered with the degree of order, S [$\equiv 2(g_{\mathrm{Fe}}-0.5)$], at 0.94 calculated from the refined (RIETAN2000[14]) occupancy of Fe at its correct site (g_{Fe}). Micrographs were taken for the samples by a scanning electron microscope (SEM; Hitachi: S4500). Magnetization measurements were performed with a superconducting-quantum-interference-device (SQUID) magnetometer (Quantum Design: MPMS-XL5). Electrical resistivity was measured using a standard four-probe technique with a commercial apparatus (PPMS; Quantum Design: System-Model 6000).

Figure 1 shows SEM micrographs for several typical SFMO homocomposites. The large grains (component B) are clearly surrounded by the smaller ones (component A). For the parent ($x=0$) sample, the average grain size (D_B of component B) is ~ 3.8 μm. For the composite samples the average grain sizes (D_A) of component A are ~ 1.0 μm when $T_s=950$ °C, and ~ 2.3 μm when $T_s=1100$ °C.

We define the magnetoresistance ratio (MR) by $(\rho_0-\rho_H)/\rho_H$, where ρ_H and ρ_0 are resistivities at a finite applied field (H) and at $H=0$, respectively. In Fig. 2, plots of MR vs H are shown for homocomposites with various x and T_s. All the samples exhibit two distinguishable regions in the field dependence of MR. That is, with increasing H, MR increases rapidly for $H \leqslant 0.5$ T, but rather moderately for $H > 0.5$ T. In Fig. 2(a) the data for the $x=0.2$ composites sintered at various T_s are compared. It is seen that the MR value at 300 K depends weakly on T_s, but that at 5 K obviously depends on T_s, reaching a maximum at $T_s=950-1000$ °C. Therefore, we decided to sinter homocomposites at 950 °C regardless the value of x. In Fig. 2(b), the composites with $x=0.05-0.3$ have achieved a clear enhancement in MR at both 5 and 300 K, compared with the $x=0$ sample. In order to see the enhancement more clearly, we depict the x dependence of MR ratios at 0.5 and 7 T and at 5 and 300 K in Fig. 3. In the same figure, also plotted is "LFMR" obtained by extrapolating the high-field MR to zero field. The $x=0.2$ sample exhibits the largest LFMR and MR at 7 T and 5 K, whereas the $x=0.05$ sample exhibits the largest MR at 0.5 T and 300 K. Overall, the $x=0.2$ sample is concluded to have gained the largest MR enhancement. It should be noted that the maximum LFMR value of 36% measured for the $x=0.2$ composite is a little higher than the predicted value based on a model of second-order tunneling through interfacial spin sites at grain boundaries (for manganese oxides).[15]

To further investigate the origin of MR enhancement, we plot $\Delta\rho/\rho_0 \equiv (\rho_0-\rho_H)/\rho_0$ as a function of m^2 ($m \equiv M/M_s$, where M_s is the saturation magnetization) instead of H in Fig. 4. The m^2 values were taken from the magnetization measurements at the same temperature of the MR vs H measurements. It is seen that $\Delta\rho/\rho_0$ for all the five samples exhibits a similar proportionality to m^2 in the low field region: $\Delta\rho/\rho_0 \propto m^2$, or $\Delta\rho/\rho_0=\alpha m^2$. The constant α depends on x, which reaches the maximum at $x \approx 0.2$. As M approaches M_s, i.e., $m^2 \to 1$, the relation deviates from linearity such that $\Delta\rho/\rho_0=\alpha m^2+\beta m^4$. The linearity in terms of m^2 was attributed to the spin-polarized tunneling between magnetic domain boundaries.[16–18] As evidenced with the SEM micrographs of the homocomposites, every large grain of component B with a high value of S is surrounded by several smaller grains of component A (with a low value of S). An m^2 dependence arises in principle whenever the MR ratio depends only on relative orientation of any two adjacent interfacial spin sites. The deviation from the linear dependence on m^2 may reflect some higher-order correlations between next-neighbor or next-next-neighbor grains of various spin polarization.

From Fig. 4, it is observed that MR is most sensitive to m^2 for $x=0.2$ at 5 K, whereas at 300 K, it shows similar

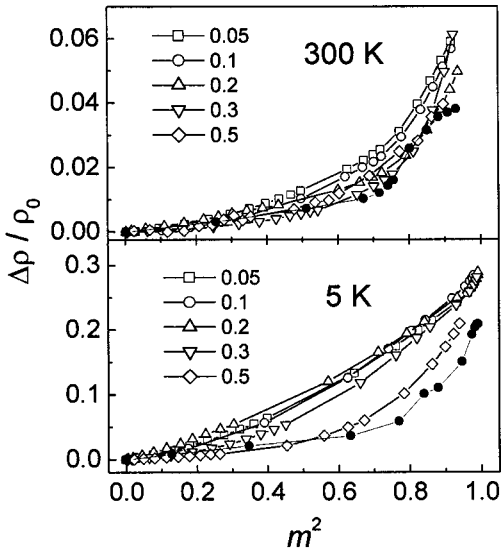

FIG. 4. $\Delta\rho/\rho_0$ as a function of m^2 for the homocomposites with $x=0-0.5$ sintered at 950 °C for 8 h. The solid circles represent the data of parent Sr_2FeMoO_6 (component B).

sensitivities to the change in m^2 for the samples with $x = 0.05$, 0.1, and 0.2. The fact that the MR vs m^2 slope is largest for $x = 0.2$ suggests that the component A grains are likely to reduce higher-order correlations between the component B grains, leaving the MR value dependent mainly on m^2. It is noteworthy that the MR sensitivities of the parent SFMO sample to the change in m^2 at both 5 and 300 K are much lower than those of the composites, demonstrating that the tunneling effects in the homocomposites become much more enhanced by homocompositing. After all, the enhancement in LFMR for the present homocomposites could be ascribed to the enhanced spin-polarized tunneling due to the greater intergranular grain boundary effects.

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