Temperature Dependence of Resistivity of $Sr_2CoMoO_{6−δ}$ Films

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We investigate the temperature dependence of the resistivity and magnetoresistance of a polycrystalline $Sr_2CoMoO_{6−δ}$ film deposited on (100)-$SrTiO_3$ substrate prepared by the pulsed laser deposition method. X-ray diffraction, Raman and magnetoresistance results demonstrate clearly the coexistence of a ferromagnetic metallic and an antiferromagnetic (or paramagnetic) insulating domain. Percolative transition between these two phases as the temperature varies, which is believed to induce a metal-insulator transition at around $T_C$, has been directly observed in our measurements of the temperature dependence of the sample resistivity. Thus we have provided new direct evidence that a phase separation scenario also exists in the ordered double-perovskite structure materials.

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Since the observation of most significant colossal magnetoresistance (CMR) effect close to the magnetic transition temperatures, there has been an intense search for compounds with magnetic transition temperatures substantially higher than the $T_C$ ($\sim 200$ – $350K$) in manganites. Recently, it has been reported that the transition-metal oxides with the ordered double-perovskite structure, $A_2MMoO_6$ ($A$ is a rare-earth metal and $M$ is a transition metal), exhibits a pronounced negative CMR at lower magnetic fields and higher temperatures compared to the doped manganites. The reason for this improved MR property in these compounds at a relatively higher temperature arises primarily from the fact that they have a surprisingly high magnetic transition temperature ($Sr_2FeMoO_6$ 415$K$; $Sr_2CoMoO_6$ 350$K$) compared to manganites. The largest MR response is expected close to the magnetic transition temperature $T_C$. The combination of large MR effect and high $T_C$ value makes this family of perovskites promising for practical applications.

Up to present, many researchers have reported the structural, magnetic, and electrical properties of the double-perovskite transition-metal oxides, especially for the Fe-based compounds. To the best of our knowledge, however, the behavior of resistivity at high temperature especially near $T_C$ is less addressed and the temperature dependence of the resistivity-temperature curve. This is the first time that such a mixed-phase phenomenology has been observed to appear in the ordered double-perovskite structures materials.

A Thin film of $Sr_2CoMoO_{6−δ}$ of thickness 700 nm was deposited on a (100) $SrTiO_3$ (STO) substrate by pulsed laser deposition. The substrate temperature during deposition was kept at 500 °C in high vacuum (10$^{-7}$ Torr). The crystal structure and phase purity of the samples were examined by X-ray diffraction using Cu $Ka$ radiation. The micro-Raman spectrum was measured in the backscattering geometry using an ISA Jobin-Yvon-Spex T64000 Raman spectrometer with an Olympus microscope attachment. The 514.5 nm line of an argon-ion laser was used as the excitation source. The electrical resistivity $ρ$ was measured using the standard four-probe technique. The magnetoresistance ratio, MR, is defined as $MR(%) = \Delta ρ/ρ_0 \times 100\%$, where $\Delta ρ = ρ_H − ρ_0$, $ρ_0$ and $ρ_H$ are the resistivities in an applied magnetic field and in zero field, respectively.

Fig. 1 depicts the X-ray diffraction pattern for the deposited $Sr_2CoMoO_{6−δ}$ thin films on STO at room temperature. It shows that the film was polycrystalline, and a minor amount of $SrMoO_4$ was also detected. The peak, labeled “∗”, corresponds to the peak of the $SrMoO_4$ im-
purity phase. All the other peaks corresponding to the main phase of Sr₂CoMoO₆₋δ can be indexed according to the space group I4/mmm.

Fig. 2 shows the Raman spectra of the sample at room temperature. The peak at 882.3 cm⁻¹, labeled "•", corresponds to the strongest Raman line of the SrMoO₄ impurity phase. The presence of the SrMoO₄ impurity in the sample reinforces the conclusion obtained in the XRD analysis in Fig. 1.

Fig. 3 shows the temperature dependence of the resistivity at zero field and at 1T respectively for the sample in the temperature range from 80 – 300K. At the lower temperature range, the resistivity decreases exponentially with temperature, showing a semiconducting-like or thermally activated behavior. The temperature dependence of the magnetoresistivity ratio MR(%) = (ρ₀ − ρ_H)/ρ₀ × 100% for polycrystalline Sr₂CoMoO₆₋δ thin film at H = 1T at the temperature range from 80 to 300K.

FIG. 3: Temperature dependence of resistivity for polycrystalline Sr₂CoMoO₆₋δ thin film at zero field (solid line) and at 1T (dash line) at the temperature range from 80 to 300K. The inset is temperature dependence of the magnetoresistivity ratio MR(%) = (ρ₀ − ρ_H)/ρ₀ × 100% for polycrystalline Sr₂CoMoO₆₋δ thin film at H = 1T at the temperature range from 80 to 300K.

depends on the magnetoresistivity ratio MR(%) = (Δρ/ρ₀ × 100% (Δρ = ρ₀ − ρ_H) at 1T is presented in the inset of Fig. 3. The mMR decays as the temperature increases, comparable to that found in the other double perovskite Sr₂FeMoO₆. The MR is dominated by the grain boundary tunneling and demonstrates the existence of ferromagnetic metallic clusters. The increasing value of MR as the temperature is lowered is attributed to the weak spin thermal fluctuation at low temperatures.

Fig. 4 shows the temperature dependence of the resistivity of the Sr₂CoMoO₆₋δ film kept in vacuum (10⁻⁶ Torr) in the extended temperature range from 80 to 500K. The arrow indicates the Curie temperature (Tc) determined by Viola et al. At very low temperatures Sr₂CoMoO₆ is known to behave as a paramagnetic insulator, which may be ascribed to the absence of the 4d electrons in the hexavalent Mo⁶⁺ (4d⁰) ions and the divalent nature of the valence of the Co ions. Magnetic measurements suggest the presence of ferromagnetic domains characterized by Tc embedded in an antiferromagnetic matrix (AFM) characterized by Niel temperature TN. Contrary to the Sr₂FeMoO₆ structure, the formation of ferromagnetic clusters is not due to the double exchange mechanism, but rather to a kind of super-exchange interactions between Co²⁺ and Mo³⁺ moments. Based on a consideration of the small number of itinerant electrons introduced from the oxygen vacancies, Mo³⁺ cations should be randomly isolated and so only isolated ferromagnetic clusters can be formed. Therefore Sr₂CoMoO₆₋δ can be viewed as a canted-spin system or one containing inhomogeneous ferromagnetic clusters embedded in a paramagnetic matrix (or AFM matrix if the temperature is below TN). At low temperatures the resistivity exhibits a semiconductor-like
or thermally activated behavior. The resistivity of the $\text{Sr}_2\text{CoMoO}_6-\delta$ film is about two orders of magnitude smaller than that of the bulk $\text{Sr}_2\text{CoMoO}_6$, implying that a higher density of charge carriers (electrons) is involved in the conduction process. However, this resistivity is still too high compared to that in a metallic state. This indicates that the resistivity of the sample arises from the carrier scattering at the ferromagnetic grain boundaries. This observation is supported by the inverse temperature dependence of the measured MR shown in the insert of Fig. 3.

A conspicuous change in the resistivity $\rho$ is observed at around $T_C$. In the low-temperature ($T < T_C$) ferromagnetic phase, a metallic behavior ($\rho$ increases with temperature) is observed, while a semiconductor behavior is observed in the paramagnetic phase ($T > T_C$). The semiconducting behavior at $T$ above $T_C$ could be due to the thermal spin fluctuation of the ferromagnetic domains and the randomness of the boundary scattering. With further increase in temperature significantly beyond $T_C$, the resistivity shows a linear increase, which may be ascribed to the enhanced phonon scattering of the carriers and other localization effects.

The temperature dependence of the resistivity of $\text{Sr}_2\text{CoMoO}_6-\delta$ can be well understood from the phase separation scenario involving percolative transport through the ferromagnetic clusters in a background AFM matrix. Starting from a regime where the ferromagnetic clusters are formed dynamically (spin fluctuation) at a high temperature $T^*$ above $T_C$, the metallic state can be achieved if the temperature is decreased and the size of clusters grows gradually until eventually percolative transport through the ferromagnetic domains becomes possible. At this temperature, the carriers can move over a long distance and the metallic state is reached. Alternatively, one can image the metallic fraction to drop with increasing temperature, which is a reasonable assumption since the metallic portion of the sample originates from the ferromagnetic (FM) arrangement of spins that improves conduction. Such a spin arrangement deteriorates as the temperature increases. Moreover it is reasonable to imagine that the size of FM clusters decreases as the temperature grows. Then, a pattern of FM clusters that had been connected at low temperature (leading to a metallic behavior) may become disconnected at higher temperatures. The direct observation of the metal-insulator transition peak appearing in our temperature dependence of the sample resistivity represents evidence of the onset of percolative transition, and hence the existence of the phase separation scenario in the $\text{Sr}_2\text{CoMoO}_6-\delta$ film. The decrease in the metallic portion with increasing temperature was confirmed by a recent theoretical investigation on the random field Ising model based on the random resistor network model. However, quantitative determination of the $T^*$ at which the ferromagnetic clusters are formed is difficult and needs further investigation.

In summary, a polycrystalline $\text{Sr}_2\text{CoMoO}_6-\delta$ film was fabricated and the behavior of its resistivity at high temperature, especially around $T_C$, has been investigated. The sample can be viewed as a typical mixed-phase system with ferromagnetic metallic clusters embedded in the AFM insulating matrix. With increasing temperature, its magnetoresistance decreases until the room temperature, the sample resistivity exhibits a metal-insulator transition peak near $T_C$, which is attributed to the percolative transition between the FM metallic and AFM insulating phases. It provides the first experimental evidence that the phase separation scenario also exists in the transition-metal oxides with the ordered double-perovskite structure.

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