Modulation of the ferromagnetic insulating phase in Pr$_{0.8}$Ca$_{0.2}$MnO$_3$ by Co substitution

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Ferromagnetic insulator Pr$_0.8$Ca$_{0.2}$MnO$_3$ thin films were epitaxially grown on (LaAlO$_3$)$_{0.5}$(SrAl$_0.5$Ta$_0.5$O$_3$)$_{0.5}$ (100) substrates by pulsed laser deposition. To probe the ferromagnetic insulator state of hole-doped manganites, the Co content dependences of the structural, magnetic, and transport properties were studied. Variation of lattice constant by the substitution of Co ions is well reproduced considering that divalent and trivalent Co ions substitute for Mn ions at the perovskite B-sites. For 0 ≤ y ≤ 0.3, the Curie temperature, saturation magnetization, and magnetoresistance increase with increasing Co content, retaining the insulating properties. Detailed analyses of transport and magnetic properties indicate the contribution of both double exchange and superexchange interactions to the appearance of the ferromagnetic insulating phase.

Mixed-valent perovskite manganites R$_{1-x}$A$_x$MnO$_3$ have been widely studied because of their anomalous properties, such as colossal magnetoresistance (CMR)\cite{1}. In hole-doped manganites, ferromagnetism is usually accompanied by metallic conduction of $\sigma_F$ electrons according to the double exchange model. However, a ferromagnetic insulator (FI) state is observed in some lightly hole-doped materials, such as La$_{1-x}$Sr$_x$MnO$_3$ (0.10 < x < 0.17), La$_{1-x}$Ca$_x$MnO$_3$ (x < 0.15), Nd$_{1-x}$Sr$_x$MnO$_3$ (0.2 < x < 0.28), and Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO) (0.15 < x < 0.3)\cite{2}. It is important to determine the origin of the FI state which remains poorly understood, in order to design functional materials such as multiferroics in which ferroelectric distortions can affect the magnetic ordering\cite{2}.

The origin of the FI state in Pr$_{1-x}$Ca$_x$MnO$_3$ (0.15 < x < 0.3) has been studied both from theoretical and experimental points of view\cite{3-6}. In addition to the conventional double exchange and superexchange mechanisms, many other models have been proposed, such as the presence of several types of charge and orbital ordering (CO/OO)\cite{3, 4} or orbital ordering\cite{5, 6}. Mn-site substitution in the CO/OO state of Pr$_{1-x}$Ca$_x$MnO$_3$ (x = 0.5) is known to result in a collapse of long-range CO/OO ordering\cite{7-9}. If the FI state of Pr$_{1-x}$Ca$_x$MnO$_3$ (0.15 < x < 0.3) is related to some CO state, Mn-site substitution may affect the CO state, resulting in drastic change of magnetic and transport properties. In this paper, we have studied the effect of Co substitution at the Mn-site on structural, ferromagnetic, and insulating properties of Pr$_{1-x}$Ca$_x$MnO$_3$ (x = 0.2) to seek the origin of the ferromagnetic insulator state in hole-doped manganites.

Epitaxial Pr$_{0.8}$Ca$_{0.2}$Mn$_{1-y}$Co$_y$O$_3$ (PCMO) (0 ≤ y ≤ 0.7) thin films were grown on atomically flat (100)-oriented (LaAlO$_3$)$_{0.5}$(SrAl$_0.5$Ta$_0.5$O$_3$)$_{0.5}$ (LSAT) substrates by pulsed laser deposition at a substrate temperature of 700 °C. Pure oxygen was constantly fed into the growth chamber to maintain an oxygen pressure of 30 mTorr. The epitaxial orientation and crystalline quality of the films were evaluated by X-ray diffraction (XRD). In order to determine the in-plane lattice constant, reciprocal space mappings (RSMs) were measured by four-circle X-ray diffraction (4c-XRD). Magnetic and transport properties were characterized using the Quantum Design magnetic property measurement system (MPMS) and physical property measurement system (PPMS), respectively.

Figure 1(a) shows the XRD pattern of a PCMCO (y = 0.3) thin film. The XRD pattern without secondary phase peaks and the atomically flat surface in atomic force microscopy (AFM) image shown in the inset of Fig. 1(b) show no signature of segregation. The in-plane and out-of-plane lattice constants of PCMO (0 ≤ y ≤ 0.7), determined from RSMs around the PCMO (303) and (300) peaks, are shown in Fig. 1(b). The in-plane lattice constant was almost constant regardless of Co content and close to the lattice constant of the LSAT substrate (green line), suggesting that all PCMO films were epitaxially strained. The out-of-plane lattice constants linearly decrease with increasing the Co content, indicating successful substitution of Co ions for Mn ions at the perovskite B-site.

The magnetic field dependences of magnetization (M-H curves) are shown in Fig. 2(a). The M-H curve of a Pr$_{0.8}$Ca$_{0.2}$MnO$_3$ film shows a small coercive field and residual
magnetization. The coercive fields of the PCMO films increase drastically with increasing Co content. The Curie temperature (Tc) increase with Co content in the 0 ≤ y ≤ 0.3 range, as shown in Fig. 2(b), (c). For y > 0.5, Tc could not be determined because a clear ferromagnetic transition was not observed. To estimate the valence state of the substituting Co ions, the relative pseudo-cubic lattice constant (Δd(y) = d(y) - d(0)) is plotted in Fig. 2(d). We employ Shannon’s ion radii of Co^{2+} (divalent, high spin, 0.745 Å), Co^{II} (divalent, low spin, 0.65 Å), Co^{3+} (trivalent, high spin, 0.61 Å), Co^{III} (trivalent, low spin, 0.545 Å), Co^{4+} (tetravalent, high spin, 0.53 Å), Mn^{3+} (trivalent, high spin, 0.645 Å), and Mn^{4+} (0.530 Å[10]) to estimate Δd(y). The valency of Co doped in Pr_{0.5}Ca_{0.5}MnO_{3} are known to be divalent according to the X-ray absorption spectroscopy (XAS) study on Co-doped Pr_{0.5}Ca_{0.5}MnO_{3}[11]. As a result, Co substitution would change valency of Mn^{3+} to be Mn^{3+}[11, 12]. Here, we assume that Co ions would be divalent also in PCMO. On this assumption, Co substitution for Mn would result in decrease of two Mn^{3+} and increase of one Mn^{4+} and one divalent Co in low Co content region (y<0.4). Suppose all the Mn would become Mn^{4+} in y=0.4, further substitution of the Mn for Co would result in decrease of one Mn^{4+} and one divalent Co and increase of two trivalent Co. As shown in Fig. 2(d), experimentally observed Co content dependence of Δd are close to the estimated lines for Co^{2+} & Co^{3+} (orange thick line) as well as 0.8Co^{3+}+0.2Co^{4+} (green dotted line). Co valency would be divalent considering the XAS study on Co-doped Pr_{0.5}Ca_{0.5}MnO_{3}[11], which favors the former estimation line. These discussions suggest that Co ions might exist as Co^{2+} in low Co content region (y<0.4), and mixture of Co^{2+} and Co^{3+} in high Co content region (y>0.4). Though the spin state of trivalent Co cannot be determined from this simplified discussion, Co^{3+} might exist considering the small energy difference (~30 meV) between Co^{3+} and Co^{III} reported in La_{1−x}Sr_{x}Co_{0.3}MnO_{3}[13]. Figure 2(e) shows the saturation magnetization relative to the non-substituted PCMO. The lines shown in the figure were calculated by counting unpaired spins. The experimental data increase more rapidly than all the calculated lines for various valence state of Co including Co^{2+} & Co^{3+} suggested from the lattice constant variation, indicating that the enhancement of magnetization cannot be explained simply by an increase of unpaired spins at the B-site ions, and enhancement of ferromagnetic interactions between B-site ions should be also considered.

According to the simple double exchange model, an increase of magnetic interactions between B-site ions should result in an increase of hopping conduction. The temperature dependence of resistivity was measured for the ferromagnetic samples (0 ≤ y ≤ 0.3). All samples show insulating properties that were robust up to an external magnetic field of 9 T, as shown in Fig. 3(a). This behavior is different from that of the metallic Co-substituted Pr_{0.5}Ca_{0.5}MnO_{3} phase at low temperature[7]. Negative magnetoresistance, as is also seen in the conventional double exchange manganites, was observed as shown in Fig. 3(b). The magnetoresistance (MR) ratio measured above the Curie temperature increase with increasing Co content as shown in the inset of Fig. 3(b). MR below Tc could not be measured due to the high resistivity of the PCMO films.

The decrease of bond length and increase of the M-O-M bond angle by Co substitution [14, 15] and the increase of the hole-concentration in Mn-site induced by Co substitution[12] would result in increase of magnetic interaction between B-site ions according to the double exchange model. The increase of Tc, saturation magnetization, and MR ratio with
increasing Co content in the $0 \leq y \leq 0.3$ ranges may be related to this effect. To confirm the increase of the hopping conduction in PCMCO, we carefully analyzed the temperature dependence of resistivity ($\rho$-$T$ curve) by fitting the data with variable range hopping (VRH) and Arrhenius models. The multiple correlation functions ($R^2$) of these fittings are plotted in the inset of Fig. 3(a). As Co content increases, the $R^2$ of the VRH model increase, which would enhance the double exchange interactions.

Besides double exchange interactions, another possible mechanism that contributes to the ferromagnetism of PCMCO is superexchange interactions. According to the Kanamori-Goodenough rule[16, 17], superexchange interactions for Mn$^{3+}$-O-Mn$^{3+}$, Mn$^{4+}$-O-Mn$^{3+}$, and Mn$^{4+}$-O-Mn$^{4+}$ favor antiferromagnetic coupling. By low-level, $0 \leq y \leq 0.3$, Co substitution, superexchange interactions for Mn$^{2+}$-O-Co$^{2+}$ and Mn$^{4+}$-O-Co$^{2+}$ can be formed. These include the ferromagnetic superexchange interactions for Mn$^{4+}$-O-Co$^{2+}$, which should contribute to the ferromagnetism. In highly substituted level ($y>0.4$), all the Mn ions would be Mn$^{4+}$ assuming that all the Co ions are divalent, resulting in vanishing of double exchange interaction between Mn ions. Alternatively, antiferromagnetic Mn$^{4+}$-O-Mn$^{4+}$, Co$^{2+}$-O-Co$^{2+}$, Co$^{3+}$-O-Co$^{3+}$, and Co$^{3+}$-O-Co$^{3+}$ interactions become dominant. These interactions compete with the Mn$^{4+}$-Co$^{2+}$ double exchange interactions and ferromagnetic Mn$^{4+}$-O-Co$^{2+}$ superexchange interactions in PCMCO, possibly forming unconventional magnetic phases with small magnetization as is observed in $y=0.5, 0.7$ (not shown).

In summary, we have studied the effect of Co substitution on the structural, magnetic, and transport properties of Pr$_{0.8}$Ca$_{0.2}$MnO$_3$ epitaxial thin films. Insulating properties were retained for all Co substitution levels. The detailed study on magnetic and transport properties suggest that both double exchange and superexchange interactions contribute to the ferromagnetic insulator phase in PCMCO, demonstrating the effectiveness of the B-site substitution to control the ferromagnetic properties of hole-doped perovskites by modulating both double exchange and superexchange interactions.

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