Soft x-ray absorption spectroscopy study of Mo-rich $SrMn_{1-x}Mo_xO_3$ ($x \geqslant 0.5$)

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Electronic structures of perovskite oxides of $SrMn_{1-x}Mo_xO_3$ in the Mo-rich regime ($x \geqslant 0.5$) have been investigated by employing soft x-ray absorption spectroscopy (XAS). Mn $2p$ XAS spectra of $SrMn_{1-x}Mo_xO_3$ indicate that the valence states of Mn ions are divalent and that they remain nearly unchanged for $x \geqslant 0.5$. On the other hand, the Mo $3p$ XAS spectra of $SrMn_{1-x}Mo_xO_3$ show some changes, suggesting that the valence states of Mo ions decrease with increasing x for $x \geqslant 0.5$. These conclusions are supported by the unoccupied Mn $3d$ and Mo $4d$ states, observed experimentally in the O $1s$ XAS spectra of $SrMn_{1-x}Mo_xO_3$.

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$R_{1-x}A_xMnO_3$-type manganese perovskite oxides (R, trivalent rare-earth ion; A, divalent Ca, Sr, Ba, etc.), having mixed-valent Mn ions, exhibit the colossal magnetoresistance (CMR) phenomena, the charge-ordered states near the half-filling ($x = 1/2$) with a concomitant first-order metal-insulator (M-I) transition, and the rich phase diagram.[1,2] Likewise, doping of the Mn site with different transition-metal (TM) elements shows interesting phenomena, such as large room-temperature magnetoresistance (MR) and M-I transition in double perovskites.[3] It was reported that a Mo substitution in $LaMnO_3$ induces ferromagnetism (FM), which originates from a double-exchange (DE) interaction between Mn^{3+} and Mn^{2+} ions.[4] The advantage of Mo substitution for Mn is that a large variation in the Mn valence is possible due to the high valency of a Mo ion (Mo^{5+} or Mo^{6+}), while the structural disorder in the Mn lattice is relatively small.

$SrMnO_3$ is also a parent compound of the widely studied mixed-valent perovskite manganites, and it is a G-type antiferromagnetic (AFM) insulator ($T_N \sim 233$ K) with tetravalent Mn^{4+} ions.[5,6] The ordered half-substitution in $SrMn_{1-x}Mo_xO_3$ corresponds to a double perovskite, Sr_2MnMoO_6, which is a monoclinically distorted AFM insulator ($T_N \sim 12$ K).[7] For Sr_2MnMoO_6, the valence states of the Mn-Mo ions have been controversial between (Mn^{2+}-Mo^{6+})[7–9] and (Mn^{3+}-Mo^{5+}).[10] Band structure calculations suggest that (Mn^{2+}-Mo^{6+}) is more likely.[11–13] The other end member $SrMoO_3$ in $SrMn_{1-x}Mo_xO_3$ is a paramagnetic metal.[14] In particular, $SrMoO_3$ is known to have the lowest resistivity among all the oxides.[15] In the Mo-rich regime, the M-I transition occurs in $SrMo_{1-y}Mn_yO_3$ for $y \geqslant 0.03$, accompanied by the change in the magnetic property from Pauli paramagnetism to Curie–Weiss paramagnetism for $y \geqslant 0.01$. The lattice constant increased with increasing Mn doping in $SrMo_{1-y}Mn_yO_3$, which suggested the existence of Mn^{2+} states, since the radius of a Mn^{2+} ion (0.67 Å) is similar to that of a Mo^{4+} ion (0.65 Å) while that of a Mn^{4+} ion (0.53 Å) is much smaller than that of a Mo^{4+} ion (0.65 Å).

In our previous study on the electronic structures of $SrMn_{1-x}Mo_xO_3$ in the low-concentration regime of the Mo substitution,[16] we have found that the valence states of Mn ions decrease gradually from the high-spin (HS) tetravalent state (Mn^{4+}, $3d^3$) at $x = 0$ to the HS divalent state (Mn^{2+}, $3d^5$) at $x = 0.5$. The origin of the decreasing valence states of Mn ions with increasing x for $x \leqslant 0.5$ was due to the higher valence states of Mo ions that were close to being hexavalent (Mo^{6+}) for $x \leqslant 0.5$ in $SrMn_{1-x}Mo_xO_3$. Nevertheless, no work has been reported yet on the electronic structures of $SrMn_{1-x}Mo_xO_3$ for $x \geqslant 0.5$. Therefore it is important to determine the valence states of both Mn and Mo ions in $SrMn_{1-x}Mo_xO_3$ in the Mo-rich regime ($x \geqslant 0.5$).

In this work, we investigate the electronic structures of $SrMn_{1-x}Mo_xO_3$ in the Mo-rich regime ($x \geqslant 0.5$) by employing soft x-ray absorption spectroscopy (XAS), which is known to be a powerful experimental tool for studying the valence and spin states of TM ions in solids. This work provides the experimental evidence for the decreasing valence states of Mo ions in $SrMn_{1-x}Mo_xO_3$ for $x \geqslant 0.5$.

High-quality polycrystalline samples of $SrMn_{1-x}Mo_xO_3$ ($x \geqslant 0.5$) were synthesized by standard solid-state reaction methods. X-ray diffraction and neutron powder diffraction measurements showed that all the samples employed in this work have no impurity phase. The $SrMn_{1-x}Mo_xO_3$ samples for $0.5 \leqslant x \leqslant 0.75$ are monoclinically distorted double perovskites. Figure 1 shows the temperature-dependent resistivity $\rho(T)$ of $SrMn_{1-x}Mo_xO_3$ for $x \geqslant 0.5$. As x increases from $x = 0.5$, $\rho(T)$ decreases rapidly. This trend reflects the itinerant nature of Mo $4d$ states, which is consistent with the measured Mo $3p$ XAS (see Fig. 3).

XAS measurements were performed at the U7 beamline of the Pohang Light Source (PLS). The chamber pressure was better than 3×10^{-10} Torr. All the samples were cleaned *in situ* by repeated scrapings with a diamond file to remove the surface contamination. XAS spectra were obtained at room

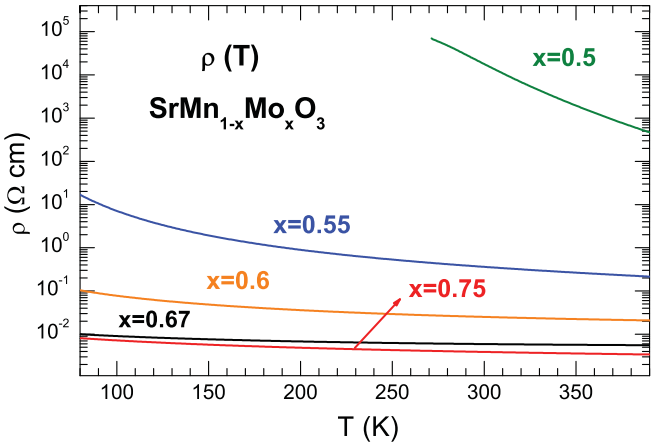

FIG. 1. (Color online) Temperature-dependent resistivity data for $SrMn_{1-x}Mo_xO_3$ ($x \geqslant 0.5$).

temperature by employing the total electron yield mode with a photon energy resolution of ~100 meV at $h\nu \approx 600$ eV. All the XAS spectra were normalized to the incident photon flux.

Figure 2 compares the measured Mn $2p$ XAS spectra of $SrMn_{1-x}Mo_xO_3$ ($x \geqslant 0.5$). All the spectra are split into L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) parts due to the $2p$ core-hole spin-orbit coupling. It is clearly shown that the Mn $2p$ XAS spectra remain essentially the same with increasing x for $x \geqslant 0.5$. TM $2p$ XAS is highly sensitive to its valence state by reflecting the $2p$ core-hole final-state multiplets due to the interaction between the $2p$ hole and the $3d$ electrons, where the number of $3d$ electrons plays an important role. Therefore the TM $2p$ XAS spectra of TM oxides represent the valence states of TM ions very well.

By comparing these Mn $2p$ XAS spectra to those of reference manganese oxides, such as MnO_2 (Mn^{4+}),[17] Mn_2O_3 (Mn^{3+}),[18] and MnO (Mn^{2+}),[19] the valence states of Mn ions

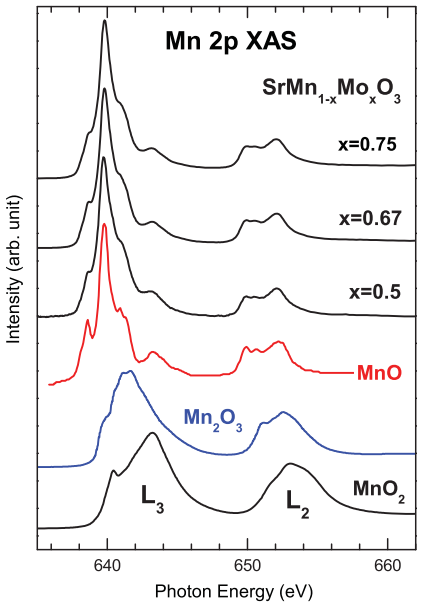

FIG. 2. (Color online) Comparison of the Mn $2p$ XAS spectra of $SrMn_{1-x}Mo_xO_3$ ($x \geqslant 0.5$) with those of MnO (Mn^{2+}), Mn_2O_3 (Mn^{3+}), and MnO_2 (Mn^{4+}).

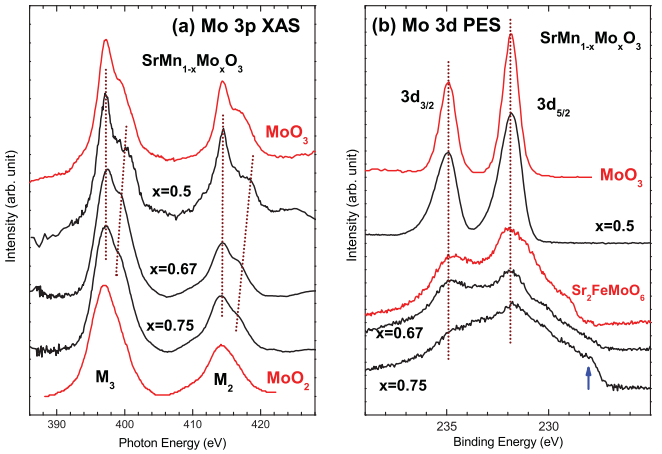

FIG. 3. (Color online) (a) Comparison of the Mo $3p$ XAS spectra of $SrMn_{1-x}Mo_xO_3$ ($x \geqslant 0.5$) with those of MoO_3 and MoO_2. (b) Comparison of the Mo $3d$ core-level PES spectra of $SrMn_{1-x}Mo_xO_3$ ($x \geqslant 0.5$) with those of MoO_3 and Sr_2FeMoO_6.

in $SrMn_{1-x}Mo_xO_3$ can be identified. The Mn $2p$ XAS spectra of reference Mn oxides show that, as the nominal valence states of Mn ions increase from Mn^{2+} to Mn^{3+} and Mn^{4+}, the positions of the main peaks shift toward a high energy with the accompanying line shape change. This comparison provides evidence that the formal valence states (v) of Mn ions in $SrMn_{1-x}Mo_xO_3$ remain approximately $v \approx 2$ for $x \geqslant 0.5$. This finding makes a contrast to the case for $x \leqslant 0.5$ in $SrMn_{1-x}Mo_xO_3$, where the valence states of Mn ions decrease gradually from being tetravalent (Mn^{4+}, $3d^3$) at $x = 0$ to being divalent (Mn^{2+}, $3d^5$) at $x = 0.5$. Further, this finding implies that, as x increases from 0.5 in $SrMn_{1-x}Mo_xO_3$, the valence states of Mo ions should decrease from being hexavalent (Mo^{6+}) at $x = 0.5$.

Figure 3(a) compares the Mo $3p$ XAS spectra of $SrMn_{1-x}Mo_xO_3$ ($x \geqslant 0.5$), in comparison with those of reference Mo oxides, such as hexavalent MoO_3 (Mo^{6+}, $4d^0$) (top) and tetravalent MoO_2 (Mo^{4+}, $4d^2$)[20] (bottom). The peak positions and the linewidths of the Mo $3p$ XAS spectra of reference Mo oxides, having different nominal valence states, are very similar to each other. This is probably due to the rather delocalized nature of $4d$ TM electrons (see Fig. 1). The main differences between MoO_3 (Mo^{6+}) and MoO_2 (Mo^{4+}) are their line shapes: the Mo $3p$ XAS spectrum of hexavalent MoO_3 exhibits a double-peak structure clearly, while that of tetravalent MoO_2 exhibits a single, broad structure. The measured Mo $3p$ XAS spectrum for $x = 0.5$ is very similar to that of MoO_3, showing a double-peak structure for both M_3 ($3p_{3/2}$) and M_2 ($3p_{1/2}$) parts. This finding supports the previous finding that Mo ions at $x = 0.5$ in $SrMn_{1-x}Mo_xO_3$ are hexavalent.[16] With increasing x from $x \geqslant 0.5$, the line shape of the Mo $3p$ XAS spectrum becomes broad, and the line shape for $x = 0.75$ becomes very similar to that of MoO_2, which has nominally tetravalent Mo^{4+} ions. It is not easy to tell how the peak positions change with x in $SrMn_{1-x}Mo_xO_3$ because the double peaks at $x = 0.5$ seem to merge with increasing x. Nevertheless, Fig. 3 shows that the valence states of Mo ions decrease from being hexavalent (Mo^{6+}) at $x = 0.5$ to the lower valence states at $x > 0.5$.

Figure 3(b) compares the Mo 3*d* core-level photoemission spectroscopy (PES) spectra of $SrMn_{1-x}Mo_xO_3$ for $x \geqslant 0.5$ to those of reference oxides of MoO_3 and Sr_2FeMoO_6, which are chosen as a formally hexavalent Mo^{6+} system and the Mo^{5+}-Mo^{6+} mixed-valent system,[21] respectively. The Mo 3*d* PES spectra of $SrMn_{1-x}Mo_xO_3$ were obtained at the U7 beamline at room temperature from the same samples from which the XAS data were obtained. The data for MoO_3 are taken from Ref. 22, while that for Sr_2FeMoO_6 is taken from Ref. 21. Note that the Mo 3*d* PES spectrum of $SrMn_{1-x}Mo_xO_3$ with $x = 0.5$ is very similar to that of MoO_3, indicating that the valence states of Mo ions are nearly hexavalent (Mo^{6+}) at $x = 0.5$. In contrast, the Mo 3*d* PES spectra of $SrMn_{1-x}Mo_xO_3$ with $x = 0.67$ and $x = 0.75$ are much broader than that with $x = 0.5$ and they exhibit several peaks in contrast to the single-peak structure in MoO_3. The appearance of the extra features at the lower binding energies (BEs) is very similar to that of Sr_2FeMoO_6, which is known to be formally mixed-valent with the Mo^{5+}-Mo^{6+} configuration and to have a metallic ground state.[21] Further, the Mo 3*d* PES spectra for $x > 0.5$ reveal the extra emission at BEs (marked with an arrow) lower than those in Sr_2FeMoO_6. These findings suggest that, for $x > 0.5$, the valence states of Mo ions are lower than those of Mo^{6+} ions and also lower than those in Sr_2FeMoO_6. In other words, for $x > 0.5$, Mo ions are mixed-valent either with the Mo^{4+}-Mo^{6+} configuration or with the Mo^{4+}-Mo^{5+}-Mo^{6+} configuration.

The top of Fig. 4 shows the O 1*s* XAS spectra of $SrMn_{1-x}Mo_xO_3$ for $x \geqslant 0.5$. The O 1*s* XAS spectra of TM oxides represent the unoccupied TM 3*d* and *sp* states, as well as the other conduction-band states via the hybridization with the O 2*p* states.[23] The lowest-energy peaks in the O 1*s* spectra, which are marked as the bars in red and black, are identified as the unoccupied Mn 3*d* and Mo 4*d* states,[23] respectively. The broad peaks around $h\nu \sim 535$ eV are due to the unoccupied Sr 4*d* states,[23] and the peaks at ~540–545 eV are assigned to the unoccupied Mn 4*s*/4*p* and Mo 5*s*/5*p* states.

This figure reveals that, at $x = 0.5$, the unoccupied Mn 3*d* states lie closer to the Fermi level (E_F) than the unoccupied Mo 4*d* states. With increasing x from $x = 0.5$, the positions of the Mo 4*d* states shift down toward E_F. This trend can be explained by a simplified ionic model, shown in Fig. 4 (bottom) as a schematic energy diagram. Mn ions are divalent for $x \geqslant 0.5$, having the $3d^5$ ($t_{2g}^3 \uparrow e_g^2 \uparrow$) configuration (see Fig. 2). On the other hand, the valence states of Mo ions are hexavalent (Mo^{6+}) at $x = 0.5$, with the configuration of $4d^0$ (t_{2g}^0), and they decrease to either Mo^{4+} or Mo^{5+} states with increasing x (see Fig. 3). Note that Mn and Mo in $SrMn_{1-x}Mo_xO_3$ have the HS and low-spin states, respectively.[24] Hence the lowest-energy peaks in the O 1*s* XAS with $x = 0.5$ will correspond to the unoccupied Mn $t_{2g} \downarrow$ states, and the unoccupied Mo $t_{2g} \uparrow\downarrow$ states lie higher than the unoccupied Mn $t_{2g} \downarrow$ states. If Mo ions are tetravalent (Mo^{4+}), having the $4d^2$ ($t_{2g}^2 \uparrow\downarrow$) configuration, then the partially filled Mo t_{2g} states for Mo^{4+} ions will be located closer to E_F than the vacant Mo t_{2g} states for Mo^{6+} ions. Therefore, as the valence state of a Mo ion decreases, the positions of the unoccupied Mo 4*d* states are expected to

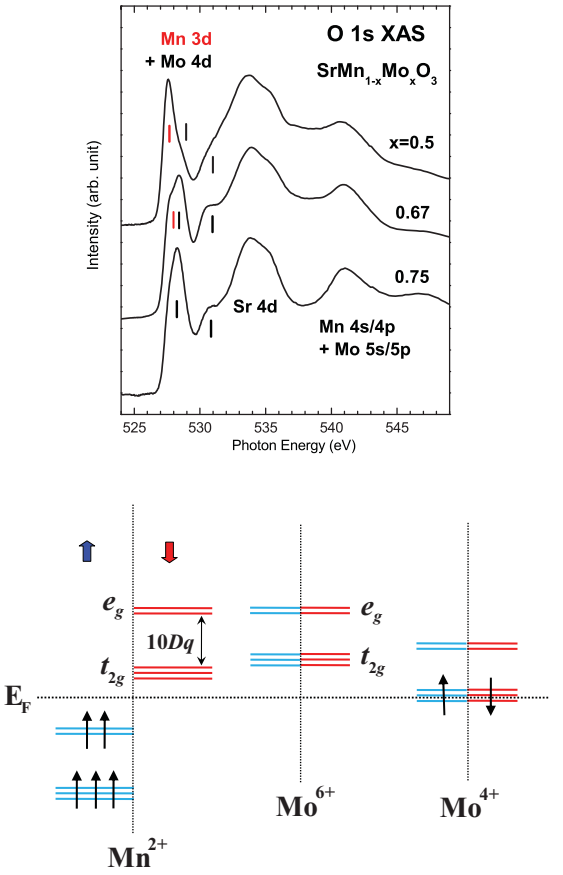

FIG. 4. (Color online) (Top) O 1*s* XAS spectra of $SrMn_{1-x}Mo_xO_3$ with $x = 0.5$, 0.67, and 0.75. Red and black bars are identified as the unoccupied Mn 3*d* and Mo 4*d* states, respectively. (Bottom) Schematic energy diagram for HS Mn^{2+} ($3d^5$, $t_{2g}^3 \uparrow e_g^2 \uparrow$), Mo^{6+} ($4d^0$), and Mo^{4+} ($4d^2$, $t_{2g}^2 \uparrow\downarrow$) ions, respectively.

TABLE I. Valence states of Mn and Mo in $SrMn_{1-x}Mo_xO_3$.

		$x = 0$	$0 < x < 0.5$	$x = 0.5$	$0.5 < x < 1$	$x = 1$
Mn		4+	xMn = 2+;	2+	2+	
			$(1 - 2x)$Mn = 4+			
	Average	4+	$(4 - 6x)/(1 - x)$	2+	2+	
Mo			6+	6+	$(1 - x)$Mo = 6+;	4+
					$(2x - 1)$Mo = 4+	
	Average		6+	6+	$2(1 + x)/x$	4+

shift toward E_F due to the partial filling of the Mo t_{2g} states. This explains the observed trend in the O 1*s* XAS spectra reasonably well.[25]

The previous[16] and present findings for $SrMn_{1-x}Mo_xO_3$ suggest that, when a Mn^{4+} ion in $SrMnO_3$ is replaced by a Mo^{4+} ion, there occurs charge transfer from a Mo ion to a neighboring Mn ion, resulting in the Mo^{6+}-Mn^{2+} configuration, as compared to the initial Mo^{4+}-Mn^{4+} configuration. That is, the valence states of Mn and Mo in $SrMn_{1-x}Mo_xO_3$ are expected to vary with x as described in Table I in the ionic picture, even though the itinerant character is more appropriate to describe the Mo 4*d* electronic states in $SrMn_{1-x}Mo_xO_3$ for $x > 0.5$. Then the average valence state of Mn for $0 \leqslant x \leqslant 0.5$ is given by $(4 - 6x)/(1 - x)$, while that of Mo for $0.5 \leqslant x \leqslant 1$ is given by $2(1 + x)/x$.

In conclusion, we have studied the electronic structures of $SrMn_{1-x}Mo_xO_3$ ($x \geqslant 0.5$) by employing XAS. The measured Mn 2*p* XAS spectra indicate that the valence states of Mn ions are nearly divalent and that they remain nearly unchanged for $x \geqslant 0.5$. On the other hand, the Mo 3*p* XAS and Mo 3*d* core-level PES spectra for $x \geqslant 0.5$ show the clear changes that imply the decreasing valence states of Mo ions from Mo^{6+} at $x = 0.5$ to the lower valence states (Mo^{4+} or Mo^{5+}) at $x > 0.5$. These conclusions are supported by the trends in the unoccupied Mn 3*d* and Mo 4*d* states in the O 1*s* XAS spectra, which occur due to the changes in their valence states.

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[25] More detailed understanding of the O 1*s* XAS requires the comparison of the O 1*s* XAS spectra with the calculated unoccupied partial densities of states (PDOSs) of $SrMn_{1-x}Mo_xO_3$ for the corresponding x value, where the effects of the Mn-O and Mo-O hybridization are included.