**X-Ray Spectroscopic Studies of A-Site Ordered Perovskite LaMn$_3$B$_4$O$_{12}$ ($B$=V, Cr)**

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We investigated the electronic structure of LaMn$_3$V$_4$O$_{12}$ (LMVO) and LaMn$_3$Cr$_4$O$_{12}$ (LMCO) by X-ray absorption spectroscopy (XAS) and resonant X-ray emission spectroscopy (RXES) measurements around Mn 2$p$ edges. The Mn 2$p$-XAS spectra showed that the Mn valence is trivalent for LMCO and divalent for LMVO. These results indicate that the A$^\prime$-site can accommodate not only Jahn-Teller ions but also non-Jahn-Teller ions. The Mn 2$p$-RXES spectra showed the difference of the hybridization between Mn-3$d$ and O-2$p$ orbitals. According to theoretical calculation results, LMCO is candidates for the negative charge transfer energy compound.

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I. INTRODUCTION

A-site ordered perovskites AA$^\prime$$_3$B$_4$O$_{12}$ show intriguing physical properties such as colossal dielectric constant, colossal magneto-resistance, and heavy fermion behavior [1]. It has been widely known to Jahn-Teller distorted ions such as Cu$^{2+}$ and Mn$^{3+}$ can be accommodated into square-coordinated A$^\prime$-site (A$^\prime$O$_4$ unit) in the A-site ordered perovskites and A$^\prime$O$_4$ units align perpendicularly to each other. This special alignment plays important roles for interesting physical properties, especially for magnetic properties. For example, CaCu$_3$B$_4$O$_{12}$ ($B$ = Ge, Sn, and Ti) and their solid solutions show unusual transitions from ferromagnetic CaCu$_3$Ge$_4$O$_{12}$ to antiferromagnetic CaCu$_3$Ti$_4$O$_{12}$ to ferromagnetic CaCu$_3$Sn$_4$O$_{12}$. The ferromagnetic-to-antiferromagnetic transition is different from the known change by the bond angles mechanism of the superexchange interaction and has not been observed previously in any ferromagnetic-antiferromagnetic compounds [2]. While Mn ions sit at A-site, AMn$_3$B$_4$O$_{12}$ ($A$ = La and Y; $B$ = Ti, V, Cr, and Co) shows the various magnetic properties such as anti ferromagnetism, ferrimagnetism, and spin glass [3, 4]. Moreover, it was proposed in previous paper that Mn ions at A$^\prime$-site show not only trivalent but also divalent or lower divalent. However, there are few spectroscopic studies. Recently, we succeeded in more two compounds LaMn$_3$V$_4$O$_{12}$ (LMVO) and LaMn$_3$Cr$_4$O$_{12}$ (LMCO). We carried out the Mn 2$p$ X-ray absorption spectroscopy (XAS) and resonant X-ray emission spectroscopy (RXES) measurements for LMVO and LMCO in order to estimate valence of the Mn ions and to investigate the detail electronic structure directly.

II. EXPERIMENTAL

LMVO and LMCO were synthesized under high pressure and high temperature as described in the literature [3]. RXES and XAS measurements were carried out at the BL27SU of SPring-8 in Japan. XAS at the Mn 2$p$ edge was performed in the total electron yield mode and normalized by the photocurrent from a clean gold mesh. RXES spectra were recorded with a high-resolution grazing-incidence grating Rowland-mount spectrometer in which the energy resolution was set to be 0.7 eV [5]. RXES measurements were carried out with the depolarization.
TABLE I: These values are used in theoretical calculation about Mn 2p XAS spectra. Theoretical XAS spectrum reproduced experimental spectrum using these parameter values. $V(e_g)$, $U_{dd}$, and $U_{dc}$ are the hybridization energy between the Mn 3d and O 2p ligand states, the Coulomb interaction energy between Mn 3d states and the Coulomb interaction between the Mn 3d and 2p core-hole states, respectively. $\Delta$ corresponds to the energy of charge transfer from O 2p orbitals to Mn 3d orbitals. 10Dq corresponds to the strength of the crystal field.

<table>
<thead>
<tr>
<th>unit (eV)</th>
<th>$\Delta$</th>
<th>$U$</th>
<th>$U_{dc}$</th>
<th>$V$</th>
<th>10Dq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{3+}$</td>
<td>-3.0</td>
<td>7.0</td>
<td>8.24</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Figure 2: (a) Mn 2p-XAS spectra for LaMn$_3$Cr$_4$O$_{12}$ and (b) YMn$_3$Co$_4$O$_{12}$.

III. RESULTS AND DISCUSSION

Figures 1(a) and (b) show Mn 2p XAS spectra of LMVO and LaMn$_3$Ti$_4$ScO$_{12}$ (LMTSO), respectively. Both spectra shows four peaks and were similar to each other. These spectral shape are due to multipe effects. This result are consistent with the fact that LMVO and LMTSO are insulating. The valence of Mn ions in LMTSO is divalent estimated by magnetic measurements [6]. Taking account for the spectral shape of LMVO, The valence of Mn ions in LMVO are divalent (electronic configuration: $d^5$).

Figures 2(a) and (b) show Mn 2p XAS spectra of LMCO and YMn$_3$Co$_4$O$_{12}$ (YMCO), respectively. Mn 2p XAS spectrum of LMCO is very different from that of YMCO. The spectral shape of YMCO is relatively similar to that of the ordinary perovskite LaMnO$_3$ which has positive charge transfer (CT) energy [7, 8]. We assume that Mn ions of YMCO have positive CT energy and the electronic configuration of Mn ions are mainly $3d^4$. On the other hand, the spectral shape of LMCO is relatively to MnO. This shows that Mn electron configuration of LMCO are not simple $3d^4$ but mainly $3d^5$. This result indicates that Mn ions of LMCO have negative CT energy. According to Ref. [3], the valence of Mn ions in LMCO were trivalent estimated by Bond valence sums calculations from the structural data.

In order to confirm that the charge transfer energy of Mn ions is negative, we have performed the theoretical calculation about Mn 2p XAS spectra. We have adopted the full multiplet calculation with charge transfer. The detail of this calculation were described in Ref. [9]. In this calculation, five parameters were used and these values were shown in Table I. The local symmetry of Mn ions at A’-site is adopted D$_{4h}$, because Mn site is square-planar coordination [3].

Figures 3 (a) and (b) show theoretical Mn 2p XAS spectra and experimental one, respectively. Theoretical spectrum relatively reproduced experimental spectrum. This indicates that the negative CT is important to understand spectral shape of LMCO.

Figure 4 shows Mn 2p-RXES spectra for LMVO (red) and LMCO (blue) excited at energy of Peak A. Inset shows Mn 2p$_{3/2}$ XAS spectra.
t_{2g} for Peak D and e_g - e_g for Peak D') excitations, and CT excitation, respectively. This result indicated that Mn-3d levels were divided into four levels and corresponds that the local symmetry of Mn ions is D_{4h}. The peak positions of d-d excitation for LMCO and LMVO are same. This indicate that 3d electronic structure is similar to each other. While, the intensity of the CT peak for LMVO was significantly suppressed than that of LMCO. The result implies that Mn-3d and O-2p orbitals strongly hybridize for LMCO compares to those for LMVO. RXES results supported that Mn electronic configuration is mainly 3d^5. The CT peak is originated from the hybridization between the Mn-3d and O-2p orbitals. The Mn-3d electrons are delocalized and strongly hybridized with the O-2p orbital in the wide energy range when the CT energy is negative. These mechanism were reported in previous paper [10].

IV. CONCLUSION

In conclusion, we measured Mn 2p-XAS and 2p-RXES spectra for LMVO and LMCO. The Mn 2p-XAS spectra showed that the Mn valence is trivalent for LMCO and divalent for LMVO. These results indicate that the A'-site can accommodate not only Jahn-Teller ions but also non-Jahn-Teller ions. The Mn 2p-RXES spectra showed the difference of the hybridization between Mn-3d and O-2p orbitals.

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