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Composition dependence of valence states in epitaxial $LaCo_{1-x}Mn_xO_3$ thin films studied by X-ray absorption spectroscopy

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Introduction

Ferromagnetic semiconductors with high Curie temperatures are of great interest for applications to spinbased multifunctional devices. In the search for new ferromagnetic semiconductors with high Curie temperatures (Tc), double-perovskite manganites exhibiting ferromagnetic semiconducting properties near to room temperature have received a renewed interest. La_2CoMnO_6 is a ferromagnetic semiconductor that has a potential of applying to spintronics devices because of its high ferromagnetic transition temperature (Tc ~ 240 K). The ferromagnetism of $LaCo_{0.5}Mn_{0.5}O_3$ is explained by the mechanism due to a superexchange interaction in Co-O-Mn, which is predicted theoretically by Goodenough - Kanamori (G-K) rules. However, electronic states of transition metals responsible for the ferromagnetic interaction have not been elucidated yet. G-K rules predict both $Co^{2+}(d^7)$-O-$Mn^{4+}(d^3)$ and $Co^{3+}(d^6)$-O-$Mn^{3+}(d^4)$ [1] interactions to exhibit a ferromagnetic behavior. In this study, X-ray absorption spectroscopy (XAS) of $LaCoO_3$-$LaMnO_3$ composition spread films was carried out to evaluate the valence states of transition metal ions for studying the origin of ferromagnetism in $LaCo_{0.5}Mn_{0.5}O_3$.

Experimental

Epitaxial $LaCoO_3$-$LaMnO_3$ composition spread films were fabricated on $LaAlO_3$ (100) substrates using a pulsed laser deposition method. During deposition, the substrate temperature was kept at 600 ºC at an oxygen pressure of 100 mTorr. Composition and structures of the films were characterized by X-ray fluorescence (XRF) and X-ray diffraction (XRD), respectively. XAS spectra were obtained by measuring the sample drain current at an undulator BL-2C beamline.

Results and discussion

Figure 1 shows Co 2*p*- 3*d* absorption spectra (a) and Mn 2*p*-3*d* absorption spectra (b) at room temperature. With increasing the incorporated Mn into $LaCo^{3+}O_3$, The shape of Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks are becoming change, as shown in Fig.1 (a). Park *et al*. reported that Co $2p_{3/2}$ spectra of $LaCo^{3+}O_3$ are quite different from that of $Co^{2+}O$ [2]. By comparing our Co *2p-3d* XAS spectra with the reported spectra, it is indicated that the valency of Co varies from Co^{3+} to Co^{2+} as a result of Mn substitution in $LaCo^{3+}O_3$. Mn $2p_{3/2}$ spectra also show changes in shape with the substitution of Co by Mn, as shown in Fig. 1 (b). This suggests that the replacement of Co by Mn increases the valency of Mn from Mn^{3+} to Mn^{4+}, which is consistent with $La_{1-x}Sr_xMnO_3$ XAS spectra obtained by Abbate *et al*. [3]. Thus, the valency changes from Co^{3+} to Co^{2+}, and from Mn^{3+} to Mn^{4+} due to the charge transfer from Mn to Co were clearly observed. This charge transfer results in a ferromagnetic semiconductor $LaCo_{0.5}Mn_{0.5}O_3$ consisting of mainly Co^{2+} and Mn^{4+}. Therefore, it is suggested that a superexchange interaction between Co^{2+} and Mn^{4+} via an oxygen ion rather than Co^{3+} and Mn^{3+} is the origin of ferromagnetism in $LaCo_{0.5}Mn_{0.5}O_3$.

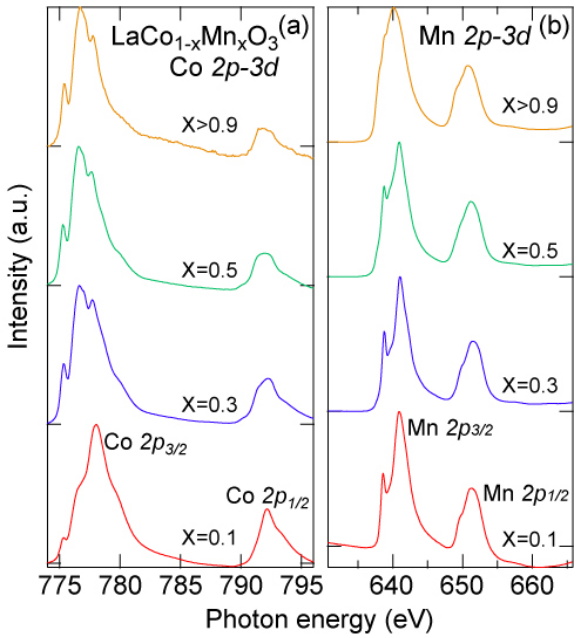

Fig. 1: XAS spectra of $LaCo_{1-x}Mn_xO_3$: (a) Co 2p-*3d*, (b) Mn *2p-3d*.

References

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