Composition dependence of valence states in epitaxial LaCo$_{1-x}$Mn$_x$O$_3$ 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$_2$CoMnO$_6$ 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 LaCo$_{0.5}$Mn$_{0.5}$O$_3$ 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 LaCo$_{0.5}$Mn$_{0.5}$O$_3$ 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 °C 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 2p- 3d absorption spectra (a) and Mn 2p-3d 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$_2$ [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$_x$MnO$_3$ XAS spectra obtained by Abbate et al. [3]. Thus, the valency changes from Co$^{2+}$ to Co$^{3+}$, 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$_3$.

References


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