Valence Changes in the $La_{1-x}Ca_xMnO_3$ studied by NEXAFS study

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The $La_{1-x}Ca_xMnO_3$ compounds belong to a family of perovskite-like manganite system which shows the colossal-magnetoresistance (CMR) properties. The Mn valence states in $La_{1-x}Ca_xMnO_3$ system consist formally of Mn^{3+} and Mn^{4+} ions. The magnetic and electronic properties of the CMR compounds have been traditionally explained by the double-exchange model which considers the transfer of an electron (or a hole) between neighboring Mn^{3+} and Mn^{4+} ions. Generally, the valence states in $La_{1-x}Ca_xMnO_3$ have been controlled by a function of composition. The $La_{1-x}Ca_xMnO_3$ compounds controlled valence states show very interesting changes in the electronic and magnetic properties [1,2].

The polycrystalline $La_{1-x}Ca_xMnO_3$ films were prepared by a laser ablation method on a $LaAlO_3(100)$ single crystal. The targets were prepared by mix and annealing of La_2O_3, CaO, and Mn_2O_3 powders in proportion to the stoichiometric composition. The near edge x-ray absorption fine structure (NEXAFS) spectra were taken at the U7 undulator beamline of the Pohang Light Source in Korea.

In this study, the valence states in $La_{1-x}Ca_xMnO_3$ films were controlled by various deposition conditions such as composition, temperature, thickness, etc. These films showed different Mn valence states according to the variation of deposition condition. It is found that the deposition condition in the film growth plays an important role for the formation of $La_{1-x}Ca_xMnO_3$ phase. According to the La $M_{4,5}$, Ca $L_{2,3}$, Mn $L_{2,3}$, and O K NEXAFS spectra, the amount formed of Mn^{4+} ions in the $La_{1-x}Ca_xMnO_3$ film changes with the composition, deposit-temperature, and thickness.).

In O K-edge, the inflection points of O K-edge for Mn oxides ($Mn^{2+}O$, $Mn^{4+}O_2$, and $KMn^{7+}O_4$) shift towards the lower energy with increasing the number of valence for Mn. The shift of O K-edge to the lower energy might mean a reduced number of Mn valence electrons. From this energy shift, we can obtain the information on the valence state of Mn in $La_{1-x}Ca_xMnO_3$.

This work was supported by the KOSEF through q-Psi and Grant Number R04-2002-000-00009-0 and by Korea Research Foundation Grants (KRF-2001-015-DP0193 and KRF-2001-015-DS0015).

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