X-ray Absorption Spectra of Delaffosite Oxides CuCr$_{1-x}$Mg$_x$O$_2$

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1 Introduction

Delaffosite oxides CuM$O_2$ ($M$ = metal element) have various important physical properties both in fundamental and applicational terms. For example, CuAlO$_2$ is the first $p$-type transparent oxide semiconductor [1], and CuFeO$_2$ is a typical multiferroic compound [2]. This family have also potential for thermoelectric materials [3] because of its layered structure of edge-shared MO$_6$ octahedrons, being the same as thermoelectric NaCoO$_2$ [4]. Hole-doped CuCr$_{1-x}$Mg$_x$O$_2$ is one of such candidates; in CuCrO$_2$, $3d$ electrons of the Cr$^{3+}$ ions under the Oh local symmetry fill up the narrow Cr$^{3+}$d$^{3}$t$_{2g}$ band and thus a rapid change of density of states at the Fermi level ($E_F$) may be realized near the t$_{2g}$ band edge in the hole-doped system CuCr$_{1-x}$Mg$_x$O$_2$, a high conductivity delaffosite [3]. However, whether the doped hole will go into the Cr$^{3+}$d states or not is unknown. In order to observe valence changes of the Cu and Cr ion in this system, we performed x-ray absorption spectroscopic measurements.

2 Experiment

Polycrystalline samples of CuCr$_{1-x}$Mg$_x$O$_2$ ($x=0$, 0.02, 0.03) were prepared by the standard solid-state reaction [3]. Soft x-ray absorption spectroscopy (XAS) measurements were performed at BL-2C of Photon Factory in KEK. The samples were fractured in situ right before measurements in ultrahigh vacuum (better than $1.2\times10^{-7}$ Pa) at 300 K.

3 Results and Discussion

Figure 1 shows XAS spectra of CuCr$_{1-x}$Mg$_x$O$_2$ ($x=0$, 0.02, 0.03) at the Cr L$_{2,3}$ and Cu L$_3$ edges. The Cr L$_{2,3}$ spectra in Panel (a) are of the typical Cr$^{3+}$ one [5] and show no observable change with x. By contrast, the Cu L$_3$ edge at x=0 is the typical Cu$^{2+}$ spectrum and the prepeak at 926.5 eV, which is associated with the Cu$^{2+}$ signal [6], systematically increases with x. These facts are indicating that the hole is not doped into the Cr states but into the Cu states.

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References


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