UVSOR-II BL5U

Electronic Structure of Pseudo-one Dimensional $Ba_3Co_2O_6(CO_3)_{0.7}$

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Cobalt oxides such as Na_xCoO_2 have attracted much attention because of their fascinating transport and magnetic properties. Recently it has been found that a barium cobalt oxycarbonate $Ba_3Co_2O_6(CO_3)_{0.7}$, which has pseudo-one dimensional structure with Co-O chains consisting of face-sharing CoO_6 octahedra along the *c* axis, shows a fairly large thermoelectric power factor of 0.9 $mWm^{-1}K^{-2}$ at 300 K with the thermoelectric power of about +120 $\mu V\ K^{-1}$ and metallic behavior of its electric conductivity above 300 K [1]. In this report, we have investigated its valence-band electronic structure by photoelectron spectroscopy to understand the physical properties.

Photoelectron measurements were carried out at the beamline BL-5U of UVSOR-II. Single crystalline specimens of $Ba_3Co_2O_6(CO_3)_{0.7}$ was prepared in size of 5 x 0.5 x 0.5 mm^3 by a flux method [1], and their clean surfaces was obtained by *in situ* fracturing the specimens in perpendicular to the *c* axis.

Figure 1 shows typical photoelectron spectra recorded at 20 K with the excitation photon energies $h\nu$ of 60 and 75 eV as well as their difference spectrum. Each spectrum is normalized with the integrated intensity and subtracted the background by an iteration method [2]. There are features A to H observed in the spectra; the features A to C are ascribed to the hybridized bands of the Co 3*d* and O 2*p* states, while the features D, F, G and H are assigned to the CO_3-derived states, Ba 5*p* spin-orbit doublets and O 2*s* state, respectively. The feature E is attributed to the surface components. The remarkable suppression of the features A and B at $h\nu$ = 60 eV is due to the Co 3*p*-3*d* resonance, which indicates the relatively large Co 3*d* contribution to the features A and B while the O 2*p* one to the feature C.

Figure 2 shows detailed spectra near the Fermi level E_F measured at $h\nu$ = 40 eV and several temperatures *T* in comparedison with reference Au spectra. $Ba_3Co_2O_6(CO_3)_{0.7}$ reveals large reduction in intensity towards E_F but clear finite intensity at E_F. This may suggest the electron doping into the low-spin bands of $Co^{4+}(t_{2g}3d^5)$, which causes the positive thermoelectric power of 81 or 141 $\mu V\ K^{-1}$ at high temperatures for the Co^{4+} concentration *x* of 0.7 [3], consistent with the observed value. Although a 1/8-power-law dependence of the intensity on the binding energy E_B might be expected in one-dimensional fermion system [4], the anomalous exponents from 0.5 at 20 K to 0.8 at 200 K are obtained for E_B = 0.01~0.1 eV, suggesting the larger short-range interaction at the lower temperature. A small hump at E_B ~ 0.02 eV observed at *T* = 20 K might also imply opening of a pseudogap or a magnetic ordering, which causes the recently observed reduction in the electric conductivity at low temperatures [5].

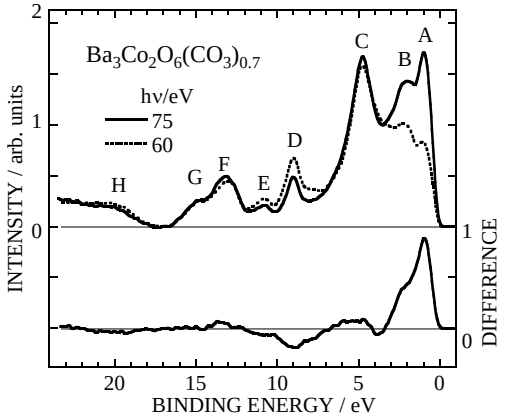

Fig.1. Valence-band spectra of $Ba_3Co_2O_6(CO_3)_{0.7}$.

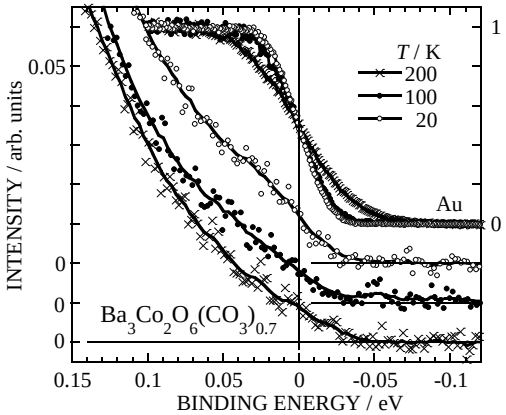

Fig.2. Valence-band spectra near the Fermi level.

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