Photoemssion study of doping dependent metal-insulator transition in Ru pyrochlores (Sm,Ca)$_2$Ru$_2$O$_7$ and (Sm,Bi)$_2$Ru$_2$O$_7$

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Pyrochlore-type Ru oxides $A_2$Ru$_2$O$_7$ show a variety of electrical and magnetic properties for different $A$-site ions [1]. This system is particularly interesting in that both filling-control and valence-control metal-insulator transition can be realized. Sm$_{2-x}$Ca$_x$Ru$_2$O$_7$ (0 $\leq x \leq$ 0.6) shows a metal-insulator transition at $x \sim 0.45$ with increasing Ca concentration, i.e., through doping holes to the Ru 4$d$ $t_{2g}$ band. Sm$_{2-x}$Bi$_x$Ru$_2$O$_7$ (0 $\leq x \leq$ 2.0) exhibits a Mott insulator-to-metal transition at $x \sim 0.6$ with increasing Bi concentration, i.e., through changing the Ru 4$d$ $t_{2g}$ band width. The Ru-O-Ru bond angle between RuO$_6$ octahedra changes from 132$^\circ$ (Sm end) to 139$^\circ$ (Bi end) in Sm$_{2-x}$Bi$_x$Ru$_2$O$_7$ [2,3].

In the present work, we have studied the electronic structures of Sm$_{2-x}$Bi$_x$Ru$_2$O$_7$ and Sm$_{2-x}$Ca$_x$Ru$_2$O$_7$ directly across the metal-insulator transition: core-level energy shift by x-ray photoemission spectroscopy (XPS) and spectral change in the valence band by ultra-violet photoemission spectroscopy (UPS) and x-ray absorption spectroscopy (XAS). By comparing the XPS and UPS spectra of Sm$_{2-x}$Bi$_x$Ru$_2$O$_7$ and Sm$_{2-x}$Ca$_x$Ru$_2$O$_7$, we discuss the mechanism of metal-insulator transition in those two systems. Spectral changes observed in the Ru 4$d$ $t_{2g}$ band are different for Ca and Bi doping but their intensity changes at the Fermi level reflect the tendency of their transport properties in both systems. The Sm$_{2-x}$Ca$_x$Ru$_2$O$_7$ system shows almost the same amount of monotonic energy shift in the Ru 3$d$ core level, O 1$s$ core level and the O 2$p$ band, which is expected from the increase of hole density in the Ru 4$d$ $t_{2g}$ band. This also matches well with the results of O 1$s$ x-ray absorption spectra. On the other hand, the Sm$_{2-x}$Bi$_x$Ru$_2$O$_7$ system doesn't show monotonic energy shift in each state, but shows spectral weight transfer within the Ru 4$d$ $t_{2g}$ band.