Valance state of a new-mixed-anion compound revealed by XANES

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Mixed anion compounds consisting of multiple anion species are attracting much attention as one of new functional material groups [1]. Among them, we are focusing on oxyhydrides, especially searching new materials with an ordered anion structure [2].

Recently, we have succeeded in synthesizing a new oxyhydride EuVO₂H with a layered square planar structure associated with anion ordering, and found using thin film reduces the impurities. Unlike the conventional oxyhydrides, this material may be a rare case where the valence state of rare earth ions changes in the reaction process. To clarify this fact, it is essential to identify exact valence states of Eu and V of EuVO₂H. Here, we measured X-ray absorption near edge structure (XANES) using the pure thin film of EuVO₂H.

EuVO₂H thin film was synthesized by pulse laser deposition. The sample used for XANES measurement was obtained by reducing the EuVO₂H thin film with metal hydride. The XANES experiment was performed by fluorescence yield mode at Eu L3-edge (6950-7050 eV) and V K-edge (5450-5550 eV) at Ritsumeikan University SR Center BL-3.

XANES at Eu L3-edge at room temperature of EuVO₂H thin film exhibits the clear peaks at 6975 and 6983 eV which are attributed to divalent and trivalent europium. This means that the sample measured in the experiment is in the mixed valence state of Eu ion. Considering the charge neutral condition, the valence of V is also presumed to be a mixed valence. In fact, as a result of XANES at V K-edge, it was found that the X-ray absorption edge was shifted to a lower energy side than EuVO₃ or V₂O₃ having an electronic state of V³⁺. This indicates that V ion in EuVO₂H was a mixed valence state of V²⁺ and V³⁺.

Before the measurement, it was thought that all of Eu in EuVO₂H was in a divalent state and all in V were in a trivalent state. However, the experimental result was different from those prediction. On the other hand, this result is interesting because it suggests that EuVO₂H may be an electron-doped material in Mott insulator. It is an important research subject to clarify the interesting physical properties from magnetization and electrical resistance measurements.