

Relation between XANES Pre-edge and XRF $K\beta_5$ as the Changes of Chemical State, Local Symmetry and Coordination Number

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It is well known that an intense pre-edge peak (PP) exists in K-edge XANES spectrum of early transition metal compounds possessing MO_4 species, whereas not for MO_6 species (Fig. 1). In this study, representative XANES spectra of 3d transition metal compounds at K-edge were selected from scientific publications to give an overview of the PP features with regard to the intensity, assignments and general tendencies related to various factors (the selection rule, coordination number, number of d-electrons and symmetry of the coordination sphere) [1]. The intense PP is assigned due to electric dipole transition of 1s electron to the p-component in d-p hybridized orbital, and the d-p mixing depends strongly on the coordination symmetry. The transition of a 1s electron to 3d orbital gives weak PP due to the electric quadrupole transitions for any symmetry. The intensity of PP for a compound with a tetrahedral center changes as a function of the number of 3d electron regardless of the kind of element.

The $K\beta_5$ line is emitted by the $1s^{-1} \rightarrow 3d_{1/2, 3/2}^{-1}$ ($K \rightarrow M_{4,5}$) electric quadrupole hole transition, and the intensity is intrinsically to be weak. But remarkable enhancement behavior has been confirmed in the $17 \leq Z \leq 30$ (Zn) region [2], where it is interpreted to be due to formation of d-p hybridized orbital. Electron transition process for X-ray absorption and emission spectroscopy is considered to be equivalent and complementary. Then a compound with an intense PP in K-edge XANES would give a relatively large $K\beta_5$ peak. It was confirmed in a case for vanadium compounds (Fig. 2), for example.

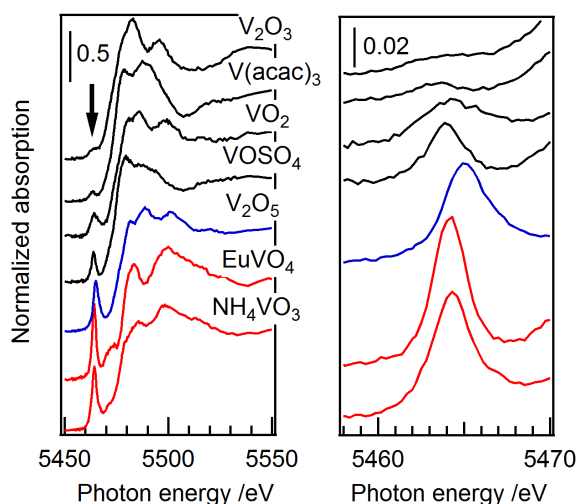


Fig. 1 V K-edge XANES and the preedge peak.

Red: VO_4 , blue: VO_5 , black: VO_6 species.

[1] T. Yamamoto: *X-ray Spectrom.*, **37**, 572 (2008).

[2] I. Török, T. Papp, J. Pálinkás, M. Budnar, A. Mühleisen, J. Kawai, J. L. Campbell: *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms*, **114**, 9 (1996).

[3] S. Fazinić, M. Jakšić, L. Mandić, J. Dobrinić: *Phys. Rev. A*, **74**, 062501 (2006).

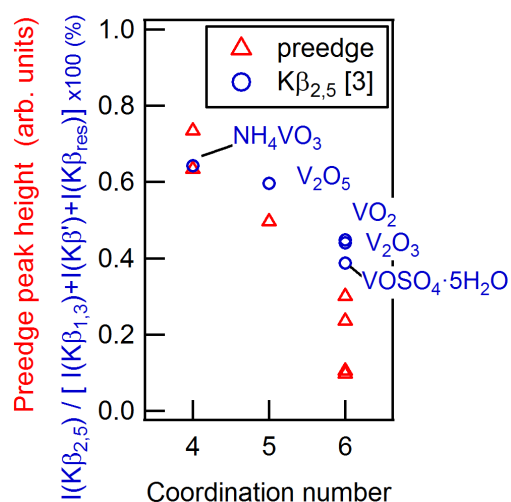


Fig. 2 Relative $K\beta_{2,5}$ [3] and preedge-peak intensity vs. number of coordinated oxygen atom to V^{n+} .