X-ray Fluorescence Analysis of Hexavalent Chromium Using Kβ Satellite Peak Observed as Counterpart of X-ray Absorption Near-Edge Structure Pre-Edge Peak

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ABSTRACT: A Kβ satellite peak in X-ray fluorescence (XRF) spectra is observed as a counterpart of the pre-edge peak of the X-ray absorption near edge structure (XANES). In Kβ emission of chromium, a small satellite peak is observed at 5.983–5.988 keV only for hexavalent chromium compounds such as CrO3, Na2CrO4·2H2O, Na2CrO4·4H2O, K2Cr2O7, K2CrO4, Zn2CrO4(OH)2, 2H2O, PbCrO4, and BaCrO4, together with the main peak at 5.947 keV, while trivalent chromium compounds such as Cr2O3 and Cr(OH)3·nH2O show only the main peak at 5.947 keV. This corresponds to the fact that the K pre-edge peak in XANES is observed only for the hexavalent chromium compounds. The electronic level causing the satellite peak is almost at the same energy level as that causing the pre-edge peak. Our finding not only affects the interpretation of the origin of the pre-edge peaks but also leads to the simple speciation method of chromium compounds using XRF.

Figure 1. XANES K-edge spectra for Cr2O3, Cr(OH)3·nH2O, CrO3, Na2Cr2O7·2H2O, Na2CrO4·4H2O, Na2Cr2O7·2H2O, Na2CrO4·4H2O, and PbCrO4. The spectra are vertically deviated for clarity.

Figure 1. XANES K-edge spectra for Cr2O3, Cr(OH)3·nH2O, CrO3, Na2Cr2O7·2H2O, Na2CrO4·4H2O, Na2Cr2O7·2H2O, Na2CrO4·4H2O, and PbCrO4. The spectra are vertically deviated for clarity.

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it can be interpreted through the $O_b$ and $T_d$ character tables of group theory. The same discussion is also applicable to Kβ X-ray fluorescence spectra.15,16

Many researchers have intensively investigated the fine structures of X-ray fluorescence (XRF) spectra.17–20 It has been reported that the oscillation similar to the extended X-ray absorption fine structure (EXAFS) was observed in lower energy than the main Kα peak of XRF and that the similar information as EXAFS spectra was obtained without using a synchrotron radiation facility.21–25 Fluorescence spectra generally show counterparts of absorption spectra because both involve transitions among the same electronic levels. There have, however, been no reports on the fine structures of the XRF spectra showing the counterpart of the XANES pre-edge peak. In this study, we present the first observation of the counterpart of the pre-edge peak of Cr K-edge absorption spectra in Cr Kβ emission spectra.

**EXPERIMENTAL SECTION**

Two types of trivalent chromium compounds and eight types of hexavalent chromium compounds were measured: Cr$_2$O$_3$, Cr-(OH)$_3$·$n$H$_2$O, CrO$_3$, K$_2$Cr$_2$O$_7$, K$_2$CrO$_4$, Na$_2$Cr$_2$O$_7$·$2$H$_2$O, Na$_2$CrO$_4$·$4$H$_2$O, Zn$_2$Cr$_2$O$_7$(OH)$_2$·$2$H$_2$O, PbCrO$_4$, and BaCrO$_4$ (Kanto Chemical Co., Inc., Tokyo, Japan; reagent grade). Each sample was pressed into a pellet of 13 mm o.d. In order to examine the oscillation similar to the extended X-ray absorbtion (EXAFS) spectra was obtained without using a synchrotron radiation facility. Thus, the spectra were also taken for Cr$_2$O$_3$, Cr(OH)$_3$·$n$H$_2$O to improve the stiffness of the pellet at the ratio of 1 part BN to 4 parts Cr(OH)$_3$·$n$H$_2$O by weight.

XRF spectra were taken with a wavelength dispersive X-ray fluorescence spectrometer (XRF-1700; Shimadzu Co., Ltd., Kyoto, Japan). A rhodium anode X-ray tube was used for excitation with a high voltage of 40 kV and 95 mA. The dispersive crystal was LiF (200) ($2d = 0.40267$ nm), and the X-ray detector was a scintillation counter with NaI (TI). The 2θ scan range was from 57° to 65° by a 0.01° step, and the counts were accumulated for 50 s for each step. The XRF spectra were fitted with a pseudo-Voigt function and a Lorentz function using a nonlinear least-squares method based on the generalized reduced gradient algorithm. XANES spectra, for comparison, were also taken for Cr$_2$O$_3$, Cr(OH)$_3$·$n$H$_2$O, CrO$_3$, Na$_2$Cr$_2$O$_7$·$2$H$_2$O, Na$_2$CrO$_4$·$4$H$_2$O, and PbCrO$_4$ at beamline BL38B10 of Spring-8 (Japan Synchrotron Radiation Research Institute, JASRI, Hyogo, Japan). The spectra were collected in transmission mode using two ion chambers for $I_0$ and $I$.

**RESULTS AND DISCUSSION**

In the XANES spectra, a single peak was observed in the pre-edge region of the spectra of the hexavalent chromium compounds, at about 12 eV smaller than the Cr K absorption edge, and the pre-edge peak was not observed for the trivalent chromium compounds, as shown in Figure 1. Figure 2 shows Cr Kβ XRF spectra after background subtraction and normalization. All the spectra were almost the same around the main peak $Kβ^{1,3}$ ($P_{3/2}$, $P_{1/2}$ $→$ $P_{1/2}$) at 5.947 keV. However, a small shoulder was observed only for hexavalent chromium compounds in the tail region of 5.97–6.00 keV. The spectral curves for Cr$_2$O$_3$, K$_2$Cr$_2$O$_7$, K$_2$CrO$_4$, Na$_2$Cr$_2$O$_7$·$2$H$_2$O, Na$_2$CrO$_4$·$4$H$_2$O, Zn$_2$Cr$_2$O$_7$(OH)$_2$·$2$H$_2$O, and PbCrO$_4$ were almost the same, whereas the curve for BaCrO$_4$ showed a larger shoulder than the other hexavalent compounds. Similarly the spectral curves for Cr$_2$O$_3$ and Cr(OH)$_3$·$n$H$_2$O were almost the same. The main peak was well fitted with the pseudo-Voigt function, except for the small shoulder region of the hexavalent chromium compounds. The residual error after subtracting the fitted pseudo-Voigt function from the experimental data indicated that a small satellite peak (we call this here Kβ$^{0,0}$) existed around 5.999 keV in the spectra of the hexavalent chromium compounds. Thus, the double-peak fitting, the pseudo-Voigt function for the main peak and the Lorentzian function for the satellite peak, was performed. The residual sum of squares for the hexavalent chromium compounds were substantially reduced by using the double-peak fitting, whereas those for the trivalent chromium compounds remained almost the same as the case of the single peak fitting. The fitting parameters are summarized in Table 1.

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<th>Compounds</th>
<th>$u$ (eV)</th>
<th>$σ$ (eV)</th>
<th>$h$</th>
<th>$η$</th>
<th>$u$ (eV)</th>
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*a u, peak position; σ, FWHM; h, peak height; and η, ratio of Lorentz function in pseudo-Voigt function.

Figure 2. Kβ emission spectra for Cr$_2$O$_3$, Na$_2$CrO$_4$, and BaCrO$_4$. The inset is a magnified image of satellite regions.

Table 1. Peak Parameters of Kβ Emissions for Chromium Compounds

The inset is a magnified image of satellite regions.
Figure 3. The satellite peak area vs hexavalent chromium content for five mixtures of Cr₂O₃ and Na₂CrO₄. The satellite peak area is normalized to the main peak area. The open square, □, shows the observed peak area ($I_{obs}$) containing the contribution from the trivalent chromium, which is derived from the deviation between the main peak and the fitted function. The closed square, ■, shows the net peak area ($I_{net}$) calculated by canceling the apparent contribution of the trivalent chromium.

$$I_{net} = I_{obs} - (1 - f_{hex})I_0$$  

where $f_{hex}$ is the fraction of Cr(VI) and $I_0$ is the observed satellite peak area at $f_{hex} = 0$. The calibration curve for the fraction of Cr(VI) vs the net satellite peak area showed a linear relationship. This indicates that the quantitative analysis of valence states will be possible by the analysis of the satellite peak in the XRF spectra. Figure 4 shows the comparison between the energy levels of K absorption and Kβ emission. The energy level to which an electron transits in the K pre-edge absorption (5.993 keV) is very close to the energy level from which an electron transits in the present Kβ* satellite emission (5.983–5.988 keV). Therefore, the satellite peak observed only for the hexavalent chromium compounds is a counterpart of the pre-edge peak of XANES observed only for the same hexavalent chromium compounds as well. This is the first observation of the counterpart of the pre-edge peak in XANES in the XRF spectra. The origin of the pre-edge peak in XANES has been considered to be due to the electric quadrupole transition from 1s to 3d or the electric dipole transition from 1s to a d–p hybrid orbital. Recent studies based on polarized spectra, group theory, and theoretical calculations indicated that an intense pre-edge peak is attributable to the electric dipole transition to p-character in the d–p hybrid orbital and that the electric quadrupole transition from 1s to 3d is the erroneous interpretation.¹⁴

The pre-edge features are characteristic to the transition metals with empty 3d orbital such as Cr(VI), Ti(IV), V(V), and Mn(VII). It is interesting to note that not only the transition to the electronic level corresponding to the pre-edge feature in XANES but also the transition from the same electronic level was observed in XRF. Because the 3d orbital is empty, the quadrupole transition from 3d to 1s in XRF is considered to be improbable. Our results also contradict the quadrupole transition and support the electric dipole transition from the d–p hybrid orbital relating to the symmetry of the central transition metal ion. We expect the analysis of the satellite peaks in XRF spectra would be very informative to clarify the origin of the pre-edge features, because they contain useful information on the electronic levels relating to the XANES.

The main peaks observed in the present study were rather broad (fwhm, 0.33⁻⁻⁻⁻, 0.013 keV), and the satellite peaks were superimposed on the tail of the main peaks. The energy resolution would be greatly improved by employing a double crystal X-ray monochromator or the Bragg-Brentano geometry, and simple and easy analysis without using the synchrotron radiation facility would be possible. The pre-edge peaks in XANES reflect various information on the chemical states of metal compounds such as symmetry, valence, and coordination number.¹¹ The analysis of the fine structure of XRF spectra would be an effective tool alternative to the conventional XANES analysis to obtain such information. We believe that our present findings in the fine structure of XRF spectra would promote the field of chemical state analysis.

CONCLUSIONS

We first found that the fine structures of Kβ emission in XRF spectra provide the same information as the K pre-edge feature of XANES spectra. In Kβ emission, a small satellite peak at 5.983–5.988 keV was observed only for hexavalent chromium compounds, about 40 eV higher than the main peak at 5.947 keV, corresponding to the fact that K pre-edge peaks are observed at 5.993 keV only for hexavalent chromium compounds in XANES spectra. As for the origin of the pre-edge peaks and the corresponding satellite peaks, our results contradict the quadrupole transition and support the electric dipole transition from the d–p hybrid orbital. Since the pre-edge peaks in XANES reflect the chemical states of metal compounds such as symmetry, valence, and coordination number, it is expected that the analysis of the fine structures of XRF would be a new useful tool for chemical state analysis.

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REFERENCES


