X-ray absorption near-edge structure of chromium ions in \( \alpha \)-Al\(_2\)O\(_3\)

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Abstract. Both synthetic and natural \( \alpha \)-Al\(_2\)O\(_3\) samples with different Cr concentrations were investigated by XANES. The Cr contents were analyzed using LA-ICP-MS technique prior to this experiment. XANES spectra combined with first principle calculations showed the transformation from \( \alpha \)-Al\(_2\)O\(_3\):Cr\(^{3+}\) to \( \alpha \)-Al\(_2\)O\(_3\):Cr\(^{3+}\),Cr\(^{3+}\) or \( \alpha \)-Cr\(_2\)O\(_3\) as the Cr-Cr content increased. The absorption transformation could be resulted from the change of environment around Cr\(^{3+}\) ions, i.e., the Al-O-Cr bonds decreased while the Cr-O-Cr bonds increased. Significant differences in XANES line shapes observed for synthetic and natural \( \alpha \)-Al\(_2\)O\(_3\) samples suggested the differences in local environments around Cr ions in both samples. The XANES line shape of \( \alpha \)-Al\(_2\)O\(_3\):Cr\(^{3+}\),Cr\(^{3+}\) or Cr ion pairs corresponded to the Cr content, which was also confirmed by the intensity ratios between N\(_2\)-line and sideband S of R-lines of photoluminescence spectra.

1. Introduction

Both synthetic \( \alpha \)-Al\(_2\)O\(_3\) and natural ones, known as corundum, have been used for jewelry. While pure \( \alpha \)-Al\(_2\)O\(_3\) is colorless, the presence of certain trace elements or impurities in the corundum structure can induce coloration, e.g., red by Cr, blue by Fe and Ti, and yellow by Fe. The amount of impurities ranges from a few ppm to one percent or more. Low Cr content (\( \alpha \)-Al\(_2\)O\(_3\):Cr\(^{3+}\)) gives rise to pink sapphire, higher Cr content (\( \alpha \)-Al\(_2\)O\(_3\):Cr\(^{3+}\),Cr\(^{3+}\)) produces ruby whereas Cr\(^{3+}\) in \( \alpha \)-Cr\(_2\)O\(_3\) is responsible
for the green coloration. The different local environments of Cr ions were expected between the low and high Cr contents.

X-ray absorption near edge structure (XANES) spectrometry is a powerful technique in study of electronic structure around the absorbing atom. The peak positions and line shape of XANES spectrum are strongly sensitive to valence state and symmetry of surrounding/neighboring atoms or local environments. A comparative study of two Indian natural ruby samples and a flame fusion synthetic ruby showed similar peak positions and line shape in XANES spectra [1]. With variations in Cr contents, the Cr-O distances of \( \alpha \text{-Cr}_2\text{O}_3 \) to \( \alpha \text{-Cr}_{0.07}\text{Al}_{1.93}\text{O}_3 \) measured by extended X-ray absorption fine structure (EXAFS) were estimated to be of small significance (1%) [2].

The Cr-Cr coupling was expected to play a role in XANES line shape because of the change of symmetry around \( \text{Cr}^{3+} \). For 1s shell absorption of \( \text{Cr}^{3+} \), the photo-electrons ended up in the O 2p empty states by the selection rule \( \Delta l=+1 \). The \( \text{Cr}^{3+} \) unfilled 3d states took part in the absorption processes by hybridizing with those O 2p states. The pd hybridization highly depended on the local coordination environment.

The luminescence spectrum of dilute ruby (\( \alpha \text{-Al}_2\text{O}_3;\text{Cr}^{3+} \)) was dominated by the two sharp R-lines. The Cr exchange-coupling could be observed from the existence of weaker sharp lines (N-lines) [3]. These N-lines increased in intensity relative to that of the R-lines as the concentration of chromium was increased [4].

In this study, the X-ray absorption spectra of two synthetic and two natural samples of \( \alpha \text{-Al}_2\text{O}_3 \) (from Mong Hsu, Myanmar) with different Cr concentrations were measured by XANES technique. The increase in Cr-Cr coupling corresponding to the Cr concentrations was also investigated using the intensity ratios between the luminescence N- and R-lines.

2. Experiment
The samples consisting of two synthetic and two natural \( \alpha \text{-Al}_2\text{O}_3 \) (Mong Hsu, Myanmar) with various Ti, Cr and Fe concentrations are listed in table 1. Their trace element contents were analyzed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) technique prior to this study. NIST-612 multi-element glass was used as the standard for chemical composition calculation. It must be noted that content inhomogeneity are to be expected, especially, in natural samples. Thus, for each one of the samples, three different laser ablated sites were measured and averaged out for a representative value. Samples were polished in one side perpendicular to the c-axis to ensure the orientation was uniformed for all measurements. \( \alpha \text{-Cr}_2\text{O}_3 \) powder was prepared for comparative XANES study.

| Table 1. Contents of Ti, Cr and Fe in synthetic and natural \( \alpha \text{-Al}_2\text{O}_3 \) samples analyzed by LA-ICP-MS. |
|---------------------------------------------------------------|
| Synthetic samples | Natural samples |
| \( ^{47}\text{Ti} \) | \( ^{47}\text{Ti} \) | \( ^{47}\text{Ti} \) | \( ^{47}\text{Ti} \) |
| \( ^{53}\text{Cr} \) | \( ^{53}\text{Cr} \) | \( ^{53}\text{Cr} \) | \( ^{53}\text{Cr} \) |
| \( ^{57}\text{Fe} \) | \( ^{57}\text{Fe} \) | \( ^{57}\text{Fe} \) | \( ^{57}\text{Fe} \) |
| \( \text{SYNC30} \) | 12.9 | 40.2 | 967.4 | 460.5 |
| \( \text{SYNC60} \) | 3518.6 | 6054.0 | 4339.3 | 3712.0 |
| \( \text{GMMSA} \) | 7.7 | 12.0 | 11.4 | 10.6 |

XANES measurements were performed at the X-ray absorption spectroscopy beamline (BL-8) of the Synchrotron Light Research Institute, Thailand, using a radiation beam from a bending magnet. The beamline details and performance have been reported elsewhere [5]. The XANES spectra were recorded at Cr-K-edge. A pure chromium foil was used as the standard for energy calibration, which was 5989 eV at the absorption edge. The detection was carried out in fluorescence mode using a 13-element Ultra LEGe detector. Flat surface of \( \alpha \text{-Al}_2\text{O}_3 \) samples were arranged at about 45 degrees to the light source and detectors.
Photoluminescence (PL) measurements were carried out at room temperature (25°C) using a Renishaw inVia Raman microscope. The argon laser excitation wavelength was 514.5 nm. The system was calibrated using single crystal silicon with spectral resolution of 2.0 cm⁻¹.

3. Results and discussion

Since all XANES measurements were carried out at the same angular orientation with respect to the light source, the detectors, and the c-axis of samples, the polarization dependence of the X-ray absorption cross section was presumably identical.

Figure 1(a) shows comparison of synthetic samples with two different Cr concentrations. The spectra showed the transition from $\alpha$-$\text{Al}_2\text{O}_3$:Cr³⁺ to $\alpha$-$\text{Al}_2\text{O}_3$:Cr³⁺,Cr³⁺ and $\alpha$-$\text{Cr}_2\text{O}_3$. The spectrum of $\alpha$-$\text{Al}_2\text{O}_3$:Cr³⁺ was calculated using first principle multiple-scattering code FEFF8.2 [6]. Feature A, a pre-edge peak of the calculated spectrum, was displaced to higher energy as previously reported [7]. Features B, C, and E were slightly shifted to higher energy whereas Feature D was first shifted to higher energy before being shifted back to lower energy which suggested Cr-Cr coupling, i.e., the increase in Cr concentration.

Figure 1(b) shows XANES spectra comparison of two Mong Hsu samples (GMMSA and GMMSB) with different Cr concentrations. The spectra showed transitions in similar manner to the synthetic samples except at Feature C, and not directly dependent upon the increase in Cr contents. Feature C was clearly pronounced in GMMSA while Features B and D showed small significances. This could be explained by the coupling of Cr with other trace elements, especially, high content of Ti in natural samples. The development of Feature E in $\alpha$-$\text{Cr}_2\text{O}_3$ was rather specific to eskolaite. The similarity in line shapes of SYNC60 synthetic and GMMSB natural samples suggested the possibility of them having equal contents of Cr-Cr pairs which influenced their line shapes accordingly.

The photoluminescence of Cr was not correlated to Cr content in $\alpha$-$\text{Al}_2\text{O}_3$ in a simple manner. The intensity ratios of the N₂ and the sideband S of R₁ and R₂ correlated almost linearly with Cr₂O₃ contents [8]. The linear relation was fitted and used as the Cr-Cr content calibration in this study. The PL spectrum of Cr in $\alpha$-$\text{Al}_2\text{O}_3$ was measured and demonstrated in figure 2(a). The intensity ratio of N₂/S versus Cr-Cr contents were plotted as shown in figure 2(b). This suggested that, for synthetic $\alpha$-$\text{Al}_2\text{O}_3$ samples, the higher the Cr concentration, the greater number of Cr-Cr pairs.

However, for natural samples, this may also depend on the geological environments, e.g., high concentration of Ti in this case. GMMSB with less Cr content compared to GMMSA (shown in table...
1) exhibited more Cr-Cr pairs as shown in figure 1(b). Unsurprisingly, GMMSA with more Cr concentration consisted of less Cr-Cr pairs.

Figure 2. (a) Photoluminescence spectrum of an $\alpha$-Al$_2$O$_3$ and their magnified N-lines and sidebands, and (b) a plot of intensity ratios of N$_2$-line (701.37 nm) and its sideband S (713.19 nm) of the synthetic (open circles) and natural samples (open stars) showing linear correlation.

4. Conclusion

Different contents of Cr in synthetic and natural $\alpha$-Al$_2$O$_3$ were studied by XANES. The spectra line shapes suggested the transition from $\alpha$-Al$_2$O$_3$:Cr$^{3+}$ to $\alpha$-Al$_2$O$_3$:Cr$^{3+}$,Cr$^{3+}$ and $\alpha$-Cr$_2$O$_3$ with respect to the increase in Cr-Cr contents. XANES spectra of synthetic and natural $\alpha$-Al$_2$O$_3$ (Mong Hsu ruby, Myanmar) samples differed significantly because of the different variations of Cr$^{3+}$ local environments. Trace element contents were measured by LA-ICP-MS prior to the XANES measurements. The Cr-Cr coupling corresponded to the Cr content was confirmed by intensity ratios of R- and N- lines of photoluminescence spectra.

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