**Title**
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Local Structure of Transition Elements (V, Cr, Mn, Fe and Zn) in Al$_2$SiO$_5$ Polymorphs

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Abstract. We measured XAFS spectra near the Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn K-edges in Al$_2$SiO$_5$ polymorphs to reveal the local structure around these elements in the minerals. XANES spectra show that the valence of Fe and Cr is different depending on the crystal structure and formation environments. The spectra of kyanite, a high pressure mineral, shift to high energy side. The Fe-O bond length of kyanite determined by EXAFS data analyses is the shortest of all samples.

Keywords: Andalusite, sillimanite, kyanite, transition element, mineral, XAFS

PACS: 78.70.Dm, 61.10.Ht, 92.20.Wx

INTRODUCTION

Al$_2$SiO$_5$ polymorphs are important rock forming minerals especially in metamorphic petrology, and are much studied minerals because of being index minerals of metamorphic rocks. The crystal structure of Al$_2$SiO$_5$ polymorphs depends on temperature and pressure. Sillimanite and kyanite are formed at higher temperature and higher pressure, respectively. These minerals have two Al sites and one Si site. All three polymorphs have one Al in six-coordination and one Si in four-coordination. The coordination of the remaining Al is four in sillimanite, five in andalusite, and six in kyanite. This is the principal difference in their crystal structures. It is necessary to obtain information about the occupying site and bonding state of guest transition elements, which determine the color and physical properties. Optical and Mössbauer spectroscopy measurements have been carried out on transition elements in natural and synthetic Al$_2$SiO$_5$ minerals [1-3]. In this study, XAFS spectroscopy has been applied to natural samples in order to directly investigate the local structure around transition elements in Al$_2$SiO$_5$ minerals.

EXPERIMENTAL

Samples studied are 1) andalusite from Itinga, Brazil, 2) andalusite form Minas Gerais, Brazil, 3) manganese andalusite (viridine) from Sweden, 4) kyanite from Bahia, Brazil and 5) sillimanite from Pella District, South Africa. These specimens were characterized by polarization microscope, EPMA and X-ray powder diffraction analyses.

XAFS spectra near the Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn K-edges were measured in fluorescence mode using Lytle-type and 19-element SSD detectors at BL7C and BL9C of the Photon Factory at KEK, Tsukuba, Japan. The X-ray beam was monochromatized using the Si(111) reflection. Mirrors were used to eliminate higher harmonics. Some minerals containing transition elements such as chromite, palenzoanlite, manganite and hematite, etc. were measured as reference materials.

The EXAFS interference function was extracted from the measured absorption spectra and was normalized using MacMaster coefficients according to the EXAFS workshop report [4]. The radial structure function was obtained by the Fourier transform over the k range of 3.0-12.0 Å$^{-1}$. In parameter fitting, we carried out the Fourier-filtering technique and a nonlinear least squares fitting method by comparing the observed and calculated EXAFS interference.
function. The XAFS93 programs were employed for the data analysis [5].

RESULT AND DISCUSSION

The elements which were detected in these samples are summarized in Table 1. Iron and zinc were detected in all minerals. Chromium was found in all minerals except for viridine. Manganese was detected only in viridine. No cobalt, nickel and copper were found in any sample. In comparison with the analytical values reported by Chinner et al. [6] and Abs-Wurmbach et al. [3], these samples have the same order of Fe content and lower Cr content. Andalusite from Intiga has comparatively higher contents of Fe. These samples have typical transition element contents, except for viridine, which is a Mn-rich mineral.

<table>
<thead>
<tr>
<th>Element</th>
<th>Andalusite Intiga</th>
<th>Andalusite Jenipapo</th>
<th>Viridine</th>
<th>Sillimanite</th>
<th>Kyanite</th>
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</thead>
<tbody>
<tr>
<td>Ti</td>
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<td>V</td>
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<td>Cr</td>
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<td>Co</td>
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<td>Cu</td>
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<td>Zn</td>
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</tbody>
</table>

TABLE 1: Qualitative comparison of detected transition element content. Filled circle represents > 1.0 wt%, open circle > 0.1 wt%, triangle > 0.01 wt%. Dot means that minor amounts were detected, and bar means that no element was detected.

X-ray absorption near-edge structure (XANES) spectra are quite sensitive to the three-dimensional atomic configuration around X-ray absorbing atoms, and they are useful to determine the oxidation state and local environments in host minerals. Fe and Cr K-edge XANES spectra are shown in Figs. 1 and 2. The Fe and Cr K-edge XANES spectra change significantly with different polymorphs. The different XANES spectra and threshold energies show the different valence state of the transition metal elements and the local structure of the occupying sites in each polymorph.

In Fig. 1, the Fe K-edge threshold energy of andalusite and viridine hardly changes from that of Fe$_2$O$_3$ hematite. This indicates that Fe in andalusite and viridine is trivalent. The peak maximum of the XANES spectrum for sillimanite shifts to higher energy as compared to andalusite. In addition, that for kyanite shifts significantly from sillimanite to the high energy side. Figure 3 shows first-derivatives of Fe K-edge XANES spectra of for Fe$_2$O$_3$ hematite and kyanite. The valence of iron in kyanite could coexist as trivalent and tetravalent iron ions. The peak position of Fe K-edge XANES spectra for kyanite (Fig. 1) can be compared to those for SrFeO$_{3.5}$ perovskite type compounds with tetravalent iron ions [7]. The existence of tetravalent iron ions as guest element was predicted by the optical analysis of blue sapphire.

In Fig. 2, the peaks of the Cr K-edge XANES spectra for both andalusites shift from FeCr$_2$O$_4$ chromite to the low energy side. In contrast, the peak of kyanite moves from the peak of chromite to the high energy side. The peak of sillimanite is near equal to chromite. We had estimated by the threshold energy that the average valence of chromium in sillimanite and chromite are equal, those in two andalusites are smaller and that in kyanite is larger than chromite. From the above-mentioned, the oxidation states and effective charges of transition elements in kyanite are higher than those in andalusite and sillimanite.

From the comparison of XANES patterns, all elements observed in kyanite shift to the higher energy side. Oxidation states and effective charges of transition elements in kyanite are higher than those in andalusite.
FIGURE 2. Cr K-edge XANES spectra of various Al$_2$SiC$_x$ polymorphs.

FIGURE 3. First-derivative of the Fe K-edge XANES spectra for Fe$_2$O$_3$ hematite and kyanite.

TABLE 2. Cation-oxygen bond lengths in Al$_2$SiO$_5$ polymorphs.

<table>
<thead>
<tr>
<th>Cation-oxygen bond</th>
<th>Sillimanite</th>
<th>Andalusite</th>
<th>Andalusite Josipina</th>
<th>sillimanite</th>
<th>Kyanite</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond length (Å)</td>
<td>2.006(2)</td>
<td>1.962(9)</td>
<td>1.94(2)</td>
<td>1.865(7)</td>
<td></td>
</tr>
</tbody>
</table>

Analytical EXAFS oscillations were observed for Fe K-edge EXAFS spectra in all samples. Fe-O distances obtained from least-squares fits to Fourier filtered EXAFS spectra are shown in Table 2. Figure 4 shows the Fourier-filtered spectra and least squares fits for the Fe-O bond in kyanite. The Fe-O distance in sillimanite is the longest and in kyanite the shortest. The Fe-O bond length [2.006(2) Å] in sillimanite compares with the calculated value [2.025 Å] from Shannon's ionic radii of Fe$^{3+}$ and O$^{2-}$. Fe occupies octahedral and trigonal-bipyramidal (five-coordination) sites in andalusite. The Fe-O bond distance in kyanite is relatively shorter than in andalusite and sillimanite. The Fe-O distances in the octahedral sites of CaFeO$_5$$_8$ perovskite-type compounds with tetravalent iron ions is 1.89 Å [8]. This indicates that the guest elements in kyanite have higher-valent states, because kyanite had been formed in high pressure and high oxidized conditions.

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REFERENCES