

Quantitative determination of Al/Si-order parameter in sillimanite from micrometric region using HARECXS method

*Yohei Igami¹, Takahiro Kuribayashi², Akira Miyake¹

1. Graduate School of Science, Kyoto University, 2. Graduate School of Science, Tohoku University

Sillimanite is one of the polymorphs of Al_2SiO_5 which are valuable as indicators of pressure and temperature. Structure of sillimanite consists of AlO_6 octahedral chains and Si/AlO_4 tetrahedral double chains parallel to the *c*-axis. Although the tetrahedral Si/Al ions are normally ordered, a possibility of its disordering at high temperatures has been suggested (e.g. Zen, 1969). However, the Al/Si-order parameter of sillimanite has not been successfully quantified. The main problems are that one is the difficulty of separating mullite ($\text{Al}_2[\text{Al}_{2+2x}\text{Si}_{2-2x}]\text{O}_{10-x}$, $x \approx 0.17-0.59$) from sillimanite, because mullite is very similar to sillimanite crystallographically, and another is the difficulty to distinguish Al from Si using XRD experiments because of similarity of their X-ray scattering factor.

On the other hand, Atom location by channeling-enhanced microanalysis (ALCHEMI) using TEM-EDS was carried out for determination of Al/Si-order parameter in orthoclase by Taftø & Buseck (1983). By ALCHEMI, it can distinguish the elements with similar atomic number, e.g. Al and Si, and it can be quantified the Al/Si-order parameter from the only sillimanite micrometric region. Furthermore, HARECXS (High Angular Resolution Electron Channeling X-ray Spectroscopy), which was developed from ALCHEMI recently (e.g. Soeda, 2000; Yasuda *et al.*, 2006), provides more quantitative information, because of many EDS measurements by varying the direction of incident electron beam. In this study, therefore, HARECXS experiments were carried out on sillimanite to establish the determination procedure for the Al/Si-order parameter in sillimanite.

Sillimanite crystals in Rundvågshetta, East Antarctica, which are homogeneous without characteristic textures, were examined using TEM-EDS (JEOL JEM-2100F, JED-2300T). HARECXS profiles were obtained by collecting X-ray signals as a function of electron-beam direction. The Al/Si-order parameter was determined by comparison between the obtained HARECX profiles and simulated HARECXS profiles by program ICSC (Oxley & Allen, 2003). Additionally, CBED (convergent-beam electron diffraction) patterns were also obtained to estimate sample thickness. Moreover, single crystal X-ray diffraction experiment using an automated four-circle X-ray diffractometer (Rigaku, AFC-7S, Tohoku Univ.) with $\text{MoK}\alpha$ Radiation ($\lambda = 0.71069 \text{ \AA}$) was also carried out in order to evaluate the result obtained by HARECXS.

As the result, the HARECXS profiles were successfully obtained from $1.5 \mu\text{m}$ diameter region. For quantitative analysis, two types of profiles were simulated; a profile of ordered sillimanite and that of disordered sillimanite, using the sample thickness determined by CBED. The experimental profiles were successfully fitted to linear combination of the two simulated profiles, and Al/Si-order parameter was determined. The determined results of 18 measurements were converged around 0.80 regardless of sample thickness. However, single crystal XRD experiment showed the Al/Si-O bond distances corresponding to the Al/Si-order parameter of 0.88. The discrepancy are thought to be caused by estimation error of absorption coefficient of incident electron for sillimanite which is one of the simulation parameter to affect the HARECXS simulation. It suggests that the additional absorption should be required for more precise simulation.

The above analytical procedure was also successfully applied to experimentally heat-treated sillimanite, avoiding mullite or glasses formed by heat-treatment. Furthermore, the HARECXS method can also apply to various other minerals to determine site occupancies and estimate formation environment.

Keywords: ALCHEMI, HARECXS, sillimanite, order parameter, TEM