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Determination of Al/Si order in sillimanite by high angular resolution electron channeling X-ray spectroscopy, and implications for determining peak temperatures of sillimanite

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Abstract

Sillimanite is a polymorph of Al_2SiO_5 that is widely used as an indicator of pressures and temperatures reached during metamorphism. The degree of disorder in the double chains of SiO_4 and AlO_4 tetrahedra in sillimanite, particularly at high temperatures, is of interest as a factor in the phase relations of the Al_2SiO_5 polymorphs. We determined the Al/Si order parameter (Q) of sillimanite from Rundvågshetta, Antarctica, by the high angular resolution electron channeling X-ray spectroscopy (HARECXS) method using transmission electron microscopy with energy-dispersive X-ray spectrometry. HARECXS profiles were successfully obtained from regions ~1 μm in diameter by automated control of beam tilting and X-ray detection. The obtained Q value was close to that previously estimated by single-crystal X-ray diffraction. Moreover, the Q values of annealed samples were obtained while avoiding interference from mullite or SiO_2-rich glass domains formed by annealing. For quantitative determination of Q, we also performed theoretical calculations of HARECXS profiles and evaluated sample thicknesses by convergent-beam electron diffraction. The experimentally obtained profiles were successfully fitted by a linear combination of simulated profiles of completely ordered and completely disordered sillimanite, which yielded Q values. The Q values obtained from 18 measurements showed no effect from differing sample thicknesses. Moreover, the results from annealed samples showed that Q decreases continuously with increasing annealing temperature. The temperature dependence of Q values, formulated by least-squares fitting on the basis of the Bragg-Williams approximation, yielded a transition temperature from order to disorder at 1727 °C. The obtained curve is more accurate at high temperatures than previous estimates. It indicates that the sample material reached peak temperatures greater than ~1000 °C, which is close to previous estimates of the peak metamorphic temperature of Rundvågshetta sillimanite. This study also implies that the HARECXS method is suitable for accurate analyses of other natural samples with complicated microtextures.

Keywords: ALCHEMI, HARECXS, transmission electron microscope, sillimanite, Al/Si-disordering