High-Temperature Structural Change of Sillimanite and its Phase Relation with Mullite

We conducted high angular resolution powder X-ray diffraction experiments for sillimanite (Al_2SiO_5) heated at various temperatures and pressures in order to clarify its high-temperature phase relation with mullite ($Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$). The results showed that sillimanite discontinuously transforms to mullite in composition by high-temperature annealing, and the cell parameters of remnant sillimanites indicated that tetrahedral Al and Si in sillimanite become continuously disordered as the annealing temperature is increased. Based on the results, we proposed a new *P*–*T* diagram of the Al_2SiO_5 system for geological applications.

Sillimanite (Al_2SiO_5) is a mineral of special significance to geologists as an indicator of high-temperature metamorphism. In addition, some studies reported that sillimanite annealed above ~1000°C shows a characteristic of further transformation related to mullite ($Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$, where x = 0.17–0.59 [1]), which is an important refractory mineral in material science, associated with SiO_2-rich melt [2, 3]. However, the detailed phase relation between them had remained unclear, mainly due to the difficulty of discriminating between sillimanite and mullite in crystallography. These two minerals have the same basic framework characterized by chains of edge-sharing AlO_6 octahedra linked to double SiO_4/AlO_4 tetrahedral chains parallel to the *c*-axis. The crystal structure of mullite differs from that of sillimanite only by the disordered distribution of Al and Si in the tetrahedra and the existence of an additional tetrahedral site which is coupled to the occurrence of oxygen vacancies [Fig. 1(a)] [4]. Here, we conducted X-ray diffraction experiments using a synchrotron X-ray and a high-resolution multiple-detector system at the BL-4B2 beamline [5], for sillimanites annealed under various *P*–*T* (pressure and temperature) conditions to clarify the detailed phase relation between the two phases [6]. Samples were previously annealed at the temperature of 790–1530°C under the pressure of 1 atm–2.5 GPa for 1–1711 h. For the sample annealing, we used a muffle furnace (1 atm), an internally heated pressure vessel (0.2 GPa), or a piston-cylinder apparatus (0.5–2.5 GPa). The XRD experiments were performed at room temperature.

Figure 1(b) shows representative XRD patterns obtained in this study. We successfully distinguished peaks of newly formed mullite and remnant sillimanite. The present XRD system could surely detect 1% mullite mixed with sillimanite in mass. This made it possible to detect the initiation of the very sluggish transformation from sillimanite to mullite (mullitization) which was discontinuous in composition and to obtain accurate cell parameters of each phase. Figure 2(a) shows the determined cell parameters of mullite and sillimanite in the products against annealing temperature (the *c* axis of mullite is treated as twice the length to simplify the comparison with sillimanite). We detected the changes of cell parameters of remnant sillimanite caused by high-temperature annealing. In particular, the *b* axis shows the most marked expansion, although the cell parameter that differs most between sillimanite and mullite is the *a* axis. This indicates that some structural change other than mullitization occurs in sillimanite. We investigated the same samples also by analytical electron microscope and revealed that the degree of order of tetrahedral Al and Si in sillimanite, *Q*, decreases continuously as the annealing temperature increases [7]. *Q* is the value given by $Q = 2p - 1$ in the case of stoichiometric sillimanite, where *p* is the probability of finding an Al (Si) atom on an Al (Si) site, and thus *Q* varies from 1 for total order to 0 for total disorder. The abnormal changes in the *b* axis detected in this study are attributed to the decreasing value of *Q* [6, 7].

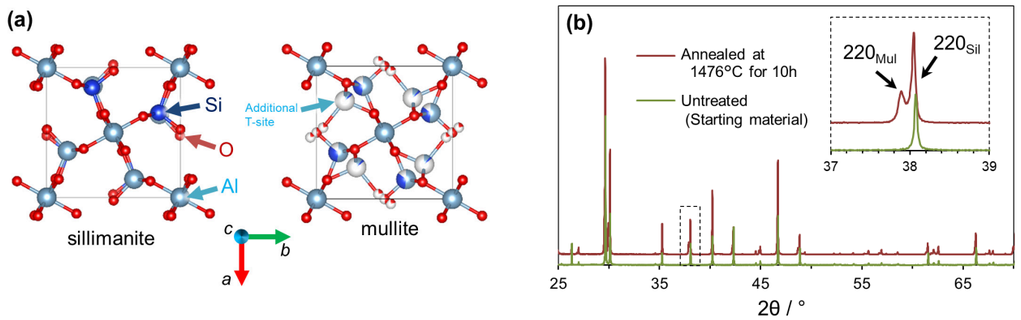

Figure 1: (a) Crystal structure of sillimanite and that of mullite (averaged structure). **(b)** XRD patterns of untreated sillimanite (starting material) and sample annealed at 1476°C for 10 h in air. The wavelength of the X-ray beam is 1.747 Å.

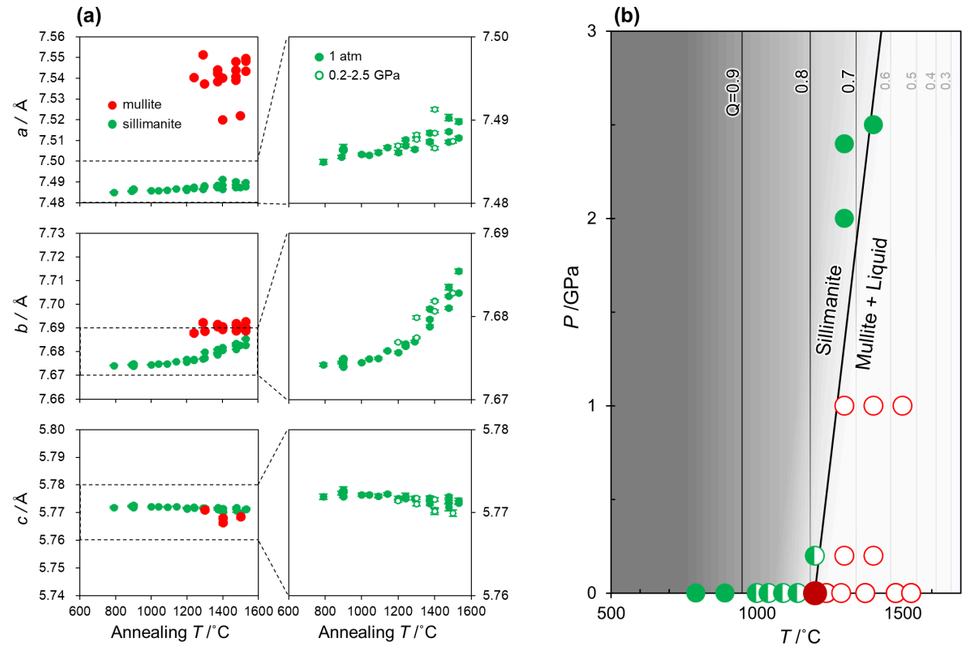

Figure 2: (a) Cell parameters of sillimanite and mullite against annealing temperature. The *c* axis of mullite is treated as twice the length to simplify the comparison with sillimanite. **(b)** *P*–*T* diagram of Al_2SiO_5 with the results of this study. The mullitization boundary and the contour of *Q* value of sillimanite determined by [7] are also shown. In the stability region of mullite + liquid, the *Q* values are shown for metastable sillimanite. Red open circles indicate that mullite is present, and green filled circles indicate that it is absent. Half-filled circles indicate that the presence of mullite is slight or unclear. The mullitization temperature at 1 atm (1200°C) determined by reaction kinetics analysis [8] is plotted by a red filled circle.

In contrast to the annealing temperature, the annealing pressure does not significantly affect the changes in cell parameters. The right panels of Fig. 2(a) show that the cell parameters of the sillimanite annealed at 0.2–2.5 GPa change with annealing temperature similarly to those of the sillimanite annealed at 1 atm. The degree of Al/Si order in sillimanite (*Q*) is almost independent of the imposed pressure.

We plotted the experimental results of this study on a *P*–*T* diagram for the Al_2SiO_5 system [Fig. 2(b)]. We also plotted the mullitization temperature of 1200°C at 1 atm, determined by [8] (a red filled circle). Based on the results, we estimated the mullitization boundary as shown in Fig. 2(b) [6]. In the figure, the contour of the *Q* value in sillimanite is also shown, which is a function of temperature [7] but is independent of pressure. This *P*–*T* diagram implies the existence of a phase with a stoichiometric Al_2SiO_5 composition and completely disordered Al and Si at above ~1700°C. However, it is difficult to observe this hypothetical phase because mullitization immediately and completely occurs at these high temperatures.

The high angular resolution XRD method in this study can be applied to the investigation of crystallographic features and the presence of fine mullites for natural sillimanite, and future studies in combination with the proposed *P*–*T* diagram [Fig. 2(b)] should yield new information about thermal histories in ultrahigh-temperature metamorphic regions above 1000°C that is easily lost.

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