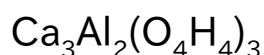


The effect of silicon incorporation on the crystal structure of katoite



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Single crystals of katoite $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{H}_4\text{O}_4)_x$ were hydrothermally synthesized from a mixture of CaO, metal Al, and amorphous SiO_2 with a molar ratio of 3:1:1 at 250 °C for 4 days. Single crystals of approximately 20 mm in diameter exhibit a rhombic dodecahedron habit with well-developed 12 equivalent {1 1 0} crystal faces. The crystal structures of katoite have been investigated by single-crystal x-ray diffraction method, electron microprobe analysis, and Raman spectroscopic technique. The crystal structures of katoite obtained have cubic space group $Im\bar{3}d$ with $a = 12.490(4)$ Å, $V = 1948.4(2)$ Å³, and with $a = 12.546(3)$ Å, $V = 1974.8(2)$ Å³, respectively. The full matrix least-squares refinements of these katoites converged to $R1 = 0.030$, $wR2 = 0.090$ for 176 unique reflections and $R1 = 0.032$, $wR2 = 0.095$ for 160 unique reflections. The chemical formula refined from the site occupancy parameters of Si were $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{4/0.26(2)}(\text{OH})_{10.96(2)}$ and $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{4/0.17(3)}(\text{OH})_{11.32(3)}$, respectively. The EPMA data for these katoites supported the incorporation of Si into the structures and showed a deficiency of Ca in the dodecahedral site. The volumes of tetrahedral site were decreased with the Si incorporation into the tetrahedral site. Since one edge of the tetrahedra is shared with an adjacent dodecahedron, the volumes of CaO_6 dodecahedra were also decreased with the Si incorporation. The resulting contractions of the coordination polyhedra led to the decrease of unit cell volume. The coordination volumes of the tetrahedra and dodecahedra lie on the straight line between grossular and hydrogrossular. The coordination volumes and rotation of AlO_6 octahedra, on the other hand, almost remained unchanged with the Si incorporation. The OH stretching of the Raman spectrum was slightly shifted to lower energy compared to that in the hydrogrossular, which is ascribed to the weakening of the hydrogen bonding interactions.

Keywords: katoite, hydrogrossular, single-crystal x-ray diffraction, EPMA, Raman spectroscopy