Crystal-chemical investigation of kalsilite from San Venanzo, Italy, using single-crystal X-ray diffraction and Raman spectroscopy

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Kalsilite, $KAlSiO_4$, is an end-member of the ternary system, $NaAlSiO_4$ (nepheline)-$KAlSiO_4$-SiO_2, which includes many important rock-forming minerals. Previous studies have provided several space groups for kalsilite: $P6_322$ [1], $P6_3$ [2], $P6_3mc$ [3], and $P31c$ [4]. In this study, a natural kalsilite, $(K_{0.92}Na_{0.07})(Al_{0.93}Fe^{3+}_{0.04}Si_{1.03})O_4$, from San Venanzo, Italy, was investigated with a Bruker X8 Apex CCD single-crystal X-ray diffractometer. The crystal is hexagonal with a=5.1589(2), c=8.6682(3) Å, and V=199.79 (13) $Å^3$. Weak diffuse scattering was observed along some strong reflections, but no twinning was detected. Observed systematic absences suggest possible space group $P6_3$ or $P6_322$, but the intensity data point to $P6_322$. The structure refinements based on $P6_322$ symmetry (25 variables, 585 reflections) with SHELX97 produced an R_1 factor of 0.0260, compared to that of 0.0271 based on $P6_3$ (43 variables, 1057 reflections). This study provides the first substantiated structure of kalsilite with its originally reported symmetry $P6_322$.

The $P6_322$ structure of kalsilite is characterized by the disordering of both O1 and O2 atoms, with O1 on the 6*h* (1/3 occupancy) and O2 on the 12*i* (1/2 occupancy) positions, as a consequence of the rigid-body motion of the $(Si,Al)O_4$ group. While the small amount of Na occupies a site that is ~0.3 Å away from the K position, the Al and Si atoms occupy the same 4*f* site. This observation agrees with the measured Raman spectrum, which exhibits a single strong Si-O-Si stretching peak at ~350 cm^{-1}.

References

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