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Wakabayashilite, $[(As,Sb)_6S_9][As_4S_5]$: Crystal structure, pseudosymmetry, twinning, and revised chemical formula

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Abstract

The crystal structure of the rare mineral wakabayashilite was solved by direct methods using intensity data collected from a twinned crystal. This study revealed that, in spite of the strong hexagonal pseudosymmetry, the structure is orthorhombic (space group $Pna2_1$) with $a_o = 25.262(1)$, $b_o = 14.563(1)$, $c_o = 6.492(1)$ Å, and $V_o = 2388.4(2)$ Å^3. The refinement of an anisotropic model led to an R index of 6.08% for 3135 observed reflections [$F_o > 4\sigma(F_o)$] and 8.71% for all 4260 independent reflections. Wakabayashilite is twinned by reticular merohedry [twin plane (110)]. There are two structural units in the structure: (1) $[M_6S_9]$ bundle-like chains running along the [001] axis, consisting of corner-sharing MS_3 trigonal pyramids (M = As, Sb), and (2) rods of As_4S_5 cage-like molecules, located in the space between three bundles and held together by van der Waals forces. The crystal chemical formula was therefore revised according to the structural results, yielding $[(As,Sb)_6S_9][As_4S_5]$ ($Z = 4$). Both the intramolecular As-S and As-As bond distances and those within the bundle-like units match closely the values commonly observed in the molecule-formed structures of other arsenic sulfides and those found in orpiment, respectively. To contribute to the understanding of the effects of light exposure on the structure of the arsenic sulfides, the crystal was exposed to filtered polychromatic light. The unit-cell parameters were measured after each exposure. The results showed that the As_4S_5 molecules do not undergo any transformations, as previously found by exposing uzonite to light.