

The crystal structure of TlAlSiO₄: The role of inert pairs in exclusion of Tl from silicate minerals

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ABSTRACT

Thallium aluminosilicate, TlAlSiO₄, synthesized hydrothermally is monoclinic with space group $P2_1/n$ [$a = 5.4095(3)$, $b = 9.4232(7)$, $c = 8.2629(6)$ Å, $\gamma = 90.01(2)^\circ$, $V = 421.20(6)$ Å³, $Z = 4$]. The crystal structure was refined to an R index of 3.8% based on 1852 observed unique reflections. The compound is a unique framework silicate with a topology similar to that of the tridymite structure. The TlO₈ polyhedron resembles a truncated rectangular pyramid, and shares its edges with three adjacent AlO₄ tetrahedra, three SiO₄ tetrahedra, and six TlO₈ polyhedra. Local understaturation at the Tl position suggested by bond-valence analysis implies that lone-pair electrons are present. The geometrical data indicate that the inert pair causes distortion of the Tl-polyhedron. Polyhedral distortion analysis using the software IVTON places the lone-pair parallel to [010], pointing to the largest base of Tl polyhedron. The rule in the valence shell electron pair repulsion model that a nonbonding pair occupies more space on the “surface” of the central atom than a bonding pair supports the orientation of inert-pair electrons in thallium provided by IVTON. The remarkable structure distortion caused by the inert-pair effect explains the rarity of Tl as a major element in silicate minerals because these cannot accommodate extremely distorted polyhedra. In contrast, about forty species of Tl-sulfide minerals exist because these structures are more flexible. Furthermore this effect probably explains why atoms such as Ge²⁺, Pb²⁺, Sn²⁺, Sb³⁺, and Bi³⁺, crystallize not as silicate phases but mainly as sulfide ones in nature.