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 P2₁/n [a = 5.4095(3), b = 9.4232(7), c = 8.2629(6) Å, γ = 90.01(2)°, 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 TlO₄ polyhedron resembles a truncated rectangular pyramid, and shares its edges with three adjacent AlO₄ tetrahedra, three SiO₄ tetrahedra, and six TlO₄ 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.

INTRODUCTION

The low content of thallium in the Earth’s crust and its geochemical similarity to potassium and rubidium promote dispersion of this element in endogenic rocks and ore formation (Mason 1966). Recent surveys on the production of subduction-related magmas (Noll et al. 1996) and the origin of Cu-Au porphyry deposits (Kamenetsky et al. 1999) reported efficient mobilization of thallium into arc magma source regions. However, thallium is sequestered in sulfide minerals, e.g., lorandite TlAsS₂, vrbaite Hg₃Tl₄Sb₂As₈S₂₀, and hutchinsonite (Pb,Tl)₂As₅S₉ (Clark 1993). The only silicate minerals containing major element concentrations of Tl are Tl-bearing ammonioleucites (Nishida et al. 1997) for which the crystal structure was determined by Rietveld refinements of synthetic TlAlSiO₄ (Krogh et al. 1991), and a thallium-leucite pseudomorph after analcime, TlAlSi₂O₆ (Kyono et al. 1999), which was identified by X-ray powder diffraction.

Even though Tl⁺ is similar to K⁺ and Rb⁺ in chemical properties and ionic size (Shannon 1976), the distinguishing characteristics of Tl depends on an inert-pair effect. The heavier members of Group 13 and 14 develop a valency two less than the normal valency, and distortion along one axis of the M-centered polyhedron often occurs due to the influence exerted by the lone pair (Cotton and Wilkinson 1988; Downs 1993). Large cations with stereochemically active lone-pair electrons (such as Tl⁺, Pb²⁺, Sn²⁺, and Bi³⁺) have received particular attention owing to their interesting structural features and physical properties (see Gillespie 1972; Moore and Araki 1976; Hawthorne and Groat 1986; Merlino et al. 1993; Cooper and Hawthorne 1995; Cooper et al. 1999 and references therein). The polyhedral distortions that result due to a ns² lone pair (n = 5, 6) of electrons in the valence shell of the central cation were discussed in detail by Gillespie (1972). Lone-pair effect in the coordination polyhedron in minerals has been studied for about Pb²⁺, Sb³⁺, and As³⁺ (e.g., Moore 1988; Moore and Araki 1976; Araki and Moore 1981). This paper determines the crystal structure of TlAlSiO₄ using single-crystal X-ray diffraction and examines if the inert-pair effect causes exclusion of thallium from silicate minerals.

EXPERIMENTAL METHODS

Standard cold-seal hydrothermal techniques were used to synthesize TlAlSiO₄ crystals. About 10 mg of low albite (Ab₈₈An₁₂) from Minas Gerais, Brazil was mixed with over 200 mg thallium nitrate and poured into a silver tube 20 mm long and 5 mm diameter). Distilled water was added to give a 70% filling ratio before sealing the tube. The silver tube was heated in an autoclave up to 500 °C for 14 days. Temperature was recorded with Pt/Pt13Rh thermocouples closely adjoining the sample position. Vapor pressure during the synthesis was estimated as 60 MPa. The experiments were stopped by allowing the autoclaves to gradually re-equilibrate to room temperature.

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