Natural kalsilite, KAlSiO₄, with P31c symmetry: Crystal structure and twinning

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Abstract

A new KAlSiO₄ polymorph was found in a granulite facies gneiss from the Punalur district, southern India. The structure was solved and refined on a twinned crystal to an R index value of 1.98% for 265 independent reflections. Metamorphic kalsilite is trigonal, space group P31c with a = 5.157 (1) Å, c = 8.706 (3) Å, V = 200.52 (9) Å³, Z = 2. The overall diffraction symmetry 6/mmm exhibited from all the crystals examined arises from a [0001] twinning, related to a mistake in the ordered Al-Si-Al-Si sequence along the c axis. The crystal structure is a stuffed derivative of tridymite, and is characterized by six-membered tetrahedral rings with ditrigonal shape. Individual layers of this structure are the same as those of P6₃, kalsilite, but are stacked along the c axis in an eclipsed manner rather than in the staggered manner of the P6₃ structure.

Introduction

At room temperature many structural modifications with a chemical formula close to KAlSiO₄ are known. All of them are tectosilicates, with structures consisting of layers of six-membered rings of Al and Si tetrahedra and K⁺ located in the large cavity. Three-dimensional connectivity is assured by apical O atoms of the tetrahedra that point up (U) and down (D) to link adjacent layers. At least three different framework topologies are known for the KAlSiO₄ phases. The high tridymite-like topology, characterized by UDUDUD rings, is found in natural and synthetic hexagonal kalsilite (Perrotta and Smith 1965; Dollase and Freeborn 1977), and in the structure of other related minerals like panunzite (Merlino et al. 1985) and trikalsilite (Bonaccorsi et al. 1988). A different framework topology is found in the structure of “O1-KAlSiO₄,” and is based on two different ring configurations, UUDUD and UUUDDD (Gregorkiewitz and Schäfer 1980). Finally, UUUDDD rings characterize the structure of the Icem KAlSiO₄ phase (Minor et al. 1978).

Kaliophilite is the other KAlSiO₄ phase that occurs in nature. Despite having a unit cell closely related to those of kalsilite, the evidence from conductivity and exchange experiments (Gregorkiewitz 1986) and thermal behavior (Cellai et al. 1992) suggests that it does not have a tridymite framework topology.

Natural kalsilite occurs mainly in K-rich, silica-under saturated volcanic rocks, but it is also found (rarely) in metamorphic rocks. The first structure refinement was carried out by Perrotta and Smith (1965) on a crystal of volcanic kalsilite with Na:K = 0.02:0.98 in the space group P6₃. In this structure, Al and Si are distributed orderly over alternating tetrahedra, and the six-membered rings are ditrigonally distorted with opposite rotations on adjacent layers so that the basal O atoms form a trigapped trigonal antiprism around the K ion. The apical O was found to be displaced by 0.25 Å from the threefold axis and therefore statistically distributed over three sites, giving Al-O-Si angles <180°. Synthetic kalsilite was produced from nepheline by ion exchange in molten KCl by Dollase and Freeborn (1977). At room temperature such crystals show intensities of the hhl, l = odd reflections different from crystal to crystal, with diffraction symmetry appearing to range continuously from that of space group P6₃, to P6₃mc. Dollase and Freeborn (1977) performed a structure refinement in space group P6₃mc, using a crystal with hhl, l = odd reflections absent. The structure is quite similar to that of natural kalsilite, but, in addition, the basal O atom was found to be disordered between two mirror-equivalent sites producing an average structure of symmetry P6₃mc that corresponds to the superposition of positive and negative ditrigonal distortions. According to Dollase and Freeborn (1977) this form can be considered as the average structure of (1120) mirror-related P6₃ domains. The domains are considered to be in a twin relationship, but with a size small enough to diffract X-rays coherently (hhl reflections systematically absent). A similar domain structure leading to apparent P6₃mc symmetry was also reported by Andou and Kawahara (1984) for synthetic kalsilite prepared by hydrothermal methods. By analogy with twinning in low quartz, Andou and Kawahara (1982) suggested that such a domain structure in kalsilite can be ascribed to the displacive high (P6₃mc) → low (P6₃) transition that they observed at 875 °C when the hhl, with l=odd reflections disappeared from their X-ray powder diffraction pattern. Later, Kawahara et al. (1987) determined the structure of the P6₃mc form using X-ray diffraction data collected from a crystal held at 950 °C. In addition, the same authors speculated on the existence of a disordered high kalsilite, with P6₃/mmc symmetry.