Low-temperature behavior of natural kalsilite with P31c symmetry: An in situ single-crystal X-ray diffraction study

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ABSTRACT

The low-temperature behavior of a natural kalsilite (ideal formula KAlSiO₄) with P31c symmetry has been investigated by in situ single-crystal X-ray diffraction. A series of intensity data collections and structural refinements have been performed at 298, 250, 200, 150, and 100 K on decreasing temperature, and 175, 225, and 275 K on increasing T. The variations of the unit-cell parameters of kalsilite as a function of T are continuous, and show no evidence of any phase transitions or thermo-elastic anomalies in this temperature range. An expansion is observed along [0001] with decreasing temperature. The axial and volume thermal expansion coefficients (α = V⁻¹∂V/∂T) between 298 and 100 K, calculated by weighted linear regression through the data points, are αₐ = 1.30(6)·10⁻⁵, αₐ = –1.5(1)·10⁻⁵, and αᵥ = 1.1(2)·10⁻⁵ K⁻¹. The main structural change on decreasing temperature is a cooperative anti-rotation of tetrahedra forming the six-membered rings lying parallel to (0001). This tetrahedral rotation is coupled with a change in the distances between the extra-framework cations and the framework O atoms. A small decrease in the tetrahedral tilts perpendicular to [0001] is responsible for the negative thermal expansion along [0001]; the implications of these mechanisms for thermal expansion in nephelines and kalsilites are discussed.

Keywords: Kalsilite, feldspathoids, low temperature, single-crystal X-ray diffraction, thermal expansion

INTRODUCTION

Kalsilite (ideal formula KAlSiO₄) is a framework silicate belonging to the “feldspathoid group.” Kalsilite occurs mainly in K-rich and silica-undersaturated volcanic rocks, probably as a result of the breakdown of silica-rich leucite in alkaline ultramafic rocks, and is usually associated with olivine, melilite, clinopyroxene, phlogopite, nepheline, and leucite. Kalsilite also occurs in metamorphic rocks.

The tetrahedral framework of kalsilite is isotypic (or homotopic) with tridymite and has topological symmetry P6₃/mmc, whereas the topochromic symmetry of kalsilite is P6₃mc as a result of Al/Si ordering within the tetrahedra (Gottardi 1979). The tetrahedral framework consists of (0001) sheets of (ordered) AlO₄ and SiO₄ tetrahedra forming six-membered rings (hereafter 6mR), pointing alternately up (U) and down (D) [i.e., 6mR//(0001)]. In the structural model described in space group P6₃mc as a result of Al/Si ordering within the tetrahedra (Gottardi 1979). The sheets are stacked along the c-axis and joined through the apical O1 atoms, which formally occupy special positions on the threefold axis. However, Perrotta and Smith (1965) found that this bridging oxygen is displaced by ~0.25 Å from the threefold axis, giving Al-O-Si bond angles <180°. The tetrahedral rings are also di-trigonomally distorted by rotation of the tetrahedra around [0001], with the sense of rotation reversed between adjacent (0001) sheets. A second set of 6-membered rings of tetrahedra occur perpendicular to (0001) [Fig. 1, hereafter 6mR⊥(0001)].

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Cellai et al. (1997) reported the crystal structure of essentially Na-free metamorphic kalsilite (i.e., K/Na molar ratio ~350). The authors showed that the structure has P31c symmetry. The crystals were ubiquitously twinned across (0001) so that hkl reflections of the first individual were superimposed on the hkl reflections from its twin. The structural model of P31c kalsilite shows an identical configuration of the tetrahedral sheets with those of the P6₃mc structure. However, the sheets are stacked in an eclipsed manner, with the same rotation of the 6mR//(0001) in succeeding sheets (Cellai et al. 1997) (Fig. 1). In the structural model described in space group P31c, the bridging oxygen between the sheets lies on the triad axis, giving an unusual Si-O-Al angle of 180°. The authors reported no experimental evidence for splitting of the bridging oxygen off the threefold axis, but a strong anisotropy of the thermal ellipsoid of the apical oxygen was observed, which is probably due to a static or dynamic disorder of the oxygen position, and the apparent inter-sheet Al-O-Si bond angle 180° is just an artifact of averaging.

A significant number of experiments has been devoted to the thermo-elastic behavior, high-temperature structural modification and phase-stability of kalsilite (Tuttle and Smith 1958; Sahama 1962a, 1962b; Henderson and Roux 1976, 1977; Dollase and Freeborn 1977; Gregorkiewitz and Schäfer 1980; Andou and Kawahara 1982, 1984; Henderson and Taylor 1982, 1988; Abbott 1984; Merlino 1984; Kawahara et al. 1987; Hovis and Roux 1993; Xu and Veblen 1996; Capobianco and Carpenter 1989; Carpenter and Cellai 1996; Cellai et al. 1999; Hovis and...