X-ray study of the trigonal → hexagonal phase transition in metamorphic kalsilite

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ABSTRACT

High-temperature annealing experiments on metamorphic kalsilite (KAlSiO₄) indicate that there is an irreversible phase transition from the P31c to P6₃, structure at ~200 °C. Powder X-ray investigations indicate that the transformation is incomplete. The proportion of P6₃ phase increases as a function of temperature, attaining 70% for the powdered sample at ~500 °C. At higher temperatures, the fraction of sample transforming to P6₃ phase seems to be independent of temperature, and probably depends on the structural state of the starting material as influenced by mechanical grinding. Transformation proceeds by tetrahedral rotation such that successive (001) sheets undergo opposite-sense rotations. The transition behavior differs for single crystals, which had not been mechanically ground; at 500 °C single crystals transformed completely into the P6₃ phase. Single-crystal structure refinements of the P6₃ phase indicate that the structure is similar to that of volcanic kalsilite. Both apical and basal O atoms show large anisotropic displacement parameters, but the displacement of the apical oxygen does not exhibit the trigonal distribution that has been observed in volcanic kalsilite. The more pronounced positional disorder in volcanic kalsilite is due to the presence of sodium.

INTRODUCTION

The rock-forming feldspathoid kalsilite (KAlSiO₄) occurs mainly in K-rich silica undersaturated volcanic rocks, and in metamorphic rocks. The first structure refinement by Perrotta and Smith (1965) on a crystal of volcanic kalsilite with Na:K ~0.02:0.98 gave the space group P6₃, (low kalsilite). The structure (Fig. 1) is characterized by AlO₄ and SiO₄ tetrahedra forming an ordered three dimensional framework which consists of six-membered rings of tetrahedra pointing alternately up (U) and down (D) (tridymite framework topology UDUDUD). All rings are ditrigonally distorted, and are stacked along the c direction, joined via the apical O atoms in a staggered configuration, which means that all ditrigonal rings in one sheet point in one direction and all the rings in the next sheet point in the opposite direction. The apical oxygen was found to be displaced by 0.25 Å from the threefold axis and appears to be randomly distributed among three sites, giving intersheet Al-O-Si bond angles <180°. However the X-ray refinement of Perrotta and Smith ended up with a large R value (R = 5.9%) which is not uncommon in the structures of the kalsilite-nepheline series (K,Na)AlSiO₄. Cellai et al. (1997) determined the crystal structure of Na-free metamorphic kalsilite on a twinned crystal. Their refinement converged to a final R-value of 1.98% and showed that the structure has P31c symmetry. A difference Fourier map did not show evidence for splitting of the apical oxygen position, and a model with the apical oxygen on the triad axis was therefore adopted. However, the strong anisotropy of the thermal ellipsoid of the apical oxygen could result from some kind of disorder (static or dynamic) of the oxygen, and the apparent intersheet Al-O-Si bond angle of 180° is probably not real. Individual sheets of P31c kalsilite are essentially the same as those of the P6₃ structure but are stacked in an eclipsed manner, so that ditrigonal rings in succeeding sheets point in the same directions. P31c kalsilite is isotypic with the P31c phase of KLiSO₄ (Bansal et al. 1980; Zhang et al. 1988; Rajagopal et al. 1991; Bhakay-Tamhane et al. 1985, 1991) and RbLiCrO₄ (Makarova et al. 1993). By studying the change in intensities of hhl reflections in metamorphic kalsilite, an irreversible structural phase transition involving the symmetry change P31c → P6₃ on heating from room temperature was proposed by Carpenter and Cellai (1996).

Synthetic kalsilite produced from nepheline by K-exchange (Dollase and Freeborn 1977) showed intensities of the hhl l = odd reflections differing from crystal to crystal. Dollase and Freeborn performed a structure refinement in space group P6₃mc using a crystal with hhl, l = odd reflections absent. Their structure is quite similar to P6₃ kalsilite; but, in addition, the basal O atoms are disordered between two mirror equivalent sites producing an average P6₃mc structure. They pointed out that (1120) mirror-related P6₃ domains generate overall P6₃mc symmetry. A similar domain structure was also reported for synthetic kalsilite prepared by hydrothermal methods (Andou and Kawahara 1984). Xu and Yebo (1996) found that kalsilite crystals prepared from nepheline by K-exchange are structurally complex, and, in particular, Na-poor and Na-free kalsilite crystals are composed of (0001) domains with P6₃ and P31c symmetries.