Phase transitions and microstructures in natural kaliophilite

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Abstract: An investigation using TEM, high temperature X-ray powder diffraction and high temperature single-crystal X-ray diffraction revealed previously unreported microstructures and phase transitions in natural kaliophilite. Measurements of unit cell dimensions from room temperature to 895°C indicate the existence of a displacive phase transition at ~725°C between two hexagonal phases with the same unit cell. A symmetry change of \( P6_322 \rightarrow P6_3 \) is tentatively suggested with the concomitant development of merohedral twins. Spontaneous strain determinations suggest that the transition is close to being tricritical in character. Above ~750°C kaliophilite crystals undergo a first order epitaxial phase transition to a different hexagonal phase with \( a = 8.9 \) Å and \( c = 8.4 \) Å. Dark and bright field images in the TEM show the presence of twins and heterogeneously distributed linear defects. These are interpreted respectively as transformation twins and stacking defects incorporated during crystal growth. The thermal evolution of kaliophilite is sufficiently different from that of kalsilite to indicate that it has a different framework topology and is not a true stuffed tridymite structure.

Key-words: kaliophilite, phase transitions, spontaneous strain, transmission electron microscopy, microstructures.

1. Introduction

The compound KAISiO₄ appears to occur in several modifications, (Table 1) two of which, kalsilite and kaliophilite, occur in nature. Kalsilite is found almost exclusively in K-rich silica undersatured volcanic rocks, while kaliophilite is known only from ejected blocks incorporated into pyroclastics. The type locality of kaliophilite is in biotite pyroxenite ejecta from Mt. Vesuvius (Bannister, 1931), but it has also been observed in ejecta belonging to different pyroclastic formations in the Alban Hills (Barbieri et al., 1970), where it is associated mainly with such minerals as clinopyroxene, garnet, melilitc, leucite, haüyne and latiumite. In the equilibrium phase diagram for NaAlSiO₄-KAlSiO₄ proposed by Tuttle & Smith (1958), natural kaliophilite with a large unit cell \((a = 27.01, c = 8.56 \) Å) is treated as a metastable phase at atmospheric pressure at all temperatures. Its relationships to the other phases are not clearly understood, however, and the occurrence of kaliophilite in ejected blocks does not preclude its having a true stability field at higher pressures. It may also be stabilised relative to kalsilite by solid solution toward nepheline.

The known phases of KAISiO₄ are all tectosilicates and are characterized by stacking of layers of six-membered rings of \([\text{AlO}_4]\) and \([\text{SiO}_4]\) tetrahedra, with \( \text{K}^+ \) in the framework cavities as the charge-balancing cation. These structural features produce unit-cell parameters which are related in

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