American Mineralogist, Volume 82, pages 1133–1140, 1997

Si-Al ordering in leucite group minerals and ion-exchanged analogues: An MAS NMR study

SIMON C. KOHN,[1,]* C. MICHAEL B. HENDERSON,[2] AND RAY DUPREE[1]

[1]Department of Physics, University of Warwick, Coventry, CV4 7AL, U.K.
[2]Department of Earth Sciences, University of Manchester, Manchester, M13 9PL, U.K.

ABSTRACT

Two series of leucite group materials, with K, Rb, and Cs as extra-framework cations, have been synthesized by ion exchange from a natural well-ordered analcite and a natural disordered leucite. ^{29}Si and ^{27}Al MAS NMR data for the analcite-derived series provide complementary information on tetrahedral cation ordering. The ordering in terms of the number of Al next-nearest neighbors, $Q^4(n\mathrm{Al})$ (short-range order), does not change significantly during ion exchange, indicating that Al and Si remain essentially fixed in their original positions. In contrast, the ordering of Al over T1, T2, and T3 (long-range order) for the analcite-derived series changes dramatically with changing alkali cation; the Al occupancies for the three analcite-derived samples expressed as T1:T2:T3 are approximately 0.25:0.50:0.25 for $KAlSi_2O_6$, 0.40:0.20:0.40 for $RbAlSi_2O_6$, and 0.15:0.70:0.15 for $CsAlSi_2O_6$. During the ion exchange, at temperatures above the cubic-tetragonal phase transitions, only one symmetrically distinct T site is present. It is proposed that on cooling through the cubic-tetragonal phase transition the structure collapses around the non-framework cations to give the lowest energy Si-Al distribution over the three T sites irrespective of the original T-site ordering in the starting material. Our data suggest that the identity of the cation in the W site affects the orientation of the framework distortions associated with the cubic-tetragonal phase transition and leads to the possibility that a particular tetrahedral cation site can take on the characteristics of a T1, T2, or T3 site. The data and their interpretation have important implications for the mechanism of this type of structural phase transition.