

X-ray diffraction and Raman spectroscopic study of clinopyroxenes with six-coordinated Si in the Na(Mg_{0.5}Si_{0.5})Si₂O₆-NaAlSi₂O₆ system

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ABSTRACT

Five clinopyroxenes containing various amounts of six-coordinated Si (^{vi}Si) in the Na(Mg_{0.5}Si_{0.5})Si₂O₆ (NaPx)-NaAlSi₂O₆ (jadeite) system have been synthesized at 15 GPa and 1600 °C and their structures studied with single-crystal X-ray diffraction and Raman spectroscopy. The results show that clinopyroxenes with ^{vi}Si ≤ 0.33 atoms per formula unit (apfu) possess *C2/c* symmetry, whereas those with ^{vi}Si ≥ 0.45 apfu crystallize with *P2/n* symmetry. There is an obvious discontinuity in the unit-cell parameters *a*, *β*, and *V* as the ^{vi}Si content increases from 0.33 to 0.45 apfu, suggesting that the *C2/c*-*P2/n* transition is first-order in character, rather than tricritical as reported for the transition from jadeite/diopside/augite to omphacite. The Mg and ^{vi}Si cations in the *P2/n* structure are completely ordered into two nonequivalent octahedral sites, M1 and M1(1), respectively, with M1 being appreciably more distorted than M1(1). With increasing mean <M1-O> distance, the mean tetrahedral <Si-O> distance increases, whereas the O3-O3-O3 angle of the tetrahedral chain decreases systematically, consistent with the structural variation trends found in the jadeite-diopside system. A comparison of the Raman spectra reveals that the *C2/c*-*P2/n* transition is characterized by the splitting of many Raman bands in *C2/c* clinopyroxenes into doublets in *P2/n*, and such splitting becomes more pronounced with increasing ^{vi}Si. For *C2/c* clinopyroxenes, all Raman bands become progressively broader with the increased substitution of (Si⁴⁺ + Mg²⁺) for Al³⁺. In addition, several new Raman bands, attributable to the presence of ^{vi}Si, are observed. Together with previous data, we suggest that the maximum ^{vi}Si content allowed for an Mg/Al dominated octahedral site is close to ~35%, above which ^{vi}Si and Mg/Al are likely to be ordered into distinct sites.

Keywords: Clinopyroxenes, six-coordinated silicon, X-ray structure refinement, Raman spectroscopy, phase transformation