

## **X-ray diffraction and Raman spectroscopic study of clinopyroxenes with six-coordinated Si in the $\text{Na}(\text{Mg}_{0.5}\text{Si}_{0.5})\text{Si}_2\text{O}_6\text{-NaAlSi}_2\text{O}_6$ system**

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### **ABSTRACT**

Five clinopyroxenes containing various amounts of six-coordinated Si (<sup>VI</sup>Si) in the  $\text{Na}(\text{Mg}_{0.5}\text{Si}_{0.5})\text{Si}_2\text{O}_6$  ( $\text{NaPx}$ )- $\text{NaAlSi}_2\text{O}_6$  (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 <sup>VI</sup>Si  $\leq$  0.33 atoms per formula unit (apfu) possess  $C2/c$  symmetry, whereas those with <sup>VI</sup>Si  $\geq$  0.45 apfu crystallize with  $P2/n$  symmetry. There is an obvious discontinuity in the unit-cell parameters  $a$ ,  $\beta$ , and  $V$  as the <sup>VI</sup>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 <sup>VI</sup>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  $\langle\text{M1-O}\rangle$  distance, the mean tetrahedral  $\langle\text{Si-O}\rangle$  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 <sup>VI</sup>Si. For  $C2/c$  clinopyroxenes, all Raman bands become progressively broader with the increased substitution of  $(\text{Si}^{4+} + \text{Mg}^{2+})$  for  $\text{Al}^{3+}$ . In addition, several new Raman bands, attributable to the presence of <sup>VI</sup>Si, are observed. Together with previous data, we suggest that the maximum <sup>VI</sup>Si content allowed for an Mg/Al dominated octahedral site is close to ~35%, above which <sup>VI</sup>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