High-pressure $P_2\overline{1}/c$-$C2/c$ phase transitions in clinopyroxenes: Influence of cation size and electronic structure

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**ABSTRACT**

The high-pressure behavior of the clinopyroxenes kanoite $\text{Mn}_n\text{Mg}_m\text{Si}_6\text{O}_{18}$, $\text{MnSiO}_3$, and $\text{CrMgSi}_2\text{O}_6$ (all space group $P_2\overline{1}/c$) was studied by single-crystal X-ray diffraction in a diamond-anvil cell at room temperature. Phase transitions from $P_2\overline{1}/c$ to $C2/c$ clinopyroxene were found and reversed at $5.06 \pm 0.14$ GPa for kanoite, $2.905 \pm 0.005$ GPa in $\text{MnSiO}_3$, and $3.60 \pm 0.03$ GPa in $\text{CrMgSi}_2\text{O}_6$. The phase transitions are first-order in character and are accompanied by a volume decrease of approximately 2.3%. The structure of high-pressure $C2/c$ kanoite was determined from single-crystal X-ray intensity data collected at 5.20 GPa, and is very similar to that of high-pressure (HP) $C2/c$-ferrosilite. Although the space group $C2/c$ is the same as for the high-temperature (HT) $C2/c$-ferrosilite, the two phases have significantly different structures. The silicate chains are extremely kinked in HP kanoite while they are almost straight in HT kanoite. Compared with the transition pressure of clinoenstatite-clinoferrosilite, the new data suggest that the effective ionic radii of M1 and M2 cations do not exclusively control the transition pressure and that the HP $C2/c$ clinopyroxenes with $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ gain additional stabilization energy from crystal field effects.

**INTRODUCTION**

Pyroxenes are major components in the Earth’s upper mantle. The stability of a $C2/c$ pyroxene polymorph at upper mantle pressures has been recently demonstrated by the combination of phase equilibria studies in the multi-anvil press (e.g., Pacalo and Gasparik 1990; Kanzaki 1991; Woodland and Angel 1997) with room-temperature X-ray diffraction (XRD) studies of clinopyroxene polymorphs in the diamond-anvil pressure cell (Angel et al. 1992; Hugh-Jones et al. 1994). The latter showed that, under compression, the low-clinopyroxene polymorphs of enstatite and ferrosilite (space group $P2_1/c$) undergo phase transitions to high-pressure clinopyroxene polymorphs with space group $C2/c$. In both enstatite ($\text{MgSiO}_3$) and ferrosilite ($\text{FeSiO}_3$) the transitions are first-order, reversible (although with hysteresis $2.5$ GPa in $\text{MgSiO}_3$), and displacive in character, but the pressure of the phase transitions are very different, approximately 6.5 GPa in $\text{MgSiO}_3$ and 1.7 GPa in $\text{FeSiO}_3$. The fact that the transition occurs at lower pressures in $\text{Fe}^{2+}$-bearing pyroxenes than in pure $\text{MgSiO}_3$ (Ross and Reynard 1998, unpublished data) implies that solution of Fe into enstatite will act to stabilize the $C2/c$ polymorph. However, the crystalchemical reasons for this stabilization have remained unclear until now.

The $P2_1/c$ to $C2/c$ symmetry change at high pressure also occurs upon heating clinoenstatite (Iishi and Kita-yama 1995), pigeonite (Smyth 1969; Smyth and Burnham 1972), clinoferrosilite (Sueno et al. 1984), and kanoite (Arlt and Armbruster 1997). But careful comparison of the structures of the HT and HP $C2/c$ polymorphs of ferrosilite suggests that they are different phases (Hugh-Jones et al. 1994). Kanoite, $\text{MnMgSi}_2\text{O}_6$, is of potential interest in this context because its transition temperature is much lower ($<250$ °C, Arlt and Armbruster 1997) than in the enstatite-ferrosilite clinopyroxenes and it therefore provides an opportunity to study the relationship between the high-temperature and high-pressure $C2/c$ forms at experimentally more tractable conditions.

To provide further insights into the crystal chemical factors influencing the structure and stability of the high-pressure $C2/c$ clinopyroxene phases and their relationship to the high-temperature forms, we have performed a single-crystal high-pressure diffraction study on kanoite, the $\text{Cr}^{2+}$-bearing pyroxene $\text{CrMgSi}_2\text{O}_6$, and $\text{MnSiO}_3$. 

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