

High-pressure behavior of Ca/Na clinopyroxenes: The effect of divalent and trivalent 3d-transition elements

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ABSTRACT

Two *C2/c* pyroxenes, CaMnSi₂O₆ and CaZnSi₂O₆, were investigated at high pressure by single-crystal X-ray diffraction. Their unit-cell parameters were determined at 9 different pressures up to 7.55 and 8.23 GPa, respectively. No evidence of phase transformations was found for either sample throughout the investigated pressure range. The pressure-volume data were fit using a third-order Birch-Murnaghan equation of state and it was possible to refine simultaneously the unit-cell volume V_0 , the bulk modulus K_{T0} and its first pressure derivative K' providing the following coefficients: $V_0 = 462.01(3) \text{ \AA}^3$, $K_{T0} = 97.3(4) \text{ GPa}$, $K' = 7.5(2)$ for CaMnSi₂O₆ and $V_0 = 444.79(2) \text{ \AA}^3$, $K_{T0} = 109.6(5) \text{ GPa}$, $K' = 7.0(2)$ for CaZnSi₂O₆. The substitution of Zn for Mn at the M1 crystallographic site causes a strong decrease of the bulk modulus (by about 11%). Intensity data were collected at several pressures for both samples. The main compression mechanism is related to the tetrahedral chain kinking and the consequent shortening of the Ca-O_{3_{long}} bond distances, which show a markedly larger decrease for the CaMnSi₂O₆ sample. Comparing the results obtained in this work with previous data for Ca/Na-bearing *C2/c* pyroxenes containing trivalent and divalent 3d-transition elements at M1 site, we identified two distinct compressibility trends: for a similar unit-cell volume at room pressure the pyroxenes with Na on M2 and trivalent cations on M1 are more compressible than those having Ca on M2 and divalent cations at the M1 site. The analysis of the structure evolution for all samples indicates that this is strongly correlated with the evolution of kinking of the tetrahedral chains and the shortening of the M2-O3 bonds.

Keywords: Pyroxenes, transition elements, high pressure, diffraction