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# High-pressure single-crystal X-ray diffraction and infrared spectroscopic studies of the $C2/m$-$P2_1/m$ phase transition in cummingtonite

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## ABSTRACT

The structural changes associated with the $C2/m$-$P2_1/m$ phase transition in cummingtonite with (Fe + Mn)/(Fe + Mn + Mg) $\approx$ 0.50 have been studied with single-crystal X-ray diffraction at various pressures up to 7.90 GPa and infrared spectroscopy up to 8.63 GPa. With increasing pressure, the crystal transforms from $C2/m$ to $P2_1/m$ symmetry at ~1.21 GPa, as determined by the appearance of reflections violating the $C2/m$ space group. Infrared spectra provide additional evidence for the phase transition: A distinct splitting of OH stretching bands results from an increase from one to two nonequivalent OH positions. The $C2/m$-$P2_1/m$ transition is of weakly displacive first-order or tricritical character with apparent slope changes in the plots of the axial ratios $a/b$ and $a/c$ as a function of pressure. The unit-cell compression is considerably anisotropic with the $a$ dimension in both $C2/m$ and $P2_1/m$ phases being the most compressible. Major structural changes for the $C2/m$-$P2_1/m$ transition include: (1) One crystallographically distinct silicate chain becomes two discontinuously, coupled by the splitting of the M4-O5 bond, as well as M4-O6, into two nonequivalent bonds, and (2) the M4-cation coordination increases from sixfold to sevenfold. More importantly, we observed a change in the sense of rotation for the A chain while the crystal structure maintains $P2_1/m$ symmetry: It is O rotated, as the B chain, at 1.32 GPa, but S-rotated at 2.97 GPa and higher pressures. As pressure increases from 1.32 to 7.90 GPa, there is a switching of the nearest bridging O atoms coordinated with the M4 cation: The M4-O5B distance contracts from 2.944 to 2.551 Å, whereas the M4-O6B distance increases from 2.754 to 2.903 Å. Compression mechanisms for the low- and high-pressure polymorphs appear to be slightly different. In the $C2/m$ phase, the behavior of the A and M4 sites controls the compression of the structure, whereas the response of the M1, M2, and M3 octahedra to pressure also plays a role in determining the compression of the $P2_1/m$ structure. The phase transition is regarded as primarily driven by the differential compression between the M4 and T sites, and the symmetry breaking provides a necessary tighter coordination for the M4 site. Based on our data, the obvious changes in the hyperfine parameters of $^{57}$Fe in grunerite between 1.0 and 3.4 GPa, observed by Zhang and Hafner (1992), are likely to result from the $C2/m$-$P2_1/m$ structural transformation.