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A new pyroxene structure at high pressure: Single-crystal X-ray and Raman study of the *Pbcn*-$P2_1cn$ phase transition in protopyroxene

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ABSTRACT

The crystal structure of $(Mg_{1.54}Li_{0.23}Sc_{0.23})Si_2O_6$ protopyroxene has been studied with single-crystal X-ray diffraction at pressures to 9.98 GPa and Raman spectroscopy to 10.4 GPa. A first-order displacive phase transformation from the *Pbcn* space group to $P2_1cn$ was observed between 2.03 and 2.50 GPa, which is characterized by a discontinuous decrease in *a*, *c*, and *V* by 1.1, 2.4, and 2.6%, respectively, and an increase in *b* by 0.9%, along with appearance of intensities of some 0*kl* reflections with $k \neq 2n$. This is the first substantiated example of protopyroxene having the symmetry predicted by Thompson (1970). Evidence for the phase transition from Raman spectroscopy is also presented. The prominent structural changes associated with the *Pbcn*-to-$P2_1cn$ transformation involve the abrupt splitting of one type of O-rotated silicate chain in low-pressure protopyroxene into S-rotated A and O-rotated B chains in high-pressure protopyroxene, coupled with a marked decrease in the O3-O3-O3 angles and a re-configuration of O atoms around the M2 site. The kinking angle of the silicate chain in the low-pressure phase at 2.03 GPa is 165.9°, whereas the angles are 147.9° and 153.9° for the A and B chains, respectively, in high-pressure phase at 2.50 GPa. Strikingly, the two types of silicate chains in the $P2_1cn$ structure alternate along the *b* axis in a tetrahedral layer parallel to (100). Such a mixed arrangement of two differently rotated silicate chains in a tetrahedral layer has not been observed in any other pyroxene structure. Compression anisotropy of the protopyroxene structure is affected by the phase transition. The relative linear compressibilities (β_a:β_b:β_c) are 1.00:1.72:0.99 for low-pressure protopyroxene, but are 1.00:1.28:1.65 for high-pressure protopyroxene. The bulk moduli of low- and high-pressure phases are 130(3) and 111(1) GPa, respectively. This study concludes that the *Pbcn*-to-$P2_1cn$ phase transition results from the differential compression between SiO_4 tetrahedra and MO_6 octahedra.