

The structure of (Ca,Co)CoSi₂O₆ pyroxenes and the Ca-M²⁺ substitution in (Ca,M²⁺)M²⁺Si₂O₆ pyroxenes (M²⁺ = Co, Fe, Mg)

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ABSTRACT

The crystal structure of three *C2/c* clinopyroxenes with composition (Ca_{0.8}Co_{0.2})CoSi₂O₆, (Ca_{0.6}Co_{0.4})CoSi₂O₆ and (Ca_{0.4}Co_{0.6})CoSi₂O₆ was refined down to $R_{4\sigma} = 2.6\%$ by single-crystal X-ray diffraction. The crystals were synthesized at $P = 3$ GPa by cooling from 1500 to 1200 °C in a piston-cylinder apparatus. At the end of the refinement cycles, electron density residuals (up to 2.1 e⁻) were observed close to the M2 site and related to the site splitting of Ca and Co in the M2 polyhedron in the two subsites M2 and M2'. Split refinement significantly improved the agreement factor and decreased the uncertainty in the atomic coordinates. Similar features were found in (Ca,Mg)MgSi₂O₆ and (Ca,Fe)FeSi₂O₆ intermediate pyroxenes.

The average structural changes related to the cation substitution at the M2 site in (Ca,Co)CoSi₂O₆, (Ca,Mg)MgSi₂O₆, and (Ca,Fe)FeSi₂O₆ pyroxenes are similar: the T tetrahedron becomes more regular, the difference between M1-O bond lengths increases, and the M2-O3 bond lengths with the furthestmost O3 oxygen atoms become longer. The changes in the M2-O bond distances are, however, not linear, and they are higher for more increased substitution. The largest structural deformation occurs on the (010) plane, with higher deformation at about 60° from the *c* axis for any composition. The orientation of the deformation ellipsoid is most related to a shift in tetrahedral chains. The scalar deformation for the cation substitution, ϵ_s , is linearly related to the cation radius of the average M2 site (IR^{M2}), i.e., the deformation is higher as the cation size decreases, following the equation: $\epsilon_s = -0.0072(12)IR^{M2} + 0.0082(13)$, $R^2 = 0.75$. Increasing deformation with cation substitution is supported as the major limiting factor for solid solution.

The displacement parameters for unsplit M2, O2, and O3 atoms increase up to the intermediate composition, indicating a local configuration for the M2 polyhedron centered by Ca and Co. However no significant change in U_{eq} of the O3 atom is observed up to 20% substitution of the smaller cation in the M2 site. Comparison with Raman spectral data suggests that local chain structural configurations occur only for the substitution of the smaller cation in the M2 site higher than 20%, and that the substitution mechanism is different for *C2/c* clinopyroxenes with lower and higher Ca content.

Keywords: CaCoSi₂O₆, single-crystal X-ray diffraction, high-pressure single-crystal synthesis, pyroxene