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Solid solutions and phase transitions in $(Ca,M^{2+})M^{2+}Si_2O_6$ pyroxenes (M^{2+} = Co, Fe, Mg)

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Abstract

The effect of the substitution of Ca with Co, on the phase transition and on the extension of the miscibility gap, was studied to model the general mechanism of phase transitions and solid solutions in $(Ca,M^{2+})M^{2+}Si_2O_6$ pyroxenes. Eleven pyroxenes with composition $Ca_{1-x}Co_{1+x}Si_2O_6$, $(0 \leq x \leq 1)$ were therefore synthesized by piston cylinder at $P = 3$ GPa, and T between 1100 and 1350 °C. The samples were characterized by SEM-EDS, XRD powder diffraction, and TEM. The results were compared with those of Ca-Fe and Ca-Mg pyroxenes. The phase diagram of Ca-Co pyroxenes is similar to that of Ca-Fe and Ca-Mg ones, with a wide asymmetric miscibility gap, and higher solubility in the Ca-rich side of the gap. The solubility on the Ca-rich side of the gap is related to the radius of the cation substituting.

The cell parameters of the Ca-Co pyroxenes undergo a sudden change at the composition of about 0.4 Ca apfu, due to the $C2/c$–$P2_1/c$ phase transition. The change in volume with composition follows an ideal trend, in the $C2/c$ phase, dictated by the ionic size of the substituting cation. Deviation from the $C2/c$ behavior are instead observed in the $P2_1/c$ field and ascribed to volume strain. The same turnover was found in Ca-Mg, Ca-Fe, and Ca-Mn pyroxenes. The $C2/c$–$P2_1/c$ transition occurs with decreasing the M2 average cation radius, down to a critical value between 0.85 and 0.88 Å, depending on the series. A stabilization of the $C2/c$ phase related to crystal field in Ca-Fe and Ca-Co pyroxenes is suggested by the analysis of the volume strain in the $P2_1/c$ field. A key finding is that a miscibility gap may develop either by lattice strain related to cation substitution, within a series where all end-members have the same structure, or for the combined effect of lattice strain and a phase transition, as is the case for pyroxenes.

Keywords: Ca-Co pyroxenes, high-pressure synthesis, phase transition, phase equilibria