

Crystal chemistry of synthetic lawsonite solid-solution series $\text{CaAl}_2[(\text{OH})_2/\text{Si}_2\text{O}_7]\cdot\text{H}_2\text{O}$ – $\text{SrAl}_2[(\text{OH})_2/\text{Si}_2\text{O}_7]\cdot\text{H}_2\text{O}$ and the $Cmcm$ – $P2_1/m$ phase transition

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ABSTRACT

Crystals of the solid-solution series of (Ca,Sr)-lawsonite were synthesized hydrothermally at 4 GPa and 600 and 800 °C in piston-cylinder experiments. Synthesis products were analyzed with SEM, EMP, and powder-XRD. Lawsonite was observed in both the orthorhombic space group $Cmcm$ and in the monoclinic space group $P2_1/m$. It is exclusively orthorhombic at low $x_{\text{Sr}}^{\text{bulk}}$ but monoclinic at high $x_{\text{Sr}}^{\text{bulk}}$; in the range $x_{\text{Sr}}^{\text{bulk}} = 0.18$ to 0.4 both polymorphs coexist and the data suggest a two-phase field between $x_{\text{Sr}}^{\text{ortho}} \sim 0.1$ –0.2 and $x_{\text{Sr}}^{\text{mono}} \sim 0.3$ –0.4 at 4 GPa/600 °C. Linear regression to the refined lattice parameters yields $a = 0.017 \cdot x_{\text{Sr}} + 5.841$ (Å), $b = 0.197 \cdot x_{\text{Sr}} + 8.787$ (Å), $c = 0.263 \cdot x_{\text{Sr}} + 13.130$ (Å), and $v = 4.62 \cdot x_{\text{Sr}} + 101.46$ (cm³/mol) for orthorhombic lawsonite and $a = 0.119 \cdot x_{\text{Sr}} + 5.306$ (Å), $b = 0.118 \cdot x_{\text{Sr}} + 13.160$ (Å), $c = 0.025 \cdot x_{\text{Sr}} + 5.833$ (Å), $\beta = 0.38 \cdot x_{\text{Sr}} + 124.07$ (°), and $v = 3.20 \cdot x_{\text{Sr}} + 101.59$ (cm³/mol) for monoclinic lawsonite. The data suggest an increasingly negative $\Delta v_{\text{ortho-mono}}$ with increasing x_{Sr} . In monoclinic lawsonite, structural expansion due to the incorporation of Sr is primarily accomplished by tilting and rotation within the Si₂O₇-group, whereas in orthorhombic lawsonite this tilting and rotation is prohibited by symmetry restrictions and expansion is mostly accomplished by an increase in lattice parameters. Combining the extrapolated Ca end-member volume for monoclinic lawsonite with published high- P data yields $K_0^{\text{mono}} = 137(3)$ GPa ($K' = 4.4$). Contrary to the Ca end-member system, the $Cmcm$ – $P2_1/m$ phase transition is quenchable within the Sr-bearing system. A tentative phase diagram for (Ca,Sr)-lawsonite at 600 °C indicates a narrow orthorhombic-monoclinic two-phase field that shifts significantly to lower pressure with increasing x_{Sr} . The $Cmcm$ – $P2_1/m$ phase transition in the Sr end-member system is located at ≤ 1 GPa at ~ 400 to 600 °C, 6 to 9 GPa below the transition in the Ca-system, and has a negative P - T slope.

Keywords: Crystal structure, lawsonite, XRD data, experimental petrology