Crystal chemistry of synthetic lawsonite solid-solution series CaAl$_2$[(OH)$_2$/Si$_2$O$_7$]·H$_2$O–SrAl$_2$[(OH)$_2$/Si$_2$O$_7$]·H$_2$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$_{Sr}^{\text{bulk}}$ but monoclinic at high x$_{Sr}^{\text{bulk}}$, in the range x$_{Sr}^{\text{ortho}}$ = 0.18 to 0.4 both polymorphs coexist and the data suggest a two-phase field between x$_{Sr}^{\text{ortho}}$ ~0.1–0.2 and x$_{Sr}^{\text{mono}}$ ~0.3–0.4 at 4 GPa/600 °C. Linear regression to the refined lattice parameters yields a = 0.017·x$_{Sr}$ + 5.841 (Å), b = 0.197·x$_{Sr}$ + 8.787 (Å), c = 0.263·x$_{Sr}$ + 13.130 (Å), and v = 4.62·x$_{Sr}$ + 101.46 (cm$^3$/mol) for orthorhombic lawsonite and a = 0.119·x$_{Sr}$ + 5.306 (Å), b = 0.118·x$_{Sr}$ + 13.160 (Å), c = 0.025·x$_{Sr}$ + 5.833 (Å), β = 0.38·x$_{Sr}$ + 124.07 °, and v = 3.20·x$_{Sr}$ + 101.59 (cm$^3$/mol) for monoclinic lawsonite. The data suggest an increasingly negative Δ$\nu_{\text{ortho-mono}}$ with increasing x$_{Sr}$. In monoclinic lawsonite, structural expansion due to the incorporation of Sr is primarily accomplished by tilting and rotation within the Si$_2$O$_7$-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 $K^m_{\text{mono}}$ = 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

INTRODUCTION

Lawsonite, CaAl$_2$Si$_2$O$_7$(OH)$_2$·H$_2$O, an index mineral for high-pressure, low-temperature metamorphism, is common in blueschist-facies metabasalts and metagreywackes. It is stable up to extremely high pressure of 12 GPa (Schmidt 1995) and a potential carrier of H$_2$O into the Earth’s depth in subduction zones. However, lawsonite is not only a carrier of H$_2$O but also of the geochemically important trace element Sr (among others) in high- and ultrahigh-pressure rocks, where it controls the whole-rock chemical budget of Sr (Tribuzio et al. 1996; Zack et al. 2002; Spandler et al. 2003). Therefore, understanding the geochemical cycle of Sr during metamorphism and especially within subduction zones requires understanding of its crystal-chemical incorporation in lawsonite.

At ambient conditions, lawsonite and its Sr-analog itoigawaite, SrAl$_2$Si$_2$O$_7$(OH)$_2$·H$_2$O, are both orthorhombic with space group Cmcm (Fig. 1a; Baur 1978; Miyajima et al. 1999). The structure is composed of single chains of edge-sharing octahedra (M site) parallel [100]. The M site is occupied by trivalent cations, preferentially by Al. Kinked Si$_2$O$_5$-groups bridge the octahedral chains in [010] and [001]; within this framework one relatively large A position forms, which is occupied by the large divalent cations Ca and Sr. Several P-T induced phase transitions have been determined for lawsonite. At low temperatures, its space group reduces to Pmcm below 273 K/0.1 MPa and to P2$_1$/cn below 155 K/0.1 MPa (Libowitzky and Armbruster 1995; Meyer et al. 2000, 2001; Martin-Olalla et al. 2001). These reversible phase transitions are mainly caused by shifts of the OH-group and H$_2$O from highly symmetric to ordered positions at low temperatures. At high pressure/room temperature, a reversible and non-quenchable phase transition from orthorhombic Cmcm to monoclinic P2$_1$/m (C112'/m) lawsonite occurs at ~8.6 GPa (Scott and Williams 1999; Daniel et al. 2000). This phase transition was also observed by Pawley and Allan (2001), however, at slightly higher pressure of ~10 to 11 GPa/room temperature. The latter authors explained the phase transition by shearing of (010)$_{ortho}$ Planes in [100]$_{ortho}$ (Fig. 1b). As a consequence, monoclinic P2$_1$/m lawsonite has two different octahedral sites M1 and M2, slightly distorted Si$_2$O$_5$-groups, and the lattice parameters of the two polymorphs are related to each other by 2a$_{ortho}$·sinβ$_{ortho}$ = b$_{ortho}$ = c$_{ortho}$ = c and c$_{mono}$ = a$_{ortho}$. Boffa-Ballaran and Angel (2003) pressurized lawsonite up to 9.82 GPa/room temperature and tested the C-centering with ω-scans of the (017) reflection, which is absent in Cmcm space group. Above 4 GPa/room tem-