

A new polymorph of eucryptite (LiAlSiO₄), ϵ -eucryptite, and thermal expansion of α - and ϵ -eucryptite at high pressure

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ABSTRACT

X-ray diffraction experiments have been carried out on β -eucryptite (LiAlSiO₄) at pressures up to 2.5 GPa and temperatures up to 1073 K in a large-volume apparatus. With room-temperature compression, we observed a phase transition to a new polymorph between 0.83 and 1.12 GPa. This transition is reversible in character. The new phase, referred to here as ϵ -eucryptite, can be indexed according to an orthorhombic unit cell with $a = 10.217(4)$ Å, $b = 8.487(4)$, Å, $c = 5.751(3)$ Å, and $V = 498.7(4)$ Å³ for XRD data at 2.2 GPa and 298 K. On heating at 2.2 GPa, ϵ -eucryptite and β -eucryptite were metastable over the temperature interval 298–873 K; at higher temperatures they underwent an irreversible phase transition to α -eucryptite.

Both hexagonal α -eucryptite and ϵ -eucryptite show anisotropic thermal expansion. For α -eucryptite, we obtained $\alpha_a = 6.71(\pm 0.25) \times 10^{-6}$ K⁻¹, $\alpha_c = 1.07(\pm 0.05) \times 10^{-5}$ K⁻¹, and $\alpha_v = 2.42(\pm 0.1) \times 10^{-5}$ K⁻¹ at 1.94(2) GPa over the temperature range 298–1073 K. For ϵ -eucryptite at 2.32(8) GPa, we find larger thermal expansion in a smaller temperature range 298–773 K, with $\alpha_a = 1.47(\pm 0.15) \times 10^{-5}$ K⁻¹, $\alpha_b = 6.65(\pm 1.33) \times 10^{-6}$ K⁻¹, $\alpha_c = 7.83(\pm 0.88) \times 10^{-6}$ K⁻¹, and $\alpha_v = 2.99(\pm 0.15) \times 10^{-5}$ K⁻¹. In combination with a previous determination of thermal expansion at ambient pressure, the pressure effect on volume thermal expansion of α -eucryptite is determined to be -2.68×10^{-6} GPa⁻¹ K⁻¹, and the temperature derivative of the bulk modulus is estimated to be -0.015 GPa/K.