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

JIANGZHONG ZHANG,¹,* AARON CELESTIAN,¹ JOHN B. PARISE,¹ HONGWU XU,² AND PETER J. HEANEY³

¹Center for High-Pressure Research and Department of Geosciences, State University of New York at Stony Brook, Stony Brook, New York 11794, U.S.A. ²Thermochemistry Facility, Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, California 95616, U.S.A. ³Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

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 αₐ = 6.71(±0.25) × 10⁻⁶ K⁻¹, αₗ = 1.07(±0.05) × 10⁻⁶ K⁻¹, and α₁ = 2.42(±0.1) × 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 αₐ = 1.47(±0.15) × 10⁻⁵ K⁻¹, αₗ = 6.65(±1.33) × 10⁻⁶ K⁻¹, α₁ = 7.83(±0.88) × 10⁻⁶ K⁻¹, and αₙ = 2.99(±0.15) × 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.

INTRODUCTION

The hexagonal aluminosilicate β-eucryptite (LiAlSiO₄) is a structural derivative of β-quartz (SiO₂) such that half of the (SiO₄)²⁻ tetrahedra are replaced by (AlO₄)³⁻ tetrahedra and the charge is balanced by the incorporation of Li⁺ into the main structural channels parallel to the c axis (Buerger 1954). As a result of Al and Si ordering over the tetrahedral framework sites and Li positional order along the channels, the a and c dimensions are doubled relative to those of β-quartz (Pillars and Peacor 1973). β-eucryptite has been of continuing interest to mineralogists due to its structural similarity to quartz (Palmer 1994; Xu et al. 1999a, 1999b). Of particular significance to the field of material sciences is its unusual thermal-expansion properties observed at ambient pressure. As already demonstrated by many experimental studies, expansion within the (001) plane of the structure is approximately canceled by contraction along the c axis, yielding negative thermal expansion along the c axis (αₙ = −2αₗ) and near-zero volume thermal expansion over the temperature range 300–1400 K (e.g., Pillars and Peacor 1973; Schulz 1974; Lichtenstein et al. 1998; Xu et al. 1999a). Explanations for this behavior have been sought for decades, and scientists have offered a variety of interpretations (see reviews by Muller 1995 and Xu et al. 1999a).

The initial objective of this study was to examine whether the remarkable thermal-expansion properties of β-eucryptite persist at elevated pressures. During compression at room temperature, however, β-eucryptite underwent a polymorphic phase transformation to a previously undescribed phase. This phase transformed to α-eucryptite during heating. We were therefore unable to determine the thermal expansion of β-eucryptite at high pressure. Instead, we offer our observations associated with these novel phase transformations, and we report the isobaric thermal expansion of α-eucryptite at 1.94 GPa and of the new polymorph at 2.32 GPa. Thermal equation of state parameters are also derived for α-eucryptite based on the present and previous volume measurements.

EXPERIMENTAL METHOD

The β-eucryptite sample (Fig. 1a) was synthesized from Li₂CO₃, Al₂O₃, and SiO₂·nH₂O powders in the molar ratio 1:1:2. The mixture was first sintered at 1373 K for 15 hours and, after regrinding, resintered at 1573 K for 24 hours. Two X-ray diffraction experiments were performed using the DIA-type and "T-cup" large-volume apparatus (Weidner et al. 1992; Vaughan et al. 1998). An energy-dispersive X-ray method was employed using white radiation from the superconducting wiggler magnet at beamline X17B of the National Synchrotron Light Source and from the bending magnet at beamline 13-BM-D of the Advanced Photon Source. The incident X-ray beam was colli-