Pressure-Induced Phase Transformation and Amorphization in Eucryptite

J. Zhang,[1] L. Wang,[1] T. Uchida[2]

[1] *CHiPR and Department of Geosciences, SUNY at Stony Brook, Stony Brook, NY, U.S.A.*

[2] *Consortium for Advanced Radiation Sources, The University of Chicago, Chicago, IL, U.S.A.*

Introduction

The hexagonal aluminosilicate β-eucryptite ($LiAlSiO_4$) is a structural derivative of β-quartz (SiO_2) such that half of the $[SiO_4]^{4-}$ tetrahedra are replaced by $[AlO_4]^{5-}$ tetrahedra and the charge is balanced by the incorporation of Li^+ into the main structural channels parallel to the *c* axis.[1] As a result of Al and Si ordering over the tetrahedral framework sites and Li positional order along the channels, the unit cell is doubled along the *a* and *c* axes relative to that of β-quartz.[2] β-eucryptite has been of continuing interest to mineralogists due to its structural similarity to quartz, one of the most common minerals in the Earth's crust.[3] 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 ($\alpha_c \approx -2\alpha_a$) and near-zero volume thermal expansion over a wide temperature range of 300-1400K.[3-6]

The initial objective in the study of Zhang et al.[7] was to examine whether these remarkable thermal-expansion properties in β-eucryptite persist at elevated pressures. During room-temperature compression up to 2.2 GPa, however, it has become evident that β-eucryptite destabilized and underwent a polymorphic phase transformation to a previously undescribed phase, ε-eucryptite, as referred in the work of Zhang et al.[7] The primary goal of the present study is to examine reversibility of this reported transformation and to study the stability of β- and ε-eucryptite at higher pressures.

Method and Materials

The starting β-eucryptite sample was synthesized from Li_2CO_3, Al_2O_3, and $SiO_2 \cdot nH_2O$ powders in the molar ratio 1:1:2. The mixture was first sintered at 1373K for 15 hours and, after regrinding, resintered at 1573K for 24 hours. X-ray diffraction experiments were performed using the "T-cup" large-volume apparatus.[8] An energy-dispersive x-ray method was employed using white radiation at beamline 13-BM of the Advanced Photon Source. The incident x-ray beam was collimated to dimensions of 100 × 200 μm, and diffracted x-rays were collected by a solid-state Ge detector at fixed angle of $2\theta = 5.536°$.

The cell assembly used in the DIA experiment is similar to those described by Vaughan et al.[8] In the room-temperature experiment of exploring the reversibility of the transformation between β- and ε-eucryptite, the data were collected at steps of 0.3-0.4 GPa on both compression and decompression in the range 0-2.8 GPa. In the higher P and T experiment, the sample was first compressed at room temperature to 13.2 GPa, followed by heating to the temperature of 1173K. Pressure was determined by EOS of NaCl and temperature by previously established calibration.

Results

Consistent with previous study by Zhang et al.,[7] β--eucryptite was found to transform into ε-eucryptite around 1.2 GPa on room-temperature compression. The transformation did not complete up to ~2.5 GPa. On decompression, ε-eucryptite disappeared at pressures between 0.5 and 1.0 GPa, and at ambient conditions ε-eucryptite was the only phase observed. These experimental results demonstrate that the β-ε transformation in eucryptite is reversible.

In the experiment at high pressure and temperature, β-eucryptite again started transforming into ε-eucryptite around 1.2 GPa. Upon further compression at room temperature, amorphization was observed at pressures above 3 GPa, as revealed by the weakening of diffraction peaks and the continuing growing of diffraction background. The amorphization, however, did not complete up to 13.2 GPa. On heating at 13.2 GPa, amorphization completed between 523 and 573K. On further heating, crystalline phases (spodumene and $LiAlO_2$ spinel) grew at temperatures between 973-1073K, which were recovered at ambient conditions.

Discussion

Pressure-induced phase transformations in β-eucryptite is associated with the open nature of its β-quartz-like framework. Open frameworks, however, often become destabilized when pressure is applied, as demonstrated in several studies on zeolites.[9] It can also be concluded from the present observations that the Li-stabilized β-quartz structure does not persist at high pressures, at least above 1.2 GPa. Amorphization of ε-eucryptite is likely attributed to the fact that it is a metastable phase at pressures above 1.2 GPa.[7] Since direct transformation from ε-eucryptite to spodumene and $LiAlO_2$ was not observed under our experimental conditions, the present observations can be viewed as one of the classic examples in which an intermediate/metastable phase (usually an amorphous phase) is often involved when transformation between the thermodynamically stable phases is kinetically hindered.

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