A Cr\textsuperscript{3+} luminescence study of spodumene at high pressures: Effects of site geometry, a phase transition, and a level-crossing

EARL O’BANNON III\textsuperscript{1,*} AND QUENTIN WILLIAMS\textsuperscript{1}

\textsuperscript{1}Department of Earth and Planetary Sciences, University of California, Santa Cruz, 1156 High Street, Santa Cruz, California 95064, U.S.A.

ABSTRACT

Cr\textsuperscript{3+} luminescence of the green Cr-bearing variety of spodumene (LiAlSi\textsubscript{2}O\textsubscript{6}) has been studied under hydrostatic conditions up to ~15 GPa. R-line luminescence is a particularly sensitive site-specific probe of the Al-site, and high-pressure phase transitions that affect the symmetry or electron density at this site should produce obvious changes in the luminescence spectra. Thus, the nature of Cr\textsuperscript{3+} luminescence is probed across known and possible phase transitions in spodumene. Discontinuous shifts of the R-lines and their sidebands to higher energy at 3.2 GPa are associated with the C2/c to P2\textsubscript{1}/c phase transition. Both R-lines and sidebands shift to lower energy after the 3.2 GPa transition up to ~15 GPa. The C2/c to P2\textsubscript{1}/c phase transition is confirmed to be first order in nature based on its observed hysteresis on decompression, and R-line and sideband measurements give no evidence of a second proposed transition up to ~15 GPa. The splitting between the R\textsubscript{1} and R\textsubscript{2} bands is dramatically enhanced by pressure, with the split decreasing at the phase transition. These trends correspond to pressure-induced shifts in the distortion of the M1 site, and a likely shift in off-centeredness of the Cr\textsuperscript{3+} ion. Pressure-induced decreases in line widths are consistent with the R-lines shifting at slower rates than the phonons to which they are most closely coupled, as demonstrated by large pressure shifts of vibronic peaks. Observations of a pressure-induced cross-over between the T\textsubscript{2} and E levels of the Cr\textsuperscript{3+} ion indicate that spodumene undergoes a shift from an intermediate strength crystal field environment to a high strength crystal field environment at pressures between ambient and 3.2 GPa.

Keywords: Spodumene, pyroxene, high pressure, phase transition, Cr\textsuperscript{3+} luminescence

INTRODUCTION

Spodumene (LiAlSi\textsubscript{2}O\textsubscript{6}) is a lithium-bearing pyroxene that crystallizes in the monoclinic crystal system with C2/c symmetry. Pyroxenes are major rock-forming minerals in the Earth’s crust, and the upper mantle. While spodumene is certainly not abundant in the Earth’s crust and upper mantle, understanding high-pressure phase transitions in C2/c pyroxenes is important for understanding the high-pressure behavior of mantle relevant pyroxenes (e.g., hedenbergite and diopside), and hence the structure of the upper mantle. High-pressure phase transitions in spodumene have been extensively studied (Arlt and Angel 2000; Pommier et al. 2003; Nestola et al. 2008; Ullrich et al. 2009). The first-order displacive C2/c to P2\textsubscript{1}/c phase transition in spodumene occurs at ~3.2 GPa and is generally well agreed upon (Fig. 1). One study (Pommier et al. 2003) reports a possible higher pressure isosymmetric phase transition in the 7.7–10.5 GPa range based on shifts in the Raman spectra of this phase, and propose that this phase transition is associated with a change in the lithium coordination number from five to six.

Arlt and Angel (2000) used single-crystal X-ray diffraction and did not report a second phase transition in spodumene up to 8.8 GPa. They do suggest that a second phase transition is likely above 10 GPa based on the high-pressure kink value of the B chain (Fig. 1). Similarly, Ullrich et al. (2009) performed both single-crystal X-ray diffraction and Raman spectroscopy of spodumene up to ~9.24 GPa and concluded that a second transition at 7.7 GPa is unlikely. Among closely related materials, a Raman and X-ray investigation of LiFeSi\textsubscript{2}O\textsubscript{6} by Pommier et al. (2005) reported a C2/c to P2\textsubscript{1}/c phase transition between 0.7 and 1.0 GPa. They also suggest possible spin crossovers at ~6.0 GPa and propose that the disappearance of several peaks in the Raman spectrum (similar to the disappearance of peaks in the spodumene Raman spectra at high pressure) at ~8.0 GPa is evidence of a P2\textsubscript{1}/c to P2\textsubscript{1}/c phase transition. Nestola et al. (2008) used X-ray diffraction to examine Li(Al\textsubscript{0.53}Ga\textsubscript{0.47})Si\textsubscript{2}O\textsubscript{6} and LiGaSi\textsubscript{2}O\textsubscript{6} and found that the C2/c to P2\textsubscript{1}/c phase transition occurs between ~1.8 and 2.1 GPa in the mixed sample and between 0.0001 and 0.4 GPa in the Ga end-member. The mixed sample was studied up to ~9.0 GPa and the Ga end-member up to ~7.5 GPa and no higher pressure phase transitions were reported.

We utilize the fluorescence of chromium to probe the response of spodumene to pressure: such fluorescence under pressure is well characterized for ruby, whose role as a pressure calibrant is well known (e.g., Mao and Bell 1986), but few other minerals have had the fluorescence of Cr\textsuperscript{3+} dopants examined under pressure (alexandrite, MgO, and MgAl\textsubscript{2}O\textsubscript{4} are notable exceptions: Kottke and Williams 1983; Jahren et al. 1992[auth: fixed per ref list]); Chopelas 1996; Jovanic 2000). Notably, most other oxide minerals examined to date under pressure utilizing Cr\textsuperscript{3+} fluorescence have nearly ideal octahedral or only slightly distorted Cr-bearing sites. Spodumene’s M1 site is, in comparison, substantially distorted (e.g., Clark et al. 1968; Arlt and Angel 2000). Hence, spodumene allows both the interrogation of the fluorescence response of Cr under pressure within...