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

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Abstract

Cr^{3+} luminescence of the green Cr-bearing variety of spodumene ($LiAlSi_2O_6$) 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^{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 $P2_1/c$ 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 $P2_1/c$ 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_1 and R_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^{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 $^4T_2$ and ^2E levels of the Cr^{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^{3+} luminescence