

High pressure Raman study of the alkali/calcium carbonate, shortite

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The high pressure behavior of shortite ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$) has been investigated using Raman spectroscopy at room pressure, and post-laser heating. Shortite is of geological importance due to its presence in the ground-mass of kimberlites, and the alkaline-/carbon-rich character of kimberlitic eruptions. This investigation focuses on shortite's high pressure behavior and is relevant to the behavior of alkali-carbonate systems within Earth's upper mantle. Raman spectroscopy of shortite was collected up to 26 GPa at 300 K. Dramatic changes in the number of modes and slopes of the pressure shifts of both lattice and carbonate-associated Raman modes at 15 GPa indicate a dramatic change in its structure; these notable changes include a drop of $\sim 30 \text{ cm}^{-1}$ in the frequency of the carbonate symmetric stretch. At 26 GPa, shortite appears to undergo irreversible amorphization, as indicated by a dramatic broadening and decrease in intensity of all modes. Indeed, after this transition, only a broad carbonate symmetric stretch is resolved. Laser heating was utilized at 26 GPa to recrystallize the sample at high pressure, and this sample was then decompressed with laser-annealing at each pressure step. At 26 GPa, the amorphized sample converted to a new high-pressure crystalline phase following laser-heating. At ~ 6 GPa on decompression, the sample converted to more than one phase, and the ultimate resulting, room pressure, annealed structure is likely a combination of shortite, nyerereite ($(\text{Na}_2\text{Ca}(\text{CO}_3)_2)$) and calcite. Thus, although there is an additional stable high pressure/high temperature phase of shortite above 26 GPa, it is not quenchable at room temperature. Hence, our results demonstrate that these two high-pressure transitions of shortite could be important for the phase equilibria of alkali-rich calcic carbonate assemblages within Earth's mantle.