

High-pressure Raman and Nd³⁺ luminescence spectroscopy of bastnäsite-(REE)CO₃F

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ABSTRACT

Bastnäsite-(Ce), a rare earth element (REE) bearing carbonate (Ce,La,Y,Nd,Pr)CO₃F, is one of the most common REE-bearing minerals and has importance from both economic and geologic perspectives due to its large REE concentration. It also provides an example of the structural interplay between carbonate groups and fluorine ions, as well as the complex bonding properties of rare earth elements. We report Raman vibrational and Nd³⁺ luminescence (⁴F_{3/2}→⁴I_{9/2}, ⁴F_{3/2}→⁴I_{11/2}, and ⁴F_{5/2+2}H_{9/2}→⁴I_{9/2}) spectra of natural bastnäsite-(Ce) to 50 GPa at 300 K. Two phase transitions are observed under compression. Bastnäsite-I remains the stable phase up to 25 GPa, where it undergoes a subtle phase transition to bastnäsite-II. This is likely produced by a change in symmetry of the carbonate ion. Bastnäsite-II transforms to bastnäsite-III at ~38 GPa, as demonstrated by changes in the luminescence spectra. This second transition is particularly evident within the ⁴F_{3/2}→⁴I_{9/2} luminescent transitions, and it appears that a new rare earth element site is generated at this phase change. This transition is also accompanied by modest changes in both the Raman spectra and two sets of luminescent transitions. Despite these transformations, the carbonate unit remains a stable, threefold-coordinated unit throughout this pressure range, with a possible increase in its distortion. Correspondingly, the rare-earth element site(s) appears to persist in quasi-ninefold coordination as well, implying that the general bonding configuration in bastnäsite is at least metastable over a ~30% compression range. All pressure-induced transitions are reversible, with some hysteresis, reverting to its ambient pressure phase on decompression.

Keywords: Bastnäsite, deep Earth, high pressure, Raman spectroscopy, rare earth elements, neodymium luminescence spectroscopy, carbon; Volatile Elements in Differentiated Planetary Interiors