High-pressure Raman and Nd$^{3+}$ luminescence spectroscopy of bastnäsite-(REE)CO$_3$F

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ABSTRACT

Bastnäsite-(Ce), a rare earth element (REE) bearing carbonate (Ce,La,Y,Nd,Pr)CO$_3$(F,OH) that is typically found associated with carbonatite deposits and is economically important due to its high content of REEs. Indeed, bastnäsite is one of the two major mineral ores for REEs, with its chief competitor being monazite. Geochemically, REEs are typically incompatible in silicate minerals; their concentration in carbonatite melts (often with bastnäsite as their crystallization product) is generally more than three orders of magnitude higher than within chondrites (Holtstam and Andersson 2007). Indeed, carbonate-bearing liquids and solids likely play a primary role in transporting and retaining rare earth elements, particularly via the samarium-neodymium isotope systematics. In addition, light REE have long been used to determine the ages of continental rocks, particularly via the samarium-neodymium isotope systematics. Further, Sr-Nd isotope systematics and Nd$^{143}$/Nd$^{144}$ variation in the mantle compared to chondrites and differentiated terrestrial crustal rocks (DePaolo and Wasserburg 1976). Bastnäsite has importance for understanding the potential behavior of REE at depth within carbon (and halogen) enriched zones of the mantle and within carbonatite melts (which are frequently halogen-enriched: e.g., Jago and Gittins 1991; Williams and Knittle 2003). Additionally, the optical and magnetic properties of rare-earth carbonate fluorides have attracted interest within the materials science community (e.g., Grice et al. 2007).

Bastnäsite virtually never occurs as an end-member in terms of its REE content, as it commonly contains a mixture of REEs (e.g., Ce, Nd, Eu, Y, etc.). Recent advances in infrared reflectance spectroscopy and high-pressure spectroscopy has been used to probe the absorption bands of bastnäsite, which can constrain the REE content (Turner et al. 2016); however, assignments to the absorptions and energy levels of different REEs have generally not been made to the observed absorption peaks. In addition, the rare earths in bastnäsite luminesce strongly; as discussed below, it appears that this fluorescence has at times been associated with hydroxyl stretching vibrations in Raman spectroscopic experiments (Frost and Dickfos 2007). In this study, we are able to assign the luminescence peaks to transitions of the neodymium ion, and probe changes to the REE site with pressure by using this Nd$^{3+}$ luminescence.

INTRODUCTION

Bastnäsite-(Ce) is a rare earth element (REE) bearing fluorocarbonate (Ce,La,Y,Nd,Pr)CO$_3$(F,OH) that is typically found associated with carbonatite deposits and is economically important due to its high content of REEs. Indeed, bastnäsite is one of the two major mineral ores for REEs, with its chief competitor being monazite. Geochemically, REEs are typically incompatible in silicate minerals; their concentration in carbonatite melts (often with bastnäsite as their crystallization product) is generally more than three orders of magnitude higher than within chondrites (Holtstam and Andersson 2007). Indeed, carbonate-bearing liquids and solids likely play a primary role in transporting and retaining rare earth elements within the Earth’s mantle (e.g., Collerson et al. 2010). In addition, light REE have long been used to determine the ages of continental rocks, particularly via the samarium-neodymium dating method (McCulloch and Wasserburg 1978), and the evolution of the depleted mantle has been probed using the distinct $^{143}$Nd/$^{144}$Nd variation in the mantle compared to chondrites and crustal rocks (DePaolo and Wasserburg 1976). Bastnäsite has significance beyond its REE content: as carbonates are thought to be the dominant species containing carbon within oxidized regions of the mantle (e.g., Brenker et al. 2007), the properties of bastnäsite can provide insight into the bonding of carbon at depth. Specifically, bastnäsite has importance for understanding the potential behavior of REE at depth within carbon (and halogen) enriched zones of the mantle and within carbonatite melts (which are frequently halogen-enriched: e.g., Jago and Gittins 1991; Williams and Knittle 2003). Additionally, the optical and magnetic properties of rare-earth carbonate fluorides have attracted interest within the materials science community (e.g., Grice et al. 2007).

Bastnäsite virtually never occurs as an end-member in terms of its REE content, as it commonly contains a mixture of REEs (e.g., Ce, Nd, Eu, Y, etc.). Visible and infrared reflectance spectroscopy has been used to probe the absorption bands of bastnäsite, which can constrain the REE content (Turner et al. 2016); however, assignments to the absorptions and energy levels of different REEs have generally not been made to the observed absorption peaks. In addition, the rare earths in bastnäsite luminesce strongly; as discussed below, it appears that this fluorescence has at times been associated with hydroxyl stretching vibrations in Raman spectroscopic experiments (Frost and Dickfos 2007). In this study, we are able to assign the luminescence peaks to transitions of the neodymium ion, and probe changes to the REE site with pressure by using this Nd$^{3+}$ luminescence.

Luminescence has been employed extensively as a probe for pressure-induced changes in crystal structure or in electronic configuration (e.g., Dolan et al. 1986; Freire et al. 1994; Bray 2001; O’Brien and Williams 2016). Neodymium luminescence has been investigated for use as a pressure calibrant 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 Nd$^{3+}$ luminescence ($^4$F$_{5/2}$→$^4$I$_{9/2}$, $^4$F$_{5/2}$→$^4$I$_{11/2}$, and $^4$F$_{5/2}$+H$_{1/2}$→$^4$I$_{9/2}$) 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 $^4$F$_{5/2}$→$^4$I$_{9/2}$ 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

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