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 competition 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 the bulk Earth content (Jones et al. 2013), and greater than four 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 143Nd/144Nd 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. 2015); 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 Dickfoss 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’Bannon and Williams 2016). Neodymium luminescence has been investigated for use as a pressure calibrant due 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

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 competition 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 the bulk Earth content (Jones et al. 2013), and greater than four 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 143Nd/144Nd 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).

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