Thermodynamics of bastnaesite: A major rare earth ore mineral

RADHA SHIVARAMAIAH1, ANDRE ANDERKO2, RICHARD E. RIMAN3, AND ALEXANDRA NAVROTSKY1,*

1Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California Davis, Davis, California 95616, U.S.A.
2OLI Systems, Inc., 240 Cedar Knolls Road, Cedar Knolls, New Jersey 07927, U.S.A.
3Department of Materials Science and Engineering, The State University of New Jersey, Piscataway, New Jersey 08854-8066, U.S.A.

ABSTRACT

Bastnaesite, \([\text{RE-CO}_3-\text{OH/F}]\) (\(\text{RE} = \text{rare earth}\)) is one of the major sources of rare earth elements found in commercial deposits at Mountain Pass, California, Bayan Obo, China, and elsewhere. Synthetic forms of bastnaesite have been explored for applications including optical devices and phosphors. Determination of thermodynamic properties of these phases is critical for understanding their origin, mining, and processing. We report the first experimental determination of formation enthalpies of several OH and F bastnaesites based on high-temperature oxide melt solution calorimetry of well-characterized synthetic samples. The formation enthalpies from binary oxides and fluorides for all the bastnaesite samples are highly exothermic, consistent with their stability in the garnet zone of the Earth’s crust. Fluoride bastnaesite, which is more abundant in nature than its hydroxide counterpart, is thermodynamically more stable. For both OH and F bastnaesite, the enthalpy of formation becomes more negative with increasing ionic radius of the RE\(^{3+}\) cation. This periodic trend is also observed among rare earth phosphates and several other rare earth ternary oxides. For a given RE, the formation enthalpies from binary oxides are more negative for orthophosphates than for bastnaesites, supporting the argument that monazite could have formed by reaction of bastnaesite and apatite at high temperature. The difference in formation enthalpy of monazite and bastnaesite provides insight into energetics of such reactions along the rare earth series.

Keywords: Rare earths, bastnaesite, stability, monazite

INTRODUCTION

Rare earth elements (RE) are technology drivers in today’s world where they are integrated into every part of modern military and civilian life, including rechargeable batteries and other energy applications, phosphors for lighting and computer displays, catalytic converters, and magnets (McLellan et al. 2013; Pathak et al. 2015; Gschneidner 1981). Their wide application has created a high demand, which makes their availability a crucial issue, or, in other words, a critical material (Alonso et al. 2012; Humphries 2010). REs occur in nature both as major and trace constituents of minerals (Keith 2011). Monazite, bastnaesite, xenotime, aeschynite, and allanite are minerals in which RE is an essential constituent. Bastnaesite, first discovered in 1818 at Bastnaes, Sweden (Glass and Smalley 1945), constitutes an important RE ore and occurs as a high-grade accessory mineral of igneous or hydrothermal origin, for example in Mountain Pass (California), Bayan Obo (China), and Wingu Hill (Tanzania) (Head and Holley 1963). The Molycorp operation at Mountain Pass, California (Pradip 1981) was the largest producer of rare earths until the late 1990s when low cost Chinese production hit the global market and now constitutes 97% of the world’s RE production. Today there is some interest in the U.S. and Canada in renewed RE mining.

Bastnaesite represents a family of RE carbonate minerals \([\text{RE(OH/F)CO}_3]\) that mostly contain light rare earths (LRE)-La, Ce, Nd, and Pr and trace amounts of heavy rare earths (HRE)-Y, Dy, Lu, Eu, and others (Donnay and Donnay 1953; Fleischer 1978). Its structure consists of RE-F sheets separated by carbonate ions and is related to other RE fluorocarbonate minerals such as parsite \([\text{CaRE}_3(\text{CO}_3)_2\text{F}_2]\), roentgenite \([\text{Ca}_2\text{RE}_3(\text{CO}_3)_5\text{F}_3]\), and synchysite \([\text{CaRE}_2(\text{CO}_3)_3\text{F}_4]\), where bastnaesite-like sheets are interlayered with sheets of CaCO\(_3\) (Vlasov 1964). As the trivalent RE ions have similar crystal chemistry to Ca\(^{2+}\), they substitute for Ca in rock-forming minerals, and these RE-bearing minerals are active participants in metamorphic reactions on the geologic timescale (Lipin and Mckay 1989). These fluorocarbonates are known to have grown from fluids containing both HF and CO\(_2\) and are potential indicators of relative abundances of CO\(_2\) and HF (Williams-Jones and Wood 1992). Being carbonates, they also can play a role in controlling the global carbon cycle, although they are not major sources or sinks of carbon. While both F and OH bastnaesites are found in nature, the F form is predominant (Williams-Jones and Wood 1992). Several reports document bastnaesites from various locations in terms of structure, composition, phase relations, and reactivity with other RE accessory minerals (Exley 1980; Smith et al. 1999).

The first efforts to synthesize bastnaesite phases date back to 1950s (Jansen et al. 1959). However it was not until the early 1970s that these phases were studied in terms of structural aspects and compositional variability. In 1973, Haschke proposed phase equilbria in the lanthanum-hydroxide-fluoride-carbonate system as a function of temperature and pressure by synthesizing a series of...