

Thermodynamics of bastnaesite: A major rare earth ore mineral

RADHA SHIVARAMAIAH¹, ANDRE ANDERKO², RICHARD E. RIMAN³, AND ALEXANDRA NAVROTSKY^{1,*}

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, [RE-CO₃-OH/F] (RE = 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 RE³⁺ 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