

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

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 [RE(OH/F)CO₃] 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 parisite [CaRE₂(CO₃)₂F₂], roentgenite [Ca₂RE₃(CO₃)₅F₃], and synchysite [CaRE(CO₃)₂F], where bastnaesite-like sheets are interlayered with sheets of CaCO₃ (Vlasov 1964). As the trivalent RE ions have similar crystal chemistry to Ca²⁺, 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 CO₂ and are potential indicators of relative abundances of CO₂ 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 equilibria in the lanthanum-hydroxide-fluoride-carbonate system as a function of temperature and pressure by synthesizing a series

* E-mail: anavrotsky@ucdavis.edu

of solid solutions in the $\text{La}(\text{OH})_{1-x}\text{F}_x\text{CO}_3$ system (Haschke 1975; Haschke and Eyring 1971). These investigations provide possible reaction paths for the geochemical formation of bastnaesite. There are recent reports on the crystallization mechanism of OH bastnaesite under hydrothermal conditions (Vallina et al. 2014). In recent years synthetic bastnaesites have gained increased attention as they are used as precursors for synthesis of rare earth oxycarbonates ($\text{RE}_2\text{O}_2\text{CO}_3$) and oxyfluorides (REOF), which are excellent host lattices for phosphors (Lee and Jung 2013; Janka and Schleid 2009). RE hydroxycarbonates are also of interest for optical technologies (Chakhmouradian and Wall 2012). Despite this renewed interest, there are no reliable thermodynamic data available in the literature for bastnaesites. Limited reports on the thermal stability of bastnaesite phases indicate that fluoride phase always persists to higher temperatures than its hydroxide counterpart (Hsu 1992). This implies that the F-phase could be stable at magmatic conditions while the OH-phase exists only in low-temperature environments (Hsu 1992). Based on solubility product and stability constant measurements from solubility and titration experiments, a speciation diagram has been proposed for the CeFCO_3 system (Pradip et al. 2013).

There is a recent report on the thermodynamic properties of bastnaesite and parasite mineral phases, where the authors report enthalpy and free energy of formation of these mineral phases measured using differential scanning calorimetry (Gysi and Jones 2015). Based on their results, they construct a quantitative mineral-fluid stability diagrams involving bastnaesite, parasite, fluorocite, calcite, and fluorite at different pressure-temperature-composition (P - T - X) conditions. However, since in reality bastnaesite is a complex solid solution whose composition varies as a function of P - T - X conditions, assuming one constant mineral composition is not sufficient for accurate thermodynamic modeling. Rather, it is crucial to have thermodynamic data for the end-members to aid in modeling the bastnaesite solid solution. In this paper we report the enthalpy of formation for some synthetic bastnaesite phases by direct measurements using high temperature oxide melt solution calorimetry. For this purpose we carried out synthesis and characterization of F-bastnaesites (La and Ce) and both polymorphs of OH-bastnaesites of several RE (La, Ce, Y, Dy, and Nd).

EXPERIMENTAL METHODS

Synthesis

A summary of the synthesis conditions of both F and OH-bastnaesites is given in Table 1. The detailed procedure used for the syntheses is described below.

F-bastnaesites. REFCO_3 (RE = La and Ce) phases were synthesized by urea hydrolysis in the presence of NH_4F as a source of F^- . In a typical synthesis 0.02

mol of $\text{RE}(\text{NO}_3)_3$ was dissolved in 20 mL of deionized (DI) water and was added dropwise to a 50 mL of solution containing 0.02 mol of NH_4F . The mixture was stirred for 30 min and 0.04 mol of urea was added. The resulting suspension was aged at 90 °C for 20 h and the precipitate obtained was separated by centrifugation, washed with DI water and dried at 60 °C.

OH-bastnaesites. REOHCO_3 (RE = La, Ce, Y, Nd, and Dy) were synthesized by three different aqueous methods, (1) urea hydrolysis and (2) base hydrolysis of RECl_3 using sodium carbonate and (3) water hydrolysis of $\text{RE}(\text{CO}_3)_3$. In a typical synthesis by urea hydrolysis 0.02 mol of RECl_3 and 0.01 mol of urea were dissolved in 50 mL of DI water and stirred at room temperature for 30 min. The solution was then transferred to a polytetrafluoroethylene lined autoclave and heated at 180 °C for 3 h. The precipitate was obtained after cooling and subsequently separated by centrifugation, washed with DI water three times, and dried at 60 °C. For base hydrolysis a 50 mM solution of RECl_3 was added to a 50 mM solution of Na_2CO_3 at room temperature, stirred at room temperature for 30 min and transferred to a polytetrafluoroethylene-lined autoclave, followed by hydrothermal treatment at 180 °C for 48 h. After cooling the autoclave to room temperature, the precipitate was separated by centrifugation, washed with DI water several times, and dried in an oven at 60 °C. For hydrolysis of $\text{RE}(\text{CO}_3)_3$ in water, 5g of rare earth carbonate was taken in 100 mL water and heated first at 90 °C for 20 h and then at 100 °C for 1 h. The product was separated by centrifugation and dried at 60 °C.

Characterization

Powder X-ray diffraction patterns (XRD) of the synthesized samples were recorded using a Bruker AXS D8 Advance diffractometer with $\text{CuK}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$, to identify the phases. The Rietveld technique was employed for structure refinement of all the samples using X'pert HighScore Plus software. All the structure refinements were carried out using the published structure models. When there was an impurity phase in the sample, phase fractions were obtained by two-phase refinements.

Thermogravimetric analysis (TGA) was performed to determine the water content in the samples using a Netzsch 449 thermal analysis system in a dynamic Ar atmosphere (40 mL/min, 25–800 °C, 5 °C/min, Pt crucible). The data were analyzed using Netzsch Proteus software. The overall RE content in the samples was measured by inductively coupled plasma-mass spectrometry (ICP-MS) with an Agilent Technologies 7500a instrument. A known amount of sample was dissolved in ~0.1 mL of ICP grade HCl and diluted with Millipore water. Fourier transform infrared attenuated total reflectance spectra (ATR-FTIR) of all the samples were recorded using a Bruker Model Alpha-P IR spectrometer (diamond ATR cell, 4 cm^{-1} resolution, 400–4000 cm^{-1}).

High-temperature oxide melt solution calorimetry

High-temperature oxide melt solution calorimetry was performed using a custom-built isoperibol Tian-Calvet microcalorimeter as described by Navrotsky (1977, 1997). Molten sodium molybdate was used as a solvent at 700 °C. The calorimeter was calibrated using the heat content of high purity $\alpha\text{-Al}_2\text{O}_3$. Oxygen was flushed through the glassware at 60 mL/min to maintain constant atmosphere and bubbled through the solvent at 30 mL/min using a bubbling tube to remove evolved gases, aid dissolution, and prevent local saturation of the solvent. In a typical experiment ~5 mg of loosely pelletized sample was dropped into the solvent. The measured heat effect (heat of drop solution, ΔH_{ds}), includes the heat content of the sample, the heat effect associated with desorbing and vaporizing water, decarbonation, and the heat of dissolution of the oxide component of the sample in the high-temperature solvent. Heats of drop solution of the binary oxides were taken from previously published work (Navrotsky 2014).

RESULTS AND DISCUSSION

Two F-bastnaesites (La and Ce) were successfully synthesized by urea hydrolysis in the presence of NH_4F . Among the OH-bastnaesites, two-phase pure samples with hexagonal structure (La and Nd) were synthesized. Four OH-bastnaesite samples with orthorhombic structure were prepared (La, Ce, Dy, and Y), among which the one containing Dy was phase pure and the oth-

TABLE 1. Bastnaesite samples used for calorimetric studies, their synthesis conditions, and crystal systems

Sample	Method of synthesis/ Temperature	Crystal system	% oxide impurities
LaFCO_3	Urea hydrolysis/90 °C	Hexagonal	–
CeFCO_3	Urea hydrolysis/90 °C	Hexagonal	–
LaOHCO_3 -hex	Hydrolysis of $\text{La}_2(\text{CO}_3)_3$ /90 °C	Hexagonal	–
LaOHCO_3 -ortho	Urea hydrolysis/180 °C	Orthorhombic	6.1
CeOHCO_3	Urea hydrolysis/180 °C	Orthorhombic	5.9
DyOHCO_3	Hydrolysis of REE nitrate with Na_2CO_3 /220 °C	Orthorhombic	–
YOHCO_3	Urea hydrolysis/180 °C	Orthorhombic	6.3
NdOHCO_3	Hydrolysis of REE nitrate with Na_2CO_3 /220 °C	Hexagonal	–

¹ Deposit item AM-16-55565, Supplemental Figures. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to <http://www.minsocam.org/MSA/AmMin/TOC/>).

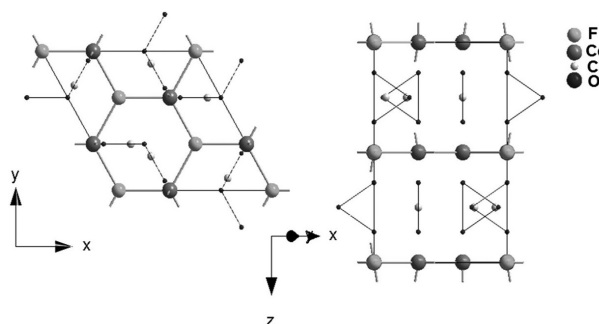
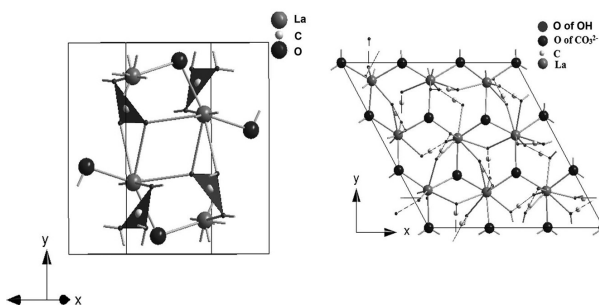
TABLE 2. Summary of results of Rietveld refinements of F- and OH-bastnaesites

Bastnaesite	Space group	Cell parameters (Å)
LaFCO ₃	$P\bar{6}2m$	$a = 7.180(8)$ $c = 4.912(6)$
CeFCO ₃	$P\bar{6}2c$	$a = 7.201(1)$ $c = 9.970(2)$
LaOHCO ₃	$P\bar{6}$	$a = 12.647(2)$ $c = 10.025(4)$
LaOHCO ₃	$Pnma$	$a = 7.270(1), b = 5.022(8)$ $c = 8.590(1)$
CeOHCO ₃	$P212121$	$a = 5.005(4), b = 8.535(7), c = 7.305(6)$
YOHCO ₃	$P212121$	$a = 4.809(1), b = 6.957(3), c = 8.466(5)$
DyOHCO ₃	$P212121$	$a = 4.834(3), b = 6.980(1), c = 8.444(2)$
NdOHCO ₃	$P\bar{6}$	$a = 12.327(1)$ $c = 9.880(4)$

ers contained oxide impurities. A summary of samples used for calorimetric measurements is given in Table 1

Rietveld fits of the PXRD patterns of the two F-bastnaesites are shown in Supplementary Figure 1¹ in the supplementary information. Both LaFCO₃ and CeFCO₃ crystallize in hexagonal crystal structure. PXRD pattern of LaFCO₃ could be refined using published crystal structure (ICSD no: 26678) with $a = 7.180(8)$ Å and $c = 4.912(6)$ Å. PXRD pattern of CeFCO₃ was refined using a published crystal structure (ICSD no: 27591) with $a = 7.201(1)$ Å and $c = 9.970(2)$ Å. The results of refinements of both F-bastnaesites are listed in Table 2. In the crystal structure of LaFCO₃, fluoride anions are present in two crystallographically distinct sites. La³⁺ cations form hexagonal layers with both the fluoride ions. Oxygen atoms of the carbonate are present in two different sites as well, resulting in two topologically different carbonate anions sandwiched between the hexagonal layers formed by La³⁺ and F⁻. CeFCO₃ exhibits a similar structure, but with an elongated c -parameter corresponding to two hexagonal layers formed by Ce and F ions, unlike in LaFCO₃ where there is one layer per unit cell. A view of crystal structure along the c -direction showing the hexagonal layers formed by Ce and F ions is shown in Figure 1a, which is isostructural with LaFCO₃. The structure along the b -direction, showing carbonate in two different orientations between these hexagonal layers, is shown in Figure 1b. The Ce³⁺ cation is in irregular coordination with eight O and three in-plane F ions, resulting in an overall coordination number of 11 for RE in a distorted tricapped trigonal prismatic arrangement.

OH-bastnaesite, on the other hand, is known to exist in two different polymorphic modifications—hexagonal and orthorhombic (Sun et al. 1986). Our attempts to synthesize both polymorphs in the Y, La, Ce, Nd, and Dy were partially successful. While most of our synthetic efforts produced a mixture of the two polymorphs, we found one methodology to successfully synthesize single-phase precipitates for each of the REOHCO₃ systems, see Table 1. Both hexagonal and orthorhombic polymorphs were obtained for LaOHCO₃ and the Rietveld fit of the PXRD patterns are shown in Supplementary Figure 2¹. The hexagonal polymorph was phase pure and the orthorhombic polymorph had La₂O₃ impurities. Two-phase refinement was performed for the orthorhombic polymorph to quantify the amount of impurity, which was found to be 6.5%. The obtained refined lattice parameters and goodness of fit parameters are listed in Table 2. The two polymorphs of OH-bastnaesites are not isostructural with F-bastnaesite, although the metal sub-lattice looks similar for the hexagonal polymorph. The crystal structures

**FIGURE 1.** Crystal structure of CeFCO₃ shown along (a) c -axis and along (b) b -axis.**FIGURE 2.** Structures of orthorhombic (left panel) and hexagonal (right panel) polymorphs of LaOHCO₃.

of both polymorphs are shown in Figure 2. In both cases each La is coordinated with 11 O atoms. Distortion in carbonate polyhedra is observed, probably due to the hydrogen bonding with OH⁻ ions. Furthermore the OH anions are not coplanar with the La cations, unlike those in LaFCO₃.

PXRD patterns of CeOHCO₃ (orthorhombic), YOHCO₃ (orthorhombic), NdOHCO₃ (hexagonal), and DyOHCO₃ (orthorhombic) are shown in Supplementary Figure 3¹. CeOHCO₃ and YOHCO₃ contained RE₂O₃ impurities, quantified to be 5.9 and 6.3 wt%, respectively. NdOHCO₃ and DyOHCO₃ were phase pure. The refined lattice parameters of all the OH-bastnaesites are listed in Table 2.

Thermogravimetric (TG) curves of the two F-bastnaesites and that of OH bastnaesites are shown in Supplementary Figure 4¹. A total mass loss of 20 and 22% was observed up to 550 °C for LaFCO₃ and CeFCO₃, respectively, which corresponds to decarbonation, leading to residual metal oxyfluorides. OH-bastnaesites showed no significant mass loss below 150 °C. A single-step mass loss was observed for CeOHCO₃ and DyOHCO₃, indicating that decarbonation and dehydroxylation occur simultaneously. In contrast, the other OH-bastnaesites showed two-step mass losses, suggesting that decarbonation and dehydroxylation occur at different temperatures.

Attenuated total reflectance (ATR) spectra of F- and OH-bastnaesites are shown in Supplementary Figure 5. Both the F-bastnaesites exhibit peaks corresponding to carbonate vibrations at 1440 and 865 cm⁻¹, whereas all the OH-bastnaesites exhibit multiple absorption bands in the same frequency range due to lowering of local symmetry of carbonate. This could be due to

distortion of the carbonate ion by the polarizing influence of the OH group. Two different kinds of distorted carbonate groups were also seen in these OH-bastnaesites. The observed peaks could be attributed to ν_1 (1070–1100 cm^{-1}), ν_2 (850–880 cm^{-1}), ν_3 (1400–1510 cm^{-1}), and ν_4 (690–730 cm^{-1}) modes of carbonate. In addition, two weak but discernable sharp peaks were observed between 3600 and 3400 cm^{-1} due to OH vibrations. The infrared spectrum of the orthorhombic polymorphs is less complicated than that of the hexagonal polymorph.

High-temperature oxide melt solution calorimetry

Enthalpies of drop solution of all the samples and the constituents used in thermodynamic cycle are listed in Table 3. Enthalpies of formation of F-bastnaesites were calculated from a mixture of constituent oxides and fluorides and the thermochemical cycle

TABLE 3. Thermochemical data for F- and OH-bastnaesites and for the constituents used for enthalpy of formation calculation

Sample	Enthalpy of drop solution (kJ/mol)	Enthalpy of formation from oxides at 298 K (kJ/mol)	Enthalpy of formation from elements (kJ/mol)
LaF ₃	95.87 ± 2.9		−1732.1 ± 1.2
La ₂ O ₃	−225.1 ± 3.16		−1791.6 ± 1.0
CeF ₃	89.58 ± 2.3		−1726.1 ± 1.6
Ce ₂ O ₃		371.6 ± 5.0	−1799.8 ± 1.8
CeO ₂	74.37 ± 0.75		−1090.4 ± 0.8
Y ₂ O ₃	−120.74 ± 0.94		−1932.8 ± 5.2
Nd ₂ O ₃	−163.36 ± 3.44		−1806.8 ± 3.0
Dy ₂ O ₃	−114.88 ± 2.2		−1863.4 ± 5.0
LaFCO ₃	162.50 ± 1.95	−173.07 ± 2.4	−1729.37 ± 2.72
CeFCO ₃	126.27 ± 1.77	−141.24 ± 2.58	−1708.85 ± 4.09
LaOHCO ₃ -hex	150.57 ± 0.45	−196.55 ± 1.64	−1628.78 ± 2.53
LaOHCO ₃ -ortho	181.40 ± 2.4	−227.38 ± 2.87	−1659.61 ± 4.48
CeOHCO ₃	115.74 ± 2.10	−166.03 ± 3.35	−1602.36 ± 3.65
DyOHCO ₃	142.85 ± 1.55	−133.72 ± 1.90	−1601.85 ± 5.15
NdOHCO ₃	149.90 ± 2.52	−165.01 ± 3.05	−1604.89 ± 5.74
YOHCO ₃	111.80 ± 4.8	−105.6 ± 4.82	−1608.49 ± 6.87

TABLE 4. Thermochemical cycle used for the calculation of enthalpy of formation of F-bastnaesites

LaFCO ₃		
(1)	LaCO ₃ F _(s, 25 °C) → 0.33La ₂ O _{3(sol, 700 °C)} + 0.33LaF _{3(sol, 700 °C)} + CO _{2(g, 700 °C)}	ΔH_1
(2)	La ₂ O _{3(s, 25 °C)} → La ₂ O _{3(sol, 700 °C)}	ΔH_2
(3)	LaF _{3(s, 25 °C)} → LaF _{3(sol, 700 °C)}	ΔH_3
(4)	CO _{2(g, 25 °C)} → CO _{2(g, 700 °C)} ^a	ΔH_4
(5)	2La _(s, 25 °C) + 3/2O _{2(g, 25 °C)} → La ₂ O _{3(s, 25 °C)}	ΔH_5
(6)	La _(s, 25 °C) + 3/2F _{2(g, 25 °C)} → LaF _{3(s, 25 °C)}	ΔH_6
(7)	C _(s, 25 °C) + O _{2(g, 25 °C)} → CO _{2(g, 25 °C)}	ΔH_7
(8)	0.33La ₂ O _{3(s, 25 °C)} + 0.33LaF _{3(s, 25 °C)} + CO _{2(g, 25 °C)} → LaCO ₃ F _(s, 25 °C)	$\Delta H_{f,ox}$
(9)	La _(s, 25 °C) + 1/2F _{2(g, 25 °C)} + C _(s, 25 °C) + 3/2O _{2(g, 25 °C)} → LaCO ₃ F _(s, 25 °C)	$\Delta H_{f,el}$
	$\Delta H_{f,ox} = -\Delta H_1 + 0.33\Delta H_2 + 0.33\Delta H_3 + \Delta H_4$ $\Delta H_{f,el} = \Delta H_{f,ox} + 0.33\Delta H_5 + 0.33\Delta H_6 + \Delta H_7$	
CeFCO ₃		
(1)	CeCO ₃ F _(s, 25 °C) + 0.165O _{2(g, 700 °C)} → 0.667 CeO _{2(sol, 700 °C)} + 0.33CeF _{3(sol, 700 °C)} + CO _{2(g, 700 °C)}	ΔH_1
(2)	CeO _{2(s, 25 °C)} → CeO _{2(sol, 700 °C)}	ΔH_2
(3)	CeF _{3(s, 25 °C)} → CeF _{3(sol, 700 °C)}	ΔH_3
(4)	CO _{2(g, 25 °C)} → CO _{2(g, 700 °C)} ^a	ΔH_4
(5)	O _{2(g, 25 °C)} → O _{2(g, 700 °C)}	ΔH_5
(6)	Ce ₂ O _{3(s, 25 °C)} + 0.5O _{2(g, 25 °C)} → 2CeO _{2(s, 25 °C)}	ΔH_6
(7)	2Ce _(s, 25 °C) + 3/2O _{2(g, 25 °C)} → Ce ₂ O _{3(s, 25 °C)}	ΔH_7
(8)	Ce _(s, 25 °C) + 3/2F _{2(g, 25 °C)} → CeF _{3(s, 25 °C)}	ΔH_8
(9)	C _(s, 25 °C) + O _{2(g, 25 °C)} → CO _{2(g, 25 °C)}	ΔH_9
(10)	0.33Ce ₂ O _{3(s, 25 °C)} + 0.33CeF _{3(s, 25 °C)} + CO _{2(g, 25 °C)} → CeCO ₃ F _(s, 25 °C)	$\Delta H_{f,ox}$
(11)	Ce _(s, 25 °C) + 1/2F _{2(g, 25 °C)} + C + 3/2O _{2(g, 25 °C)} → CeCO ₃ F _(s, 25 °C) $\Delta H_{f,ox} = -\Delta H_1 + 0.667\Delta H_2 + 0.33\Delta H_3 + \Delta H_4 - 0.165\Delta H_5 + 0.33\Delta H_6$ $\Delta H_{f,el} = \Delta H_{f,ox} + 0.33\Delta H_7 + 0.33\Delta H_8 + \Delta H_9$	

^a CO₂ = 32.07 kJ/mol and O₂ = 21.74 kJ/mol/calculated from heat capacity measurements).

used for the calculation is shown in Table 4. Because oxygen was bubbled through and over the solvent during the experiments, the dissolved state of cerium is Ce⁴⁺. The calculated enthalpy of formation of LaFCO₃ and CeFCO₃ were −173.07 ± 2.40 and −141.24 ± 2.58 kJ/mol, respectively. The strongly exothermic values indicate that these F-bastnaesites are significantly stable compared to mechanical mixture of their oxide and fluoride components and CO₂ gas.

Thermodynamic cycles used for the calculation of formation enthalpies of OH-bastnaesites from their constituent oxides are shown in Table 5. Enthalpy of formation of the two hexagonal polymorphs LaOHCO₃ and NdOHCO₃ are −196.55 ± 1.64 and −165.01 ± 3.05 kJ/mol, respectively.

Enthalpies of formation of the four orthorhombic polymorphs are −227.38 ± 2.87, −166.03 ± 3.35, −133.72 ± 1.90, and −105.60 ± 3.82 kJ/mol for La, Ce, Dy, and Y OH-bastnaesites, respectively. A plot of RE³⁺ cation radius (Shannon and Prewitt 1969) vs. enthalpy of formation is shown in Figure 3.

DISCUSSION

The recent report by Gysi and Jones (2015) on the thermodynamic properties of Ce-bastnaesite mineral with a composition (Ce_{0.5}La_{0.25}Nd_{0.20}Pr_{0.05}CO₃F), using DSC measurements with temperature ramp and under isothermal conditions yield an enthalpy of formation value of −1799.8 ± 11.9 kJ/mol. Here, the authors consider the enthalpy changes corresponding to the reaction RECO₃F → REOF + CO₂ that occurs at 824 K, for the calculation of formation enthalpy of the bastnaesite mineral. We calculated the formation enthalpy for this mineral phase from a mixture of fluorides, oxides, and CO₂ and the obtained value was −1803.7 kJ/mol. This indicates that the formation enthalpy values calculated in the present work for the end-members—LaCO₃F and CeCO₃F from a mixture of fluorides, oxides, and CO₂ indeed are reliable and can be used for the modeling of the

TABLE 5. Thermochemical cycle used to calculate enthalpies of formation of OH-bastnaesites

RECO ₃ OH (RE—La, Y, Nd, and Dy)		
(1)	RECO ₃ OH _(s, 25 °C) → 0.5RE ₂ O _{3(sol, 700 °C)} + CO _{2(g, 700 °C)} + 0.5H ₂ O _(g, 700 °C)	ΔH_1
(2)	RE ₂ O _{3(s, 25 °C)} → RE ₂ O _{3(sol, 700 °C)}	ΔH_2
(3)	H ₂ O _(l, 25 °C) → H ₂ O _(g, 700 °C)	ΔH_3
(4)	CO _{2(g, 25 °C)} → CO _{2(g, 700 °C)}	ΔH_4
(5)	2RE _(s, 25 °C) + 3/2O _{2(g, 25 °C)} → RE ₂ O _{3(s, 25 °C)}	ΔH_5
(6)	C _(s, 25 °C) + O _{2(g, 25 °C)} → CO _{2(g, 25 °C)}	ΔH_6
(7)	H ₂ + 1/2O _{2(g, 25 °C)} → H ₂ O _(l, 25 °C)	ΔH_7
(8)	0.5RE ₂ O _{3(s, 25 °C)} + CO _{2(g, 25 °C)} + 0.5H ₂ O _(l, 25 °C) → RECO ₃ OH _(s, 25 °C)	$\Delta H_{f,ox}$
(9)	RE _(s, 25 °C) + C _(s, 25 °C) + 1/2H _{2(g, 25 °C)} + 2O _{2(g, 25 °C)} → RECO ₃ OH _(s, 25 °C)	$\Delta H_{f,el}$
	$\Delta H_{f,ox} = -\Delta H_1 + 0.5\Delta H_2 + 0.5\Delta H_3 + \Delta H_4$ $\Delta H_{f,el} = \Delta H_{f,ox} + 0.5\Delta H_5 + 0.5\Delta H_6 + \Delta H_7$	
CeCO ₃ OH		
(1)	CeCO ₃ OH _(s, 25 °C) + 0.25O _{2(g, 700 °C)} → CeO _{2(sol, 700 °C)} + CO _{2(g, 700 °C)} + 0.5H ₂ O _(g, 700 °C)	ΔH_1
(2)	CeO _{2(s, 25 °C)} → CeO _{2(sol, 700 °C)}	ΔH_2
(3)	CO _{2(g, 25 °C)} → CO _{2(g, 700 °C)}	ΔH_3
(4)	O _{2(g, 25 °C)} → O _{2(g, 700 °C)}	ΔH_4
(5)	Ce ₂ O _{3(s, 25 °C)} + 0.5O _{2(g, 25 °C)} → 2CeO _{2(s, 25 °C)}	ΔH_5
(6)	H ₂ O _(l, 25 °C) → H ₂ O _(g, 700 °C)	ΔH_6
(7)	2Ce _(s, 25 °C) + 3/2O _{2(g, 25 °C)} → Ce ₂ O _{3(s, 25 °C)}	ΔH_7
(8)	C _(s, 25 °C) + O _{2(g, 25 °C)} → CO _{2(g, 25 °C)}	ΔH_8
(9)	H ₂ + 1/2O _{2(g, 25 °C)} → H ₂ O _(l, 25 °C)	ΔH_9
(10)	0.5Ce ₂ O _{3(s, 25 °C)} + CO _{2(g, 25 °C)} + 0.5H ₂ O _(l, 25 °C) → CeCO ₃ OH _(s, 25 °C)	$\Delta H_{f,ox}$
	$\Delta H_{f,ox} = -\Delta H_1 + \Delta H_2 + \Delta H_3 - 0.25\Delta H_4 + 0.5\Delta H_5 + 0.5\Delta H_6$ $\Delta H_{f,el} = \Delta H_{f,ox} + 0.5\Delta H_7 + 0.5\Delta H_8 + \Delta H_9$	

^a $\Delta H_{f,el}$ for CO₂ and H₂O is −393.51 ± 1.3 and −285.83 ± 0.42 kJ/mol, respectively (from Robie and Hemingway 1995).

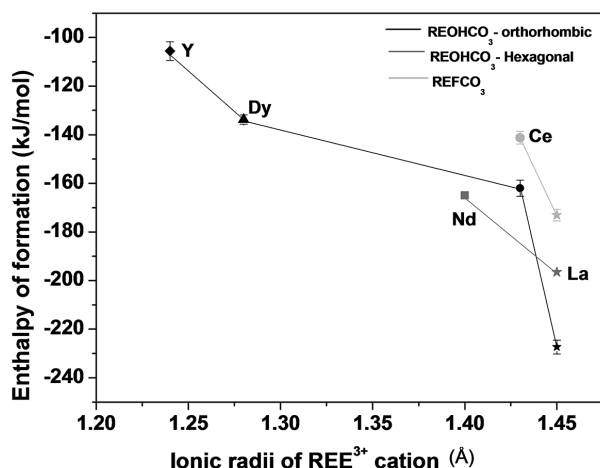


FIGURE 3. Enthalpy of formation of F/OH-bastnaesite as a function of ionic radii of RE^{3+} cation.

bastnaesite solid solution.

As seen from Figure 3, the formation enthalpies of the bastnaesite phases from RE_2O_3 , CO_2 , and H_2O or HF become increasingly negative with increase in ionic radius of the RE^{3+} cation. A similar general trend has been observed among several other ternary compounds of rare earths for a given structure, including phosphates, perovskites, aluminates, and silicates (Navrotsky 2001; Ushakov et al. 2001).

Among RE mineral phases, bastnaesite is the lowest temperature RE mineral and is stable within the garnet zone (Savko and Bazikov 2011). One of the hypotheses is that the bastnaesites could have been formed during metamorphism (Savko and Bazikov 2011). Quite similar to monazite, bastnaesites show light rare earth (LRE) selectivity and have a coordination number of 11 for RE cations. As temperature increases, bastnaesite is known to react with apatite to form monazite (Savko and Bazikov 2011; Smith et al. 1999), as represented by reaction 1.



To consider this reaction for different bastnaesites, we compare the enthalpy of formation of bastnaesites and RE phosphates. The trends in variation of formation enthalpy of monazite and bastnaesite for different RE are similar, see Figure 4a, where with increasing ionic radius of RE^{3+} , the formation enthalpy becomes more negative (this work; Ushakov et al. 2001). While the observed trends are similar, it is obvious that formation enthalpies from binary oxides are more negative for phosphates than for bastnaesites. Furthermore the difference in formation enthalpies of monazite and bastnaesite ($\Delta H_{\text{diff}} = \Delta H_{\text{f,monazite}} - \Delta H_{\text{f,bastnaesite}}$) for different RE gives an indication of the variation of enthalpy and free energy with RE for reaction 1, assuming the apatite, Ca-silicate, and fluid phases remain similar. A plot of difference in formation enthalpies of RE monazite and RE bastnaesite is shown in Figure 4b. The difference is least negative for both the F-bastnaesites, LaFCO_3 , and CeFCO_3 . The difference is comparatively more negative for OH-bastnaesites, with La being least and Y being

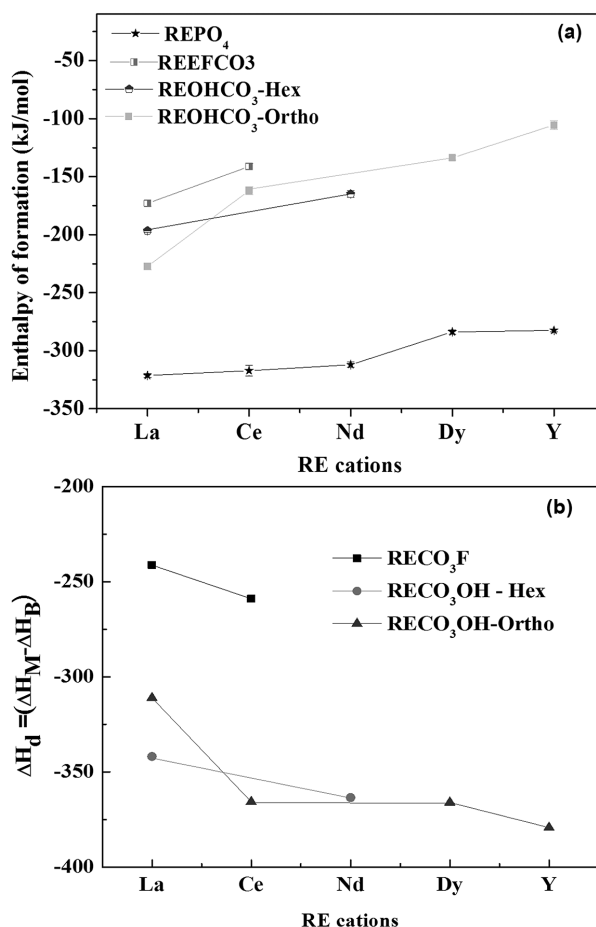


FIGURE 4. (a) A plot of enthalpy of formation values obtained for bastnaesite and monazite as a function of different RE. (b) A plot of difference in enthalpy of formation of bastnaesite and monazite calculated from elements for different REs.

most negative. The difference thus seems to become less negative with increasing radius of RE^{3+} , consistent with the LRE preference of bastnaesite. The least negative difference, observed for F-bastnaesite, both in case of La and Ce, supports the observation that natural bastnaesites are strongly Ce- and La-selective. Ce is the element that is most abundant in natural bastnaesites and La is the second. In some monazite deposits, the presence of F also indicates that monazite was formed at the expense of bastnaesite and apatite (Savko and Bazikov 2011; Smith et al. 1999), which is also supported by their energetic stabilities.

In nature F-bastnaesite is dominant and OH-bastnaesite is rare. OH-bastnaesites are known to occur only in low-temperature zones, which are essentially devoid of F. The stability relations at $P_f = 1$ kbar and $T = 400\text{--}900^\circ\text{C}$ in a part of (Ce,La)-F-H-C-O system indicate that the F-bastnaesites of both La and Ce have stability fields wider than their OH counterparts by 50 and 120 $^\circ\text{C}$, respectively (Hsu 1992). This finding is also supported by Haschke (1975). From the only two synthetic analogs available for comparison, it can be seen from Table 3 that the enthalpy of formation calculated from binary oxides of the OH-bastnaesites of both La and Ce are more negative than those of

their F counterparts calculated from a mixture of binary oxide and fluoride end-members. These values do not help for direct comparison, because they were calculated from different end-members. We thus compare the enthalpy of formation values calculated from elements for these phases as shown in Table 4 and 5. The enthalpies of formation calculated from elements indicate that the F-bastnaesites are more stable than their OH counterparts (last column of Table 3). Also, the enthalpy of reaction calculated for the conversion of RECO_3F to RECO_3OH , which corresponds to substitution of F^- by OH^- , is positive (Eq. 2) for both La and Ce (100.59 and 69.76 kJ/mol for La containing hexagonal and orthorhombic OH-polymorphs, respectively, and 106.49 kJ/mol for Ce). These positive values strongly suggest that the reaction is not spontaneous, because entropy effects are expected to be relatively small.



Thus the F-bastnaesites are thermodynamically more stable than their OH analogs. This observation explains why F-bastnaesite is more common in the Earth's crust than OH-bastnaesite and also explains the ease of formation of the former in laboratory conditions even under low F content in the aqueous phase.

IMPLICATIONS

While in reality bastnaesite is a complex solid solution with different RE and in some cases with both OH^- and F^- , in this paper we have reported the thermodynamic properties of F^- and OH^- end-members. The new data should be useful for modeling the formation of the mineral and leaching and processing of the ore. The calorimetric data confirm the increasing stability of bastnaesites with light rare earths and the greater stability and persistence to higher temperature of the fluoride end-members compared to the hydroxides, thus providing a thermodynamic justification for the pattern of bastnaesite occurrences in nature. The data provide a starting point for the modeling of complex bastnaesite solid solutions.

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REFERENCES CITED

Alonso, E., Sherman, A.M., Wallington, T.J., Everson, M.P., Field, F.R., Roth, R., and Kirchain, R.E. (2012) Evaluating rare earth element availability: a case with revolutionary demand from clean technologies. *Environmental Science and Technology*, 46, 3406–3414.

Chakhmouradian, A.R., and Wall, F. (2012) Rare earth elements: minerals, mines, magnets. *Elements*, 8, 333–340.

Donnay, G., and Donnay, J.D.H. (1953) The crystallography of bastnaesite, parisite, roentgenite, and synchisite. *American Mineralogist*, 38, 932–938.

Exley, R.A. (1980) Microprobe studies of REE-rich accessory minerals: Implications for Skye granite petrogenesis and REE mobility in hydrothermal systems. *Earth and Planetary Science Letters*, 48, 97–110.

Fleischer, M. (1978) Relative proportions of the lanthanides in minerals of the bastnaesite

group. *Canadian Mineralogist*, 16, 361–363.

Glass, J.J., and Smalley, R.G. (1945) Bastnaesite. *American Mineralogist*, 30, 601–615.

Gschneidner, K.A. (1981) Industrial Applications of Rare Earth Elements. ACS Symposium Series, 164, 1–297.

Haschke, J.M. (1975) The lanthanum hydroxide fluoride carbonate system: The preparation of synthetic bastnaesite. *Journal of Solid State Chemistry*, 12, 115–121.

Haschke, J.M., and Eyring, L. (1971) Hydrothermal equilibria and crystal growth of rare earth oxides, hydroxides, hydroxynitrates, and hydroxycarbonates. *Inorganic Chemistry*, 10, 2267–2274.

Head, E.L., and Holley, C.E. (1963) Rare-earth Carbonate, p. 51–63. *Rare Earth Research Proceedings of Third Conference*, Gordon and Breach, New York.

Hsu, L.C. (1992) Synthesis and stability of bastnaesites in a part of the system (Ce,La)-F-H-C-O. *Mineralogy and Petrology*, 47, 87–101.

Humphries, M. (2010) Rare Earth Elements: The Global Supply Chain. Congressional Research Service, The Library of Congress, Washington, D.C.

Janka, O., and Schleid, T. (2009) Facile synthesis of bastnaesite-type $\text{LaF}[\text{CO}_3]$ and its thermal decomposition to LaOF for bulk and Eu^{3+} -doped samples. *European Journal of Inorganic Chemistry*, 3, 357–362.

Jansen, G.J., Magin, G.B., and Levin, B. (1959) Synthesis of bastnaesite. *American Mineralogist*, 44, 180–190.

Keith, R.L. (2011) Principal Rare Earth Elements Deposits of the U.S.: A Summary of Domestic Deposits and a Global Perspective, 1–96. DIANE Publishing, 2011.

Lee, M.H., and Jung, W.S. (2013) Hydrothermal synthesis of LaCO_3OH and Ln^{3+} -doped LaCO_3OH powders under ambient pressure and their transformation to $\text{La}_2\text{O}_2\text{CO}_3$ and La_2O_3 . *Bulletin of the Korean Chemical Society*, 34, 3609–3614.

Lipin, B.R., and Mckay, G.A. (1989) Geochemistry and mineralogy of rare earth elements. *Reviews in Mineralogy*, 21, 259–302.

McLellan, B.C., Corder, G.D., and Ali, S.H. (2013) Sustainability of rare earths—An overview of the state of knowledge. *Minerals*, 3, 304–317.

Navrotsky, A. (1977) Progress and new directions in high temperature calorimetry. *Physics and Chemistry of Minerals*, 2, 89–104.

——— (1997) Progress and new directions in high temperature calorimetry: revisited. *Physics and Chemistry of Minerals*, 24, 222–241.

——— (2001) Systematic trends and prediction of enthalpies of formation of refractory lanthanide and actinide ternary oxide phases. *Ceramic Transactions*, 137–145.

——— (2014) Progress and new directions in calorimetry: a 2014 perspective. *Journal of American Ceramic Society*, 97, 3349–3359.

Pathak, A.K., Khan, M., Gschneider, K.A., McCallum, R.W., Zhou, L., Sun, K., Dennis, K.W., Zhou, C., Pinkerton, F.E., Kramer, M.J., and Pecharsky, V.K. (2015) Cerium: an unlikely replacement of dysprosium in high performance Nd-Fe-B permanent magnets. *Advanced Materials*, 27, 2663–2667.

Pradip (1981) The surface properties and flotation of rare earth minerals. Ph.D. thesis, University of California, Berkeley.

Pradip, Li, H.C.C., and Fuestenau, D.W. (2013) The synthesis and characterization of rare earth fluorocarbonates. *KONA Powder and Particle Journal*, 30, 193–200.

Robie, R.A., and Hemingway, B.S.S. (1995) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (105 pascals) pressure and at higher temperatures. *U.S. Geological Survey Bulletin* 2131, 468 p.

Savko, K.A., and Bazikov, N.S. (2011) Phase equilibria of bastnaesite, allanite, and monazite: bastnaesite-out isograd in metapelites of the Vorontsovskaya group, Voronezh crystalline massif. *Petrology*, 19, 445–469.

Shannon, R.D., and Prewitt, C.T. (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallographica*, B25, 927–946.

Smith, M.P., Henderson, P., and Peishan, Z. (1999) Reaction relationships in the Bayan Obo Fe-REE-Nb Deposit, Inner Mongolia, China: Implications for the relative stability of rare earth element phosphates and fluorocarbonates. *Contributions to Mineralogy and Petrology*, 134, 294–310.

Sun, J., Kyotani, T., and Tomita, A. (1986) Preparation and characterization of lanthanum carbonate hydroxide. *Journal of Solid State Chemistry*, 64, 94–99.

Ushakov, S.V., Helean, K.B., Navrotsky, A., and Boatner, L.A. (2001) Thermochemistry of rare-earth orthophosphates. *Journal of Materials Research*, 16, 2623–2633.

Vallina, B., Blanco, J.D.R., Blanco, J.A., and Benning, L.G. (2014) The effect of heating on the morphology of crystalline neodymium hydroxycarbonate, NdCO_3OH . *Mineralogical Magazine*, 78, 1391–1397.

Vlasov, K.A. (1964) Geochemistry, mineralogy and genetic types of deposits of rare elements. *Mineralogy of Rare Elements*, 2, 264.

Williams-Jones, A.E., and Wood, S.A. (1992) A preliminary petrogenetic grid for REE fluorocarbonates and associated minerals. *Geochimica et Cosmochimica Acta*, 56, 725–738.

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