

Energetics of hydroxylbastnäsite solid solutions, $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$

Vitaliy G. Goncharov^{a,b,c,d}, Haylea Nisbet^a, Andrew Strzelecki^{b,c,d},
Chris J. Benmore^e, Artaches A. Migdisov^a, Hongwu Xu^{a,f,*}, Xiaofeng Guo^{b,c,d,*}

^a Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States

^b Department of Chemistry, Washington State University, Pullman, WA 99164, United States

^c Alexandra Navrotsky Institute for Experimental Thermodynamics, Washington State University, Pullman, WA 99164, United States

^d Materials Science and Engineering Program, Washington State University, Pullman, WA 99164, United States

^e Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, United States

^f School of Molecular Sciences and Center for Materials of the Universe, Arizona State University, Tempe, AZ 85287, United States

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Abstract

Bastnäsites ($\text{LnCO}_3(\text{F},\text{OH})$) are a group of common rare earth elements (REE)-bearing minerals and are one of the primary global sources of REE. Due to the chemical similarities among REE, bastnäsites tend to occur as solid solutions instead of end members in REE containing ores. To better understand the processes and the mechanisms of formation of such deposits, it is essential to determine the thermodynamic properties of bastnäsites, including hydroxylbastnäsite (LnCO_3OH) solid solutions. In this work, we performed detailed structural and calorimetric investigations on synthetic hexagonal La–Nd hydroxylbastnäsite ($\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$, $x = 0, 0.25, 0.5, 0.75, 1$) solid solutions. X-ray diffraction confirms the crystal structure of the solid solution series in the $P6$ space group, and pair distribution function (PDF) analysis reveals local bonding environments characterized by three different types of 9-coordinated metal-oxygen polyhedra. Unit cell parameters of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ exhibit a nearly linear relation with the Nd content x , suggesting a random distribution of La and Nd in the structure. Their standard enthalpies of formation (ΔH_f°) were determined by high temperature oxide melt drop solution calorimetry, from which the enthalpies of mixing (ΔH_{mix}) were derived. The ΔH_{mix} can be fitted by a regular solution model with an interaction parameter of 12.58 ± 0.16 kJ/mol, suggesting enthalpic metastability of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ relative to the two endmembers. Combining entropy and enthalpy, we further estimated the Gibbs free energies of mixing (ΔG_{mix}) at relevant temperatures, revealing favorable temperatures under which the intermediate $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ phases can be stabilized. Such entropy-driven stabilization, as is consistent with our geochemical modeling results, may explain the enhancement of thermal stability of the solid solutions in nature. Additionally, the temperature range constrained from this study may be used to estimate the thermal history of REE bastnäsite deposit.

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Keywords: Hydroxylbastnäsite; Solid solution; Enthalpy of mixing; Configurational entropy; Thermal decomposition; Rare earth elements

1. INTRODUCTION

Rare earth elements (REE), including lanthanides (Ln) and Y, are of critical importance to the economy, renewable energy, and national security as they are vital components of many modern technologies such as phosphors, magnets,

* Corresponding authors at: Department of Chemistry, Washington State University, Pullman, WA 99164, United States (X. Guo).

E-mail addresses: hxu@lanl.gov (H. Xu), x.guo@wsu.edu (X. Guo).

electronics, catalysts, and ceramics (Adachi and Imanaka, 1998; Kagan, 2002; Hedrick, 2006; Gschneider et al., 2011; Gschneidner, 2011; McLellan et al., 2013; Pathak et al., 2015). This has led to a nearly exponential global increase in the demand of REE containing ores over the last 70 years (Zhou et al., 2017). Although REE are relatively abundant in the Earth's upper crust (a total average concentration of 169.14 ppm) (Rudnick and Gao, 2003; Zhou et al., 2017), concentrations of individual elements are highly variable. In general, the light rare earth elements (LREE: La–Gd), such as La and Ce (31 ppm and 63 ppm respectively), are considerably more abundant than heavy rare earth elements (HREE: Tb–Lu), such as Tm and Lu (0.30 ppm and 0.31 ppm respectively) (Lide, 2004; Long et al., 2010). Despite their relative abundance, the tendency for REE to concentrate in economically feasible quantities for extraction is rare (Zhou et al., 2017). In addition, due to similarities in their ionic radii in trivalent oxidation states (REE^{3+}) (Peters et al., 2020), the majority of REE minerals (e.g., bastnäsite, monazite, xenotime) are found as solid solutions. Therefore, chemistry structures and thermodynamics governing how the REE mix in the solid state plays an important role in controlling the formation and fractionation of REE in natural systems (Gramaccioli et al., 1999; Smith et al., 2000).

While there are more than 200 known REE containing minerals (Kanazawa and Kamitani, 2006; Goodenough et al., 2016), the majority of global REE supply comes from mining and processing four primary minerals: bastnäsite, monazite, xenotime, and loparite (Zhou et al., 2017; Anon, 2020). In the United States, the carbonatite hosted deposits of Mountain Pass are some the most developed sources of LREE in North America, where bastnäsite is the primary ore mineral. (Castor, 2008; Long et al., 2012; Xie et al., 2016). Both the Bayan Obo (Fan et al., 2016) and Maoniuping (Wang et al., 2001) deposits of China, are rich in bastnäsite and represent the current largest accessible REE sources in the world (Zhou et al., 2017). With a large portion of the global supplies of REE tied to bastnäsite (Williams-Jones and Wood, 1992; Schulz et al., 2019), it is imperative to develop a greater understanding of the physical and chemical properties of bastnäsite minerals. This will enable the development of more sophisticated and accurate generic models to better predict REE fractionation (Gysi and Williams-Jones, 2015; Migdisov et al., 2019; Schulz et al., 2019), ultimately enabling improved recovery margins.

Bastnäsites have a general chemical formula of $\text{Ln}(\text{CO}_3)(\text{OH}/\text{F})$, in which Ln are LREE, dominantly La, Ce, Pr, and Nd (Gysi and Williams-Jones, 2015; Shivaramaiah et al., 2016; Kim et al., 2018). Both bastnäsite (hexagonal, $P6_2m$ and $P6$) and kozoite (orthorhombic LnCO_3OH , $Pnma$ and $P2_12_12_1$) are thermodynamically stable at ambient and standard conditions (Kim et al., 2018). Although F-containing bastnäsites predominantly occur in nature (Williams-Jones and Wood, 1992; Zhongxin et al., 1992; Castor, 2008; Gysi and Williams-Jones, 2015), the OH-mineral forms LnCO_3OH , hydroxylbastnäsites, comprise an important group of LREE carbonate compounds due to i) their marked ambient stability (Rorif et al., 2005;

Vallina et al., 2014; Shivaramaiah et al., 2016; Kim et al., 2018) and ii) being crucial components of the ternary $\text{Ln}_2\text{O}_3 - \text{CO}_2 - \text{H}_2\text{O}$ system which is often encountered under geochemical conditions that drives Ln carbonate speciation (Rorif et al., 2005; Essington and Mattigod, 1985; Runde et al., 1992; Williams-Jones et al., 2012). Hydroxylbastnäsites also have simpler chemical compositions, which make them easier to synthesize in a laboratory setting for studying both their structural and thermodynamic properties (Szucs et al., 2021). This makes hydroxylbastnäsite an ideal system for systematic investigation of the bastnäsite mineral group, especially F-containing bastnäsites. (Hsu, 1992; Vallina et al., 2014; Kim et al., 2018; Szucs et al., 2021) Ultimately, studying hydroxylbastnäsite has implications towards developing a better prediction of Ln fractionation in natural systems and potential optimization of the Ln mineral extraction process (Cantrell and Byrne, 1987; Schmitt et al., 1991; Williams-Jones and Wood, 1992; Castor, 2008).

To date, there has been significant work on the determination of thermochemical properties of Ln-bearing carbonates end-members (Kim et al., 2018). The effects of heating on morphology of LnCO_3OH have been previously studied (Vallina et al., 2014; Szucs et al., 2021). The enthalpies of formations of several hydroxylbastnäsite and kozoite end-members have also been measured by calorimetric approaches, where a negative correlation between enthalpy of formation and Ln^{3+} ionic radius was revealed (Rorif et al., 2005; Shivaramaiah et al., 2016; Voigt et al., 2016; Kim et al., 2018). However, ambiguity remains on the thermodynamic stability between hydroxylbastnäsite and kozoite polymorphs. Solubility studies suggest that the hexagonal hydroxylbastnäsites are more stable than their orthorhombic kozoite counterparts (Rorif et al., 2005; Voigt et al., 2016), while the high temperature calorimetric study found the opposite (Shivaramaiah et al., 2016). A recent work by Szucs et al. in 2021 (Szucs et al., 2021) examining the solvent-mediated pseudomorphic mineral replacement of calcite by Ln-carbonates ($\text{Ln} = \text{La}, \text{Nd}, \text{Dy}$) demonstrated the following crystallization sequence occurring at low temperature hydrothermal conditions (50–220 °C): $\text{Ln}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ (lanthanite) $\rightarrow$ orth- LnCO_3OH (kozoite) $\rightarrow$ hex- LnCO_3OH (hydroxylbastnäsite). Alluding to the increased thermodynamic stability of hydroxylbastnäsite in relation to kozoite at low temperature hydrothermal conditions (Szucs et al., 2021), in agreement with high temperature calorimetric measurements (Shivaramaiah et al., 2016). Although these studies reveal the energetic trend of LnCO_3OH across the lanthanide series, they did not consider thermodynamic effects from mixing of multiple Ln cations in the hydroxylbastnäsite solid solution, which are dominantly occurring in mineral deposits (Maksimović and Pantó, 1985; Williams-Jones and Wood, 1992; Peishan et al., 1995; Schoneveld et al., 2015). These solid solutions may possess synergetic or competing enthalpic and entropic contributions (Guo et al., 2016), which can control phase equilibria of various Ln containing hydroxylbastnäsites (Kim et al., 2018). This, however, requires experimental validations to derive the thermodynamic models of various Ln cations in LnCO_3OH

(Christensen, 1973; Maksimović and Pantó, 1985; Williams-Jones and Wood, 1992; Gysi and Williams-Jones, 2015).

Moreover, Ln often function as surrogates for trivalent actinides in geological repositories (Du Fou de Kerdaniel et al., 2007; Guo et al., 2015; Tang et al., 2020; Strzelecki et al., 2020a). For example, Nd^{3+} has been shown to be an effective analog for Am^{3+} due to their similarities in ionic size, crystallographic behavior, and oxidation state (Carroll, 1993; Meinrath and Takeishi, 1993). Since geological repositories are likely to be located in hard rock below aquifers, gradual incursion of H_2O into the repository (re-saturation) is inevitable at time-scales required for the decay of nuclear fission products (Cho et al., 2014). The occurrence of CO_2 within repositories (formed by microbial or inorganic means) (Xiong and Lord, 2008), leads to the formations of low temperature CO_2 - H_2O hydrothermal conditions. Such conditions could have a significant impact on mobilization and transport of actinides with the surrounding environments (Witherspoon, 1991; Meinrath and Takeishi, 1993; Kalintsev et al., 2021; Nisbet et al., 2022). Hydroxylbastnäsites are thermodynamically stable components in the Ln_2O_3 - H_2O - CO_2 equilibrium systems. Thus, thermodynamic knowledge of LnCO_3OH can permit an evaluation of actinide behavior in H_2O - CO_2 environments relevant to geological nuclear waste storage conditions (Ringwood et al., 1979; Ewing et al., 2016).

Therefore, in this work, we systematically investigated both the structures and thermodynamics of hydroxylbastnäsite solid solutions by a combination of synchrotron X-ray diffraction and high temperature calorimetric techniques. Hexagonal $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$, $x = 0, 0.25, 0.5, 0.75$, and 1 (Fig. 1), were synthesized by hydrothermal methods. The crystal structure was determined by performing powdered X-ray diffraction (XRD) and pair distribution function (PDF) analysis. Thermal decomposition of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ under Ar was examined by thermal gravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) and evolved gas by mass spectrometry (MS). Finally, high temperature oxide melt drop solution calorimetry was used to determine the enthalpies of formation of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions from elements (ΔH°_f) and from constituent binary oxides ($\Delta H^\circ_{f,ox}$). Enthalpies of mixing (ΔH°_{mix}) of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ were then derived from the experimentally measured drop enthalpy values (ΔH°_{ds}). The outcome of this work provides fundamental thermodynamic data for the $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ system and proposes a thermodynamic rationale for hydroxylbastnäsite formation in natural systems. This study serves as the initial step towards future geochemical assessments of REE mineralization and fractionation within the greater bastnäsite mineral group.

2. EXPERIMENTAL METHODS

2.1. Synthesis

Hexagonal hydroxylbastnäsites in the stoichiometric form of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$, $x = 0, 0.25, 0.5, 0.75$, and 1, were synthesized via a previously reported hydrothermal

method (Vallina et al., 2015). 50 mM solutions of LaCl_3 and NdCl_3 (99.9%, anhydrous, Alfa Aesar) were mixed with 50 mM of a Na_2CO_3 solution by adding appropriate stoichiometric quantities for the desired phases. Immediately, an amorphous REE carbonate phase precipitated out of solution (Vallina et al., 2015). The resultant slurry was added to Teflon-lined titanium autoclaves and heated at 165 °C in a muffle furnace. The autoclaves were gently shaken every 10 mins for initial 60–100 mins of heating. After 1–14 weeks, the autoclaves were removed from the furnace and allowed to cool. Approximately, 3, 10 and 14 weeks were required for the desired synthesis of $\text{LaCO}_3\text{OH}/\text{NdCO}_3\text{OH}$ endmembers, $\text{La}_{0.25}\text{Nd}_{0.75}\text{CO}_3\text{OH}/\text{La}_{0.75}\text{Nd}_{0.25}\text{CO}_3\text{OH}$ and $\text{La}_{0.5}\text{Nd}_{0.5}\text{CO}_3\text{OH}$, respectively. Next, the products were filtered through glass vacuum filters set-up using 2.5 μm filter paper and rinsed several times with deionized water and isopropyl alcohol. The resultant powders were dried at room temperature for 12 hrs.

2.2. Characterization

Powder X-ray diffraction: $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ ($x = 0, 0.25, 0.5, 1$) samples were loaded into Kapton tubes and then transferred to beamline 6-IDD of the Advanced Photon Source (APS), Argonne National Laboratory. The wavelength of the X-ray was set to 0.123696 Å (100.233 keV). Two-dimensional (2D) diffraction images were collected using an amorphous Silicon area detector (Varex CT4343), and the geometric parameters calibrated by a CeO_2 standard. The sample to detector distance was fixed at 344 mm during the experiments. The samples were exposed to the incident X-rays for 10 s ($0.01 \text{ s} \times 1000$) to acquire diffraction images with sufficient ring intensities. The obtained 2D diffraction data were corrected for dark current, integrated and calibrated by General Structure Analysis System software version II (GSAS-II) (Toby et al., 2013) to obtain the patterns that are plotted as intensity as a function of Q ($\text{\AA}^{-1}$) (Fig. S1). Note, as a result of insufficient quantity of sample $\text{La}_{0.25}\text{Nd}_{0.75}\text{CO}_3\text{OH}$ at the time of the synchrotron XRD beamtime, we had to use the previous XRD data collected on a laboratory-based X-ray diffractometer (Bruker D8 Discover X-ray Diffractometer). The diffractometer used $\text{Cu K}\alpha_{1,2}$ radiation ($\lambda = 1.54184 \text{ \AA}$) and was equipped with a LynxEye position sensitive detector. The PXRD data were collected for approximately 1 hour in the range of $5^\circ \leq 2\theta \leq 70^\circ$ or $0.36 \text{ \AA}^{-1} \leq Q \leq 4.68 \text{ \AA}^{-1}$. All diffraction patterns were analyzed by the Rietveld method with GSAS-II, where the instrument parameters were fixed at those obtained by the fitted diffraction peaks of CeO_2 , the background by Chebyshev function (8 terms), and the peak profiles to pseudo-Voigt convolution functions (Thompson et al., 1987). The Rietveld refinements were performed to determine the crystal structures with R_{wp} ranging from 5.6% to 10.0% for high-energy XRD and 15.3% for lab-based XRD (Table 1). In additional, the pair distribution function (PDF) of X-ray scattering data was fitted using PDFgui (Farrow et al., 2007), from which $G(r)$ data were determined and plotted in Fig. S2 in Supporting Information (SI). Such procedures were also stated previously elsewhere (Xu et al., 2017; Guo

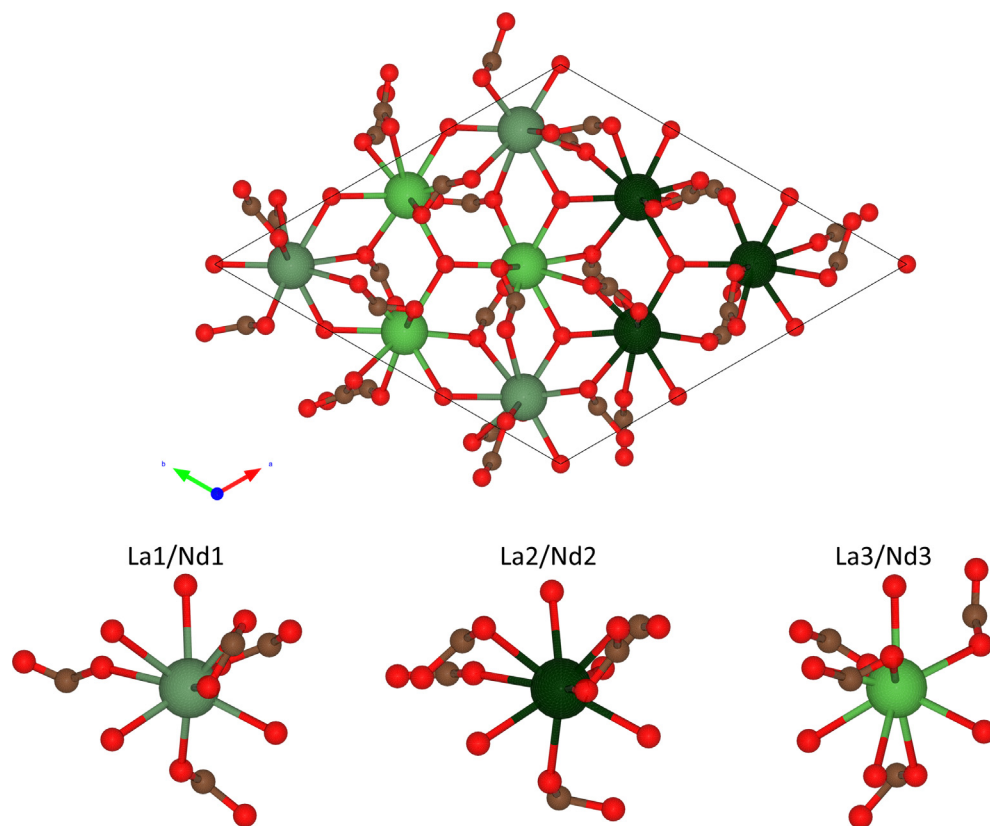


Fig. 1. Top: crystal structure of hexagonal REECO_3OH ; bottom: local REE coordination environments obtained from PDF analysis. Large green spheres – REE; small red spheres – O; small brown sphere – C.

Table 1
Summary of unit cell parameters and molar volumes of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$.

Formula	a (Å)	c (Å)	Volume (Å ³)	R_{wp} (%)
LaCO_3OH	12.622(4)	10.024(1)	1383.0(5)	5.55
$\text{La}_{0.75}\text{Nd}_{0.25}\text{CO}_3\text{OH}$	12.541(4)	9.984(1)	1359.9(5)	6.10
$\text{La}_{0.50}\text{Nd}_{0.50}\text{CO}_3\text{OH}$	12.450(8)	9.947(2)	1332.0(10)	6.63
$\text{La}_{0.25}\text{Nd}_{0.75}\text{CO}_3\text{OH}$	12.398(5)	9.925(1)	1321.2(6)	15.31
NdCO_3OH	12.351(2)	9.895(2)	1307.2(3)	7.38

et al., 2019b; Strzelecki et al., 2020b; Strzelecki et al., 2021; Marcial et al., 2021).

X-ray fluorescence: Chemical compositions and impurities of samples were examined by using a Bruker S2 PICO-FOX benchtop total reflection X-ray fluorescence (TXRF) spectrometer equipped with an air-cooled molybdenum X-ray source of 50 kV (Bruker Nano GmbH, 2010a). The instruments gain correction and resolution were calibrated prior to each series of measurements. Reusable quartz discs (3×30 mm) were employed for all measurements. No addition of an internal standard was added in this method. Measurements were collected while operating in “standardless mode” with the blank value being 0%. Each individual measurement had an acquisition time of 600 seconds. The spectra were preliminarily processed by Spectra 7 software using optimized Bayes fit technique (Bruker Nano GmbH, 2010b). Use of the Hephaestus database (Ravel and Newville, 2005) was ultimately employed in order to cor-

rectly assign the peaks presented in the XRF spectra to the appropriate fluorescence emission lines.

2.3. Thermodynamic investigations

Thermal analysis: Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ was conducted simultaneously on a TA Instrument Q600 SDT thermal analyzer with a heating rate of $10^\circ\text{C}/\text{min}$ to 900°C in a flow of ultrapure Argon (60 mL/min). The identities of evolved gases during thermal decomposition of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ were determined *in situ* by mass spectrometry (Discovery MS, TA Instruments). The sensitivity of the calorimeter was calibrated using the thermal decomposition of CaC_2O_4 and melting cycles of various metals, full description of which may be found elsewhere (Guo et al., 2014b; Olds et al., 2020; Strzelecki et al., 2020b).

High temperature oxide melt drop solution calorimetry: High temperature thermochemical experiments were performed utilizing a Calvet-type twin microcalorimeter (AlexSYS – 800) at LANL (Xu et al., 2015; Guo and Xu, 2017; Guo et al., 2018; Chung et al., 2019; Guo et al., 2019a). Dried powdered samples were pressed into ~ 5 mg pellets using a hand die. Pellets were then dropped from room temperature into the molten sodium molybdate ($3\text{NaO} \cdot 4\text{MoO}_3$) solvent (~ 15 g) contained within quartz crucibles at 700°C . A total of eight drops (four per side) were conducted per an experimental set up. O_2 gas was continuously flushed through the calorimetric chamber at 120 mL/min to maintain a constant gas environment over the solvent (Navrotsky et al., 1994). Upon the dissolution of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ pellets in the solvent, the enthalpy of drop solution (ΔH_{ds}) was obtained. The complete dissolution of trivalent Ln compounds has been previously confirmed in molten $3\text{NaO} \cdot 4\text{MoO}_3$ solvent allowing effective determination of ΔH_{ds} values (Ushakov et al., 2001; Zhang and Navrotsky, 2004; Cheng et al., 2005; Guo et al., 2014a; Guo et al., 2015; Qi et al., 2015; Strzelecki et al., 2020a; Strzelecki et al., 2020b). Instrument calibration procedures and in-depth descriptions of the calorimetric methodologies may be found in previous reports (Navrotsky, 2014; Guo et al., 2019a; Voskanyan et al., 2020).

Thermodynamic calculation for geochemical equilibrium modeling: The calculations were performed using Hch/Unitherm code (Shvarov and Bastrakov, 1999; Shvarov, 2010). The models used here were designed to evaluate the stability field of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ as a function of temperature from room temperature to 450°C , where the regular solution model determined from calorimetry was used. In highly simplified hypothetical geochemical scenarios, we have the following solid phases to be evaluated: LaCO_3OH , NdCO_3OH , and two solid solutions $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$, from reaction of NaHCO_3 and $\text{LaCl}_3/\text{NdCl}_3$ aqueous solutions. Due to the lack of the thermodynamic parameters of

Ln containing phases, determination of their estimate values was discussed in SI. Results of Hch/Unitherm modeling are deposited in *Research Data*.

3. RESULTS

LaCO_3OH and NdCO_3OH were analyzed for elemental purity via TXRF (Figs. S3 and S4). Due to the use of quartz discs for a sample substrate and silicone-based vacuum grease as an adhesion material, both spectra have a peak located at 1.74 keV, and are assigned to Si $K\alpha_{1,2}$. In addition, each spectrum has a peak located 2.96 keV (Ar argon $K\alpha_{1,2}$), corresponding to atmospheric argon. All other peaks are diagnostic of the elemental composition of the sample. For the TXRF spectrum of LaCO_3OH (Fig. S3), all sample-related peaks can be assigned to La. However, the spectrum of NdCO_3OH presented in Fig. S4 contains a single peak attributed to La $L\alpha_2$. Such impurity is a possible residual La in the synthesis reagent (NdCl_3) or a presence of minor La contamination on the TXRF sample holder (quartz disc). The quantification of La by the Spectra 7 TXRF software (Bruker Nano GmbH, 2010b) indicated less than 0.4 mol % La, which was not expected to significantly influence the enthalpic signature of NdCO_3OH (influence of possible contamination falls within the measurement uncertainty).

The XRD patterns (Figs. 2 and S1) indicate that synthesized $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions and endmembers are all single phases (space group $P\bar{6}$) belonging to LaCO_3OH , $\text{La}_{0.75}\text{Nd}_{0.25}\text{CO}_3\text{OH}$, $\text{La}_{0.5}\text{Nd}_{0.5}\text{CO}_3\text{OH}$, $\text{La}_{0.25}\text{Nd}_{0.75}\text{CO}_3\text{OH}$, and NdCO_3OH as determined by stoichiometric metal ratios of precursors used in the synthesis (Vallina et al., 2014; Shivaramaiah et al., 2016). The refined unit cell parameters and molar volumes are given in Table 1 and plotted in Fig. 3. The unit cell parameters a and c of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solution endmembers (Table 1) are in general agreement with those previously determined for

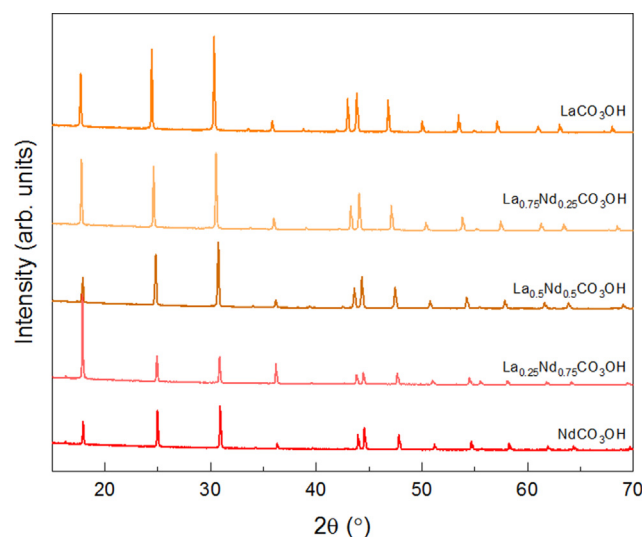


Fig. 2. XRD patterns of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions. All samples are phase pure and have XRD peaks consistent with the hexagonal $P\bar{6}$ space group.

the hexagonal polymorphs of LaCO_3OH and NdCO_3OH (Michiba et al., 2011; Shivaramaiah et al., 2016; Kim et al., 2018).

The results of TGA–DSC–MS experiments conducted up to 900 °C under Ar are shown in Fig. 4 and summarized in Table 2. The thermal decompositions of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions and two endmembers, LaCO_3OH and NdCO_3OH follow the standard decomposition pathway previously reported for dehydrated hydroxylbastnäsites (Kim et al., 2018).

High temperature oxide melt drop solution calorimetry was conducted on the dried as-synthesized samples to directly measure the enthalpy of drop solution (ΔH_{ds}) of each $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ sample. ΔH_{ds} values were then used in thermochemical cycles (Table 3), in combination with other reference ΔH_{ds} values and auxiliary data, to derive the enthalpy of mixing (ΔH_{mix}), the enthalpy of formation from constituent oxides ($\Delta H_{\text{f,ox}}$), and the standard enthalpy of formation from the elements ($\Delta H_{\text{f}}^\circ$) (Table 4).

4. DISCUSSION

4.1. Chemical and crystallographic analyses

Both of the unit cell parameter a and c were found to exhibit a nearly linear decrease with increasing Nd concentration (Fig. 3a). For the a unit cell parameter this was to occur from 12.622 Å (LaCO_3OH) to 12.351 Å (NdCO_3OH), while the unit cell parameter c was from 10.024 Å (LaCO_3OH) to 9.895 Å (NdCO_3OH). The reduction in the unit cell parameters upon substitution of La by Nd primarily arises from the smaller ionic radius of Nd^{3+} (1.163 Å) compared to La^{3+} (1.216 Å). However, the reduction in unit cell parameters was found to occur anisotropically as a parameter decreases $\sim 2.1\%$ as function of Nd content, while the c parameter decreases only $\sim 1.3\%$ as a function of Nd content. Moreover, the PDF analysis from the X-ray total scattering data resolved the first coordination shells of La- or Nd-centered polyhedra. Three different

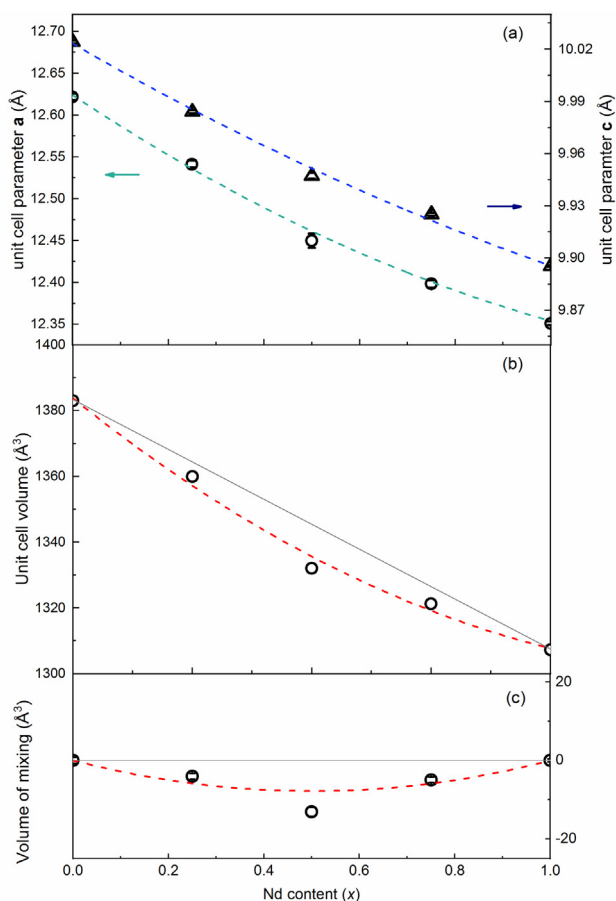


Fig. 3. Refined unit cell parameters of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions: (a) a and c parameters fitted to equations $(12.624 \pm 0.005) + (-0.38 \pm 0.03) \cdot x + (0.10 \pm 0.03) \cdot x^2$ (adjusted $R^2 = 0.9982$), and $(10.023 \pm 0.003) + (-0.16 \pm 0.02) \cdot x + (0.03 \pm 0.01) \cdot x^2$ (adjusted $R^2 = 0.9981$), respectively. Circles and triangles represent the a and c parameters respectively, with arrows denoting each to the appropriate numerical axis (a parameter left, and c parameter right); (b) cell volume V_{cell} fitted by Eq. (1) with an adjusted $R^2 = 0.9854$; (c) volume of mixing ΔV_{mix} fitted by equation $\Delta V_{\text{mix}} = (-31 \pm 6) \cdot x(1 - x) \text{ Å}^3$, with an adjusted $R^2 = 0.8095$.

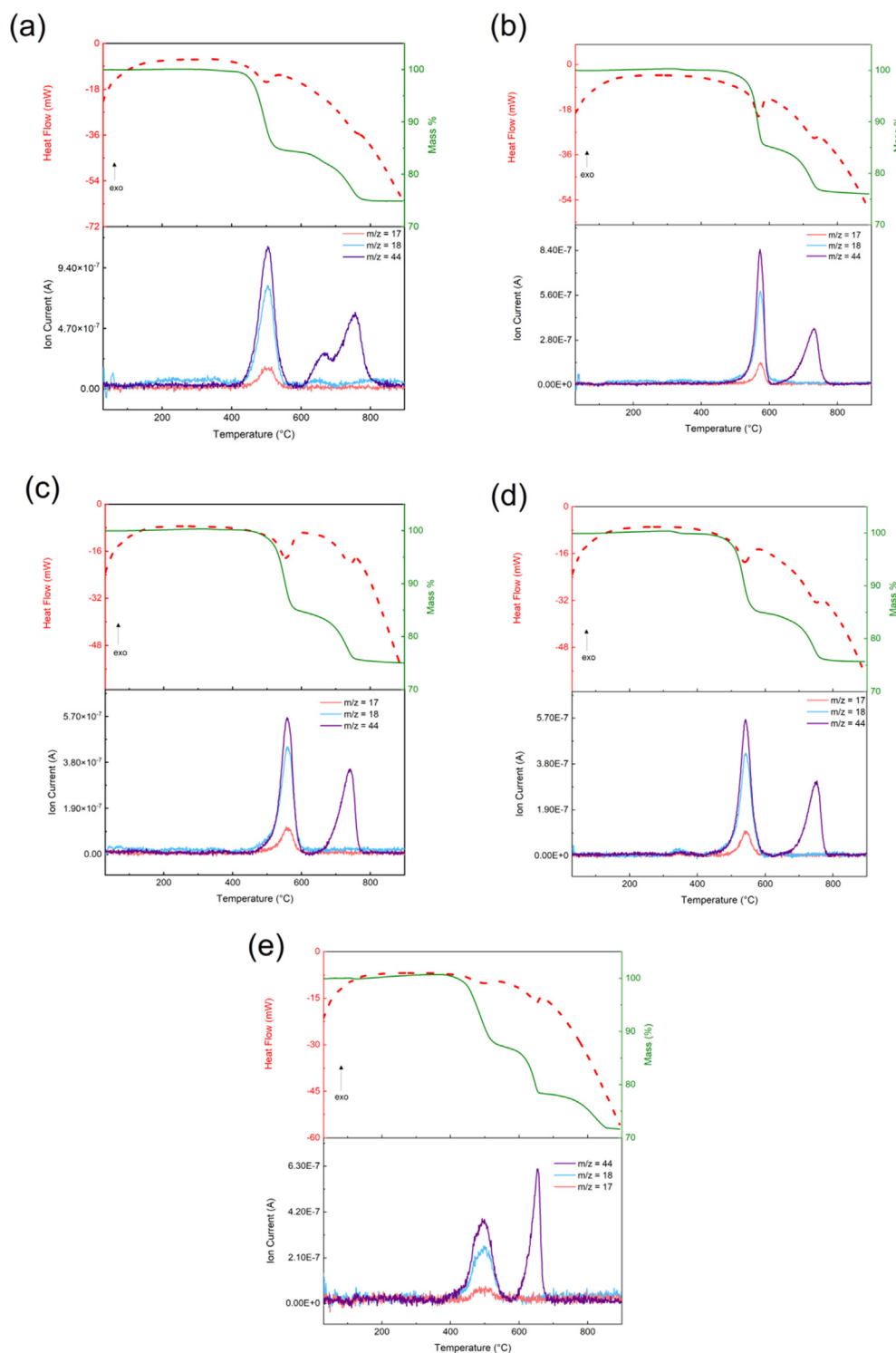


Fig. 4. TGA-DSC-MS curves of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions. Green solid and red dashed curves represent mass change and heat flow signals, respectively. The primary MS signals detected during the thermal decompositions are $m/z = 44$, $m/z = 18$ and $m/z = 17$ corresponding to CO_2 , H_2O , and OH , respectively. (a) LaCO_3OH . (b) $\text{La}_{0.75}\text{Nd}_{0.25}\text{CO}_3\text{OH}$. (c) $\text{La}_{0.5}\text{Nd}_{0.5}\text{CO}_3\text{OH}$. (d) $\text{La}_{0.25}\text{Nd}_{0.75}\text{CO}_3\text{OH}$. (e) NdCO_3OH .

9-coordinated metal polyhedra were identified (Fig. 1), each coordinated with three monodentate and one bidentate carbonate ligands, and three more oxygen connected to other type metal cations. This local structure is consistent with

the crystal structure proposed by Michiba et al. (Michiba et al., 2011) while deviating from earlier works (Christensen, 1973; Kutlu and Meyer, 1999). In comparison, the monoclinic $\text{La}_{1-x}\text{Nd}_x\text{PO}_4$ (monazite, space group

Table 2

TGA results of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ under Ar correlating experimental and theoretical mass loss % accompanying thermal decomposition.

Decomposition Steps	Temperature (°C)	Experimental Weight loss (%)	Theoretical weight loss (%)	Difference (%)
$\text{LaCO}_3\text{OH} \rightarrow \text{La}_2\text{O}_2\text{CO}_3$	462	–15.88	–14.36	1.52
$\text{La}_2\text{O}_2\text{CO}_3 \rightarrow \text{La}_2\text{O}_3$	630	–9.19	–10.19	1.00
$\text{La}_{0.75}\text{Nd}_{0.25}\text{CO}_3\text{OH} \rightarrow (\text{La}_{0.75}\text{Nd}_{0.25})_2\text{O}_2\text{CO}_3$	514	–15.87	–14.28	1.59
$(\text{La}_{0.75}\text{Nd}_{0.25})_2\text{O}_2\text{CO}_3 \rightarrow (\text{La}_{0.75}\text{Nd}_{0.25})_2\text{O}_3$	697	–8.45	–10.13	1.68
$\text{La}_{0.5}\text{Nd}_{0.5}\text{CO}_3\text{OH} \rightarrow (\text{La}_{0.5}\text{Nd}_{0.5})_2\text{O}_2\text{CO}_3$	528	–15.72	–14.19	1.53
$(\text{La}_{0.5}\text{Nd}_{0.5})_2\text{O}_2\text{CO}_3 \rightarrow (\text{La}_{0.5}\text{Nd}_{0.5})_2\text{O}_3$	705	–9.23	–10.07	0.84
$\text{La}_{0.25}\text{Nd}_{0.75}\text{CO}_3\text{OH} \rightarrow (\text{La}_{0.25}\text{Nd}_{0.75})_2\text{O}_2\text{CO}_3$	530	–15.83	–14.10	1.72
$(\text{La}_{0.25}\text{Nd}_{0.75})_2\text{O}_2\text{CO}_3 \rightarrow (\text{La}_{0.25}\text{Nd}_{0.75})_2\text{O}_3$	685	–8.09	–10.00	1.92
$\text{NdCO}_3\text{OH} \rightarrow \text{Nd}_2\text{O}_2\text{CO}_3$	440	–13.38	–14.02	0.64
$\text{Nd}_2\text{O}_2\text{CO}_3 \rightarrow \text{Nd}_2\text{O}_3$	615	–9.02	–9.94	0.92

Table 3

Thermochemical cycles for $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ based on high temperature oxide melt drop solution calorimetry in molten $3\text{NaO} \cdot 4\text{MoO}_3$ solvent at 700 °C.

Reaction	ΔH (kJ/mol)
(1) $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ (s, 25 °C) $\rightarrow$ $(1-x)/2 \text{La}_2\text{O}_3$ (sln, 700 °C) + $x/2 \text{Nd}_2\text{O}_3$ (sln, 700 °C) + $1/2 \text{H}_2\text{O}$ (g, 700 °C) + CO_2 (g, 700 °C)	$\Delta H_1 = \Delta H_{\text{ds}}^*$
(2) H_2O (l, 25 °C) $\rightarrow$ H_2O (g, 700 °C)	$\Delta H_2 = 69.00$ (Chase, 1998)
(3) CO_2 (g, 25 °C) $\rightarrow$ CO_2 (g, 700 °C)	$\Delta H_3 = 31.95$ (Chase, 1998)
(4) La_2O_3 (s, 25 °C) $\rightarrow$ La_2O_3 (sln, 700 °C)	$\Delta H_4 = -225.10 \pm 3.16$ (Cheng et al., 2005)
(5) Nd_2O_3 (s, 25 °C) $\rightarrow$ Nd_2O_3 (sln, 700 °C)	$\Delta H_5 = -163.36 \pm 3.44$ (Ushakov et al., 2001)
(6) $3/2 \text{O}_2$ (g, 25 °C) + 2La (s, 25 °C) $\rightarrow$ La_2O_3 (s, 25 °C)	$\Delta H_6 = -1791.6 \pm 2.0$ (Konings et al., 2014)
(7) H_2 (g, 25 °C) + $1/2 \text{O}_2$ (g, 25 °C) $\rightarrow$ H_2O (l, 25 °C)	$\Delta H_7 = -285.83$ (Chase, 1998)
(8) O_2 (g, 25 °C) + C (s, 25 °C) $\rightarrow$ CO_2 (g, 25 °C)	$\Delta H_8 = -393.52$ (Chase, 1998)
(9) $3/2 \text{O}_2$ (g, 25 °C) + 2Nd (s, 25 °C) $\rightarrow$ Nd_2O_3 (s, 25 °C)	$\Delta H_9 = -1807.95 \pm 0.92$ (Fitzgibbon et al., 1968)

Enthalpy of mixing of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ from LaCO_3OH and NdCO_3OH

$$\Delta H_{\text{mix}}(\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}) = -\Delta H_1 + (1-x) \Delta H_{\text{ds}}(\text{LaCO}_3\text{OH})^* + x \Delta H_{\text{ds}}(\text{NdCO}_3\text{OH})^*$$

Enthalpy of formation of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ from La_2O_3 , Nd_2O_3 , H_2O , and CO_2 at 25 °C

$$\Delta H_{\text{f,ox}}(\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}) = -\Delta H_1 + 1/2 \Delta H_2 + \Delta H_3 + (1-x)/2 \Delta H_4 + x/2 \Delta H_5$$

Standard enthalpy of formation of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$

$$\Delta H_{\text{f}}^\circ(\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}) = \Delta H_{\text{f,ox}} + (1-x)/2 \Delta H_6 + 1/2 \Delta H_7 + \Delta H_8 + x/2 \Delta H_9$$

* Experimentally measured in this work and presented in Table 4.

$\text{P2}_1/\text{n}$ solid solution has linear decreases in the unit cell parameters with increasing Nd content (Schlenz et al., 2019). Similar trends have been observed for other LnPO_4 solid solutions (Clavier et al., 2011; Heuser et al., 2018; Zaman and Antao, 2020).

The findings of the anisotropic contraction of the a and c unit cell parameters are likely attributed to other inherent structural effects of the system (Michiba et al., 2011; Shivaramaiah et al., 2016). Recent work (Shivaramaiah et al., 2016) suggested that the hexagonal hydroxyl-

bastnäsites have a similar sublattice for OH^- , but not isostructural to that of F^- in the fluoride-bastnäsite counterparts. The major difference arises from the orientation of the OH^-/F^- anion in relation to the REE cation-containing plane (Fig. 1). OH^- in hexagonal LaCO_3OH and NdCO_3OH are not coplanar to the REE cations (unlike the F^- in bastnäsites) and likely to have the ability to form hydrogen bonds with the adjacent oxygens of the carbonate polyhedra (Michiba et al., 2011; Shivaramaiah et al., 2016). Because the hexagonal hydroxylbastnäsite

Table 4

Enthalpies of drop solution (ΔH_{ds}), enthalpies of formation of hexagonal $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ from corresponding oxides ($\Delta H_{f,ox}$), and standard enthalpy of formation (ΔH_f°).

Sample	ΔH_{ds} (kJ/mol)	$\Delta H_{f,ox}$ (kJ/mol)	ΔH_f° (kJ/mol)
LaCO_3OH	$150.91^a \pm 1.07^{b(4)^c}$	-197.0 ± 1.9	-1629.3 ± 2.2
	$150.57 \pm 0.45^*$	$-196.6 \pm 1.6^*$	$-1628.8 \pm 2.5^*$
$\text{La}_{0.75}\text{Nd}_{0.25}\text{CO}_3\text{OH}$	$148.45^a \pm 0.63^{b(4)^c}$	-186.8 ± 1.3	-1621.1 ± 1.5
$\text{La}_{0.5}\text{Nd}_{0.5}\text{CO}_3\text{OH}$	$147.29^a \pm 0.94^{b(4)^c}$	-178.0 ± 1.5	-1614.3 ± 1.6
$\text{La}_{0.25}\text{Nd}_{0.75}\text{CO}_3\text{OH}$	$147.94^a \pm 0.77^{b(4)^c}$	-170.9 ± 1.6	-1609.3 ± 1.6
NdCO_3OH	$150.11^a \pm 0.48^{b(4)^c}$	-165.3 ± 1.8	-1605.8 ± 1.9
	$149.90 \pm 2.52^*$	$-165.0 \pm 3.1^*$	$-1604.9 \pm 5.7^*$

^a Averaged value.

^b Two standard deviations of the average value.

^c Number of measurements.

* Previously measured by high temperature drop solution calorimetry (Shivaramaiah et al., 2016).

polymorphs consist of alternating layers of 9-coordinated REE linked by carbonate anions, hydrogen bonding interactions of OH^- with adjacent oxygens of the carbonate polyhedra may result in a unique distortion of that polyhedra, leading to complexity of vibrational signatures of hexagonal hydroxylbastnäsites (Michiba et al., 2011; Shivaramaiah et al., 2016). Additionally, if the formations of these hydrogen bond interactions have a directional preference, it could also induce anisotropic behavior in elastic properties of hydroxylbastnäsites (Santos-Martins and Forli, 2020).

As the Nd content increases, the unit cell volume of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ decreases ($\sim 5.4\%$ from LaCO_3OH to NdCO_3OH), with a slightly negative deviation from Vegard's law (Vegard, 1921; Chai and Navrotsky, 1996), which can be described by Eq. (1):

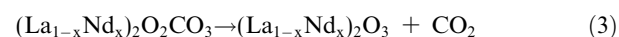
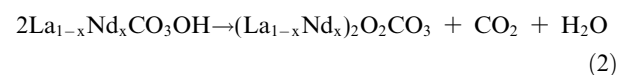
$$V_{\text{cell}} = a + bx + cx^2 \quad (1)$$

where $a = 1383.8 \pm 3.4 \text{ \AA}^3$, $b = -116.5 \pm 16.1 \text{ \AA}^3$, $c = 40.4 \pm 15.4 \text{ \AA}^3$, and an adjusted $R^2 = 0.9861$ (Fig. 3). Then the volume of mixing is given by $\Delta V_{\text{mix}} = (-31 \pm 6) \cdot x(1 - x) \text{ \AA}^3$, and is only slightly negative compared to the large unit cell volumes. A negative deviation of ΔV_{mix} from Vegard's law may be due to: *i*) local range ordering of mixed cations; *ii*) difference in bonding character of the mixed cations (Le Tonquess et al., 2019); *iii*) distortions of metal polyhedral coordination sites (Chizmeshya et al., 2003; Marcial et al., 2021). Due to the small negativity in linear deviation ($\sim 1\%$ of the total unit cell volume) and the similarity in ionic radii, short-range ordering is not expected. Second, the negative volume of mixing of Nd and La in $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ due to the difference of La^{3+} and Nd^{3+} bonding character is also unlikely due to lanthanide contraction, with their coordination behavior largely dictated by ionic radius (Karraker, 1970; Polinski et al., 2012). The slightly negative deviation of ΔV_{mix} is likely explained by the ability of the Ln coordinated OH^- groups to form hydrogen bonds with adjacent oxygens leading to slight polyhedral distortions. Due to the presence of three different types of Ln coordination environments (Fig. 1), it is difficult to ascertain the exact role of hydrogen bonding within the $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ structure. The greater reduction in the unit cell parameter a compared to c (with increasing Nd con-

tent) suggests that hydrogen bonding may likely occur along the a direction, parallel to the plane of the 9-coordinant REE-sheets. This may cause the contraction of the lattice (Aakeröy et al., 1992) unaccounted for by the ionic size differences between La^{3+} and Nd^{3+} and a slightly negative deviation in ΔV_{mix} from Vegard's law. Thus, we concluded that the mixing of La and Nd follows a near-random distribution in the metal sublattice of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$. This implies that the configurational entropy generated from the mixing of La and Nd can be well-approximated by the Boltzmann entropy formula. Although, additional studies such as computationally assisted total neutron scattering (Marcial et al., 2021) are required to validate the origin of the $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ slight deviation from Vegard's Law.

4.2. Thermal decomposition and thermal stability

The stepwise thermal decomposition of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ in an inert environment is represented by reactions (2) and (3):



Noted that the intermediate product $(\text{La}_{1-x}\text{Nd}_x)_2\text{O}_2\text{CO}_3$ only represents the mass stoichiometry derived from TGA and is not a conclusive determination; and the final product $(\text{La}_{1-x}\text{Nd}_x)_2\text{O}_3$ is assumed to be a sesquioxide solid solution (Collongues, 1992; Schweda and Kang, 2005). The summary of the thermogravimetric analysis and the representative onset temperatures of decomposition reactions are presented in Table 2. Decomposition of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ via reactions (2) and (3) is well explained by the close agreement between the experimental and theoretical weight loss % determined by TGA and supported by the evolved gas analysis by MS (Fig. 4).

To further evaluate the thermal decomposition process of hexagonal $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ and to attain higher confidence about the onset temperatures of reactions (2) and (3), the MS signal of decarbonation ($m/z = 44$) was further deconvoluted using normal distributions ($R^2 \geq 0.99$,

Figs. S5 – S9), each of which corresponds to step-wise release of CO_2 from thermal decarbonation (Head and Holley, 1962; Head and Holley, 1963; D'Assunção et al., 1993). For instance, in the thermal decomposition of LaCO_3OH (Fig. 4a, MS deconvoluted in Fig. S5), the broad heat flow peak around 470 °C is concurrent with the first $m/z = 44$ MS peak, suggesting two kinetic processes for the first decarbonation reaction (Hinode et al., 1990; D'Assunção et al., 1993). This is largely in agreement with previous thermal decomposition studies on REE hydroxycarbonates (Head and Holley, 1962; Head and Holley, 1963; Hinode et al., 1990; D'Assunção et al., 1993). However, high heating rate (≥ 10 °C/min) was known to make identifications of intermediate carbonate phases difficult (Kim et al., 2018). Thus, other intermediate carbonate phases not represented in reactions (2) and (3) may also be possible during decomposition (Hinode et al., 1990; Sharma et al., 1991). The integration of the deconvoluted $m/z = 44$ MS curves allows for approximating mole concentration of carbon lost during each deconvoluted step (Table S1), which corresponds well to the theoretical values from reactions (2) and (3). The only exception is the decomposition of NdCO_3OH (Fig. 4e, MS deconvoluted in Fig. S9), which has an additional mass loss event with an onset of 775 °C. That decomposition step corresponds to a mass loss of ~ 6 wt. % and is not accompanied by a CO_2 signal on the MS (or any other signal in the atomic mass range of 1 to 100 amu) or an apparent heat flow peak on the DSC. The additional mass loss step has been previously observed (Shivaramaiah et al., 2016), but its physical origin remains unclear.

Fig. 5 shows the onset temperatures of the decomposition reactions of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$. The decomposition temperatures of LaCO_3OH and NdCO_3OH agree with those previously determined, which decrease as the atomic

number of REE increases (Wilfong et al., 1964; Charles, 1965; Hinode et al., 1990; De Almeida et al., 2012; Kim et al., 2018). The decomposition temperatures of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions, however, exhibit a deviation towards higher temperature from that established trend. These average decomposition temperatures were fitted by an inverted second-order polynomial function (Fig. 5). Such enhanced resistance to thermal decomposition may be a result of entropically driven stabilization, with the maximum decomposition temperatures at $x = 0.5$ reflecting the theoretical configurational entropic maximum for the binary regular solid-solution system. Further support of this phenomenon can be observed from previous TGA-MS studies (Maksimović and Pantó, 1985) (Ar atmosphere and 10 °C/min heating rate) conducted on a rare naturally occurring Nd-hydroxylbastnäsite with the chemical composition of $(\text{Nd}_{0.41}\text{La}_{0.36}\text{Pr}_{0.11}\text{Sm}_{0.06}\text{Gd}_{0.02}\text{Eu}_{0.02}\text{Ca}_{0.01})_{\Sigma 0.99}(\text{CO}_3)_{1.03}[(\text{OH})_{0.55}\text{F}_{0.38}]_{\Sigma 0.93}$ (origins of this mineral will be further described in the *Geochemical implications* section). This mineral has nearly equimolar concentrations of Nd and La, while containing additional REE within its solid solution, and thus, serves as an excellent naturally occurring analog to our synthetic $\text{La}_{0.50}\text{Nd}_{0.50}\text{CO}_3\text{OH}$ sample. By comparing their onset decomposition temperatures (Fig. 4c, Table 2), very good agreements were reached for the onset temperatures of the two steps and the evolved gas content (CO_2 and H_2O). There are also slight increases in thermal stability (~ 24 and ~ 41 °C for the first and second steps, respectively) in the natural Nd-hydroxylbastnäsite, presumably due to the increased entropic effects from multiple REE mixing and additional F content, the latter of which additionally contributes to the formation of oxyfluorides (Gysi and Williams-Jones, 2015) before the second-stage decomposition that delays further thermal decomposition.

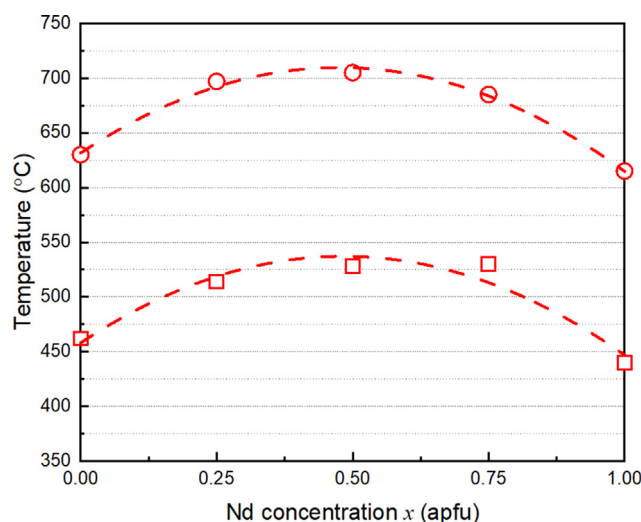


Fig. 5. Onset temperatures of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ decomposition based on TGA. The onset temperatures of the first decomposition step (reaction (2)) are represented as red squares. The onset temperatures of the second decomposition step (reaction (3)) are represented as light red circles. T1 and T2 curves are the representative onset temperatures for reactions (2) and (3), respectively. The onset of reaction (2) is fit by $T1 = -(338.4 \pm 64.3) \cdot x^2 + (327.1 \pm 67.0) \cdot x + (458.1 \pm 14.1)$ (adjusted $R^2 = 0.8668$). The onset of reaction (3) is fit by $T2 = -(345.1 \pm 21.0) \cdot x^2 + (328.3 \pm 21.9) \cdot x + (631.7 \pm 4.6)$ (adjusted $R^2 = 0.9857$).

The above discoveries emphasize two conclusions for thermal stability of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$. First, the thermal decomposition temperature of the solid solutions and their endmembers are below 475 °C under ambient pressure, confirming hydroxylbastnäsites to be low-temperature (low-T) mineral phases. Although the decomposition temperature may increase under hydrothermal (elevated P-T) conditions, these results in general support the previous hypothesis on the thermal stability of bastnäsites that OH-phases exist only in low-T environments while F-phases are stable at magmatic conditions (Hsu, 1992; Anenburg et al., 2020). Second, the entropic contribution can stabilize naturally occurring hydroxylbastnäsite solid solutions to relatively high temperatures compared to endmembers by ~ 70 °C near the equimolar of La and Nd where mixing effect is maximized. Noted such entropic effects could be greatly enhanced if more REE cations mix in the matrix (see Boltzmann entropy formula, e.g., Eq. (6)), such as in natural hydroxylbastnäsites where inclusion of several REE (particularly La, Ce, Pr, Nd) are observed (Yang, 2008; Anenburg et al., 2018; Kozlov et al., 2020; Anenburg et al., 2020). The entropically driven thermal stabilization may explain the higher decomposition temperature found in a natural fluoride-bastnäsite-(Ce) sample (Gysi and Williams-Jones, 2015), where the first onset temperature of such F-bastnäsite was reported to be 550 °C, about 100 °C above those of La- and Nd-rich hydroxylbastnäsites. The reported ~ 100 °C enhancement in thermal stability may again be a result of entropic stabilization due to the mixing of Ce, La, Nd, and Pr in fluoride-bastnäsite-(Ce).

4.3. Enthalpic determination, mixing model, and thermodynamic assessment

The enthalpies of formation of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ from binary oxides and from elements at room temperature

and under the standard condition (Table 3) were derived from experimentally measured ΔH_{ds} , $\Delta H_{\text{f,ox}}$ of two endmembers, LaCO_3OH and NdCO_3OH , obtained in this work are -197.0 ± 1.9 kJ/mol and -165.3 ± 1.8 kJ/mol, respectively, in excellent agreement with those previously determined (-196.6 ± 1.6 kJ/mol and -165.0 ± 3.1 kJ/mol, respectively) (Shivaramaiah et al., 2016). In addition, there is a negative correlation between $\Delta H_{\text{f,ox}}$ of hydroxylbastnäsite and the effective ionic radius of Ln (Fig. 6c), which is also in agreement with previous studies (Shivaramaiah et al., 2016). This implies that REE with larger ionic radii (such as La or Ce) may provide enthalpic stabilization to minor concentrations of other less energetically stable Ln species (e.g., HREE) within the LnCO_3OH phase. The dependence of $\Delta H_{\text{f,ox}}$ against Nd concentration can be fitted by the following polynomial function:

$$\Delta H_{\text{f,ox}} = a' + b'x + c'x^2 \quad (4)$$

where $a' = -197.07 \pm 0.10$ kJ/mol, $b' = 44.41 \pm 0.45$ kJ/mol, $c' = -12.67 \pm 0.42$ kJ/mol, with an adjusted $R^2 = 0.9999$. $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions all have $\Delta H_{\text{f,ox}}$ significantly below zero suggesting their thermodynamic stability compared to their corresponding binary oxides.

On the other hand, despite the demonstrated stability of OH-bastnäsites, their natural presence are still relatively rare compared to the dominating F-rich bastnäsite minerals (Williams-Jones and Wood, 1992; Hsu, 1992). This could be due to the narrower stability fields of OH-bastnäsites than those of F-bastnäsites, suggested by previous calorimetric studies on both OH- and F-bastnäsites (Fig. 7) (Shivaramaiah et al., 2016; Voigt et al., 2016). LaCO_3F has $\Delta H_{\text{f}}^\circ = -1729.4 \pm 2.7$ kJ/mol (Shivaramaiah et al., 2016), which is more negative than that of LaCO_3OH , $\Delta H_{\text{f}}^\circ = -1629.3 \pm 2.2$ kJ/mol, measured in this work.

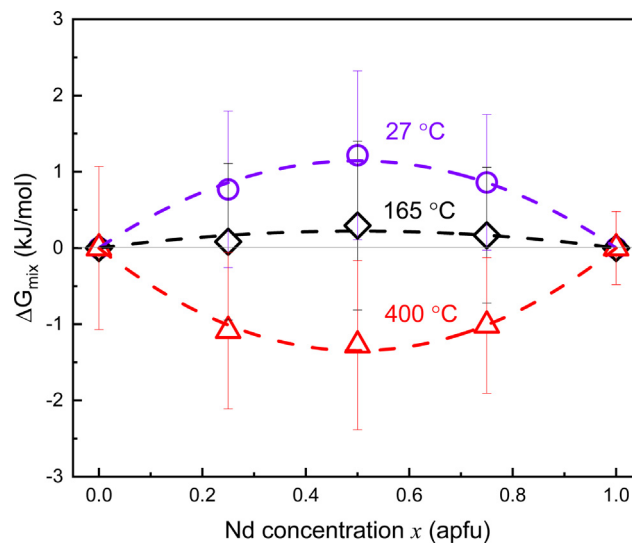


Fig. 6. (a) Enthalpies of drop solution fitted by $\Delta H_{\text{ds}} = (150.98 \pm 0.10) - (13.52 \pm 0.44) \cdot x + (12.65 \pm 0.38) \cdot x^2$ (adjusted $R^2 = 0.9984$). (b) Enthalpies of mixing fitted by $\Delta H_{\text{mix}} = (12.58 \pm 0.16) \cdot x \cdot (1 - x)$ (adjusted $R^2 = 0.9989$). (c) Enthalpy of formation of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ from their corresponding binary oxides at 25 °C, fitted by $\Delta H_{\text{f,ox}} = -(197.07 \pm 0.10) + (44.41 \pm 0.45) \cdot x - (12.67 \pm 0.42) \cdot x^2$ (adjusted $R^2 = 0.9999$).

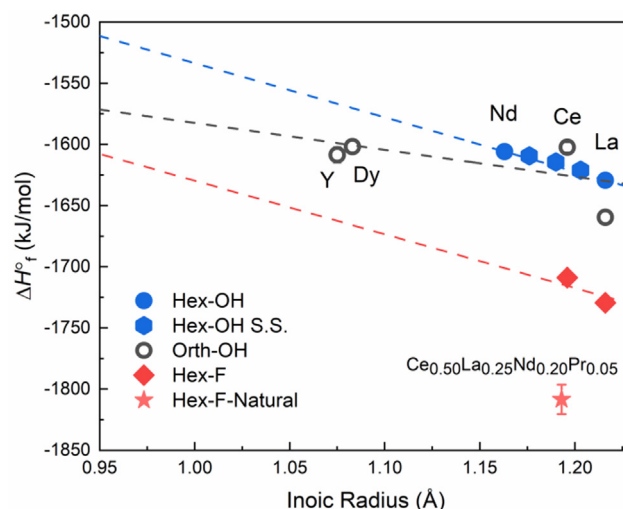


Fig. 7. The standard enthalpy of formation was plotted against the averaged ionic radius of Ln components. ΔH_f° of hexagonal LnCO_3OH and hexagonal $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions are denoted as *blue squares* and *blue hexagon*, respectively. The *blue dash* line was a linear fitting based on the hexagonal LnCO_3OH data. Orthorhombic LnCO_3OH was denoted as *black circle*, with a *black dashed* linear fitting line describing the enthalpic trend. Two hexagonal LnCO_3F were denoted as *red rhomboids* and a naturally occurring bastnäsite ($\text{Ce}_{0.5}\text{La}_{0.25}\text{Nd}_{0.2}\text{Pr}_{0.05}\text{CO}_3\text{F}$) by an *orange star*. Here the *red dashed* line has the same slope of the *blue dashed* line, which was not derived based on the fitting of just the two data, but was shown here as a qualitative comparison of the general enthalpic trend of F-bastnäsites with their and OH-counterparts. Enthalpic values of orthorhombic LnCO_3OH and hexagonal LnCO_3F ($\text{Ln} = \text{La}, \text{Ce}$) are extracted from (Shivaramaiah et al., 2016), and the enthalpic value of $\text{Ce}_{0.5}\text{La}_{0.25}\text{Nd}_{0.2}\text{Pr}_{0.05}\text{CO}_3\text{F}$ was extracted from (Gysi and Williams-Jones, 2015).

However, the energetic landscape of F-bastnäsites only was only extrapolated from two experimental (La and Ce) results. Additionally, the relative stability of LnCO_3F may also be favored by the entropic effect. This is because that the decomposition of one mole of fluoride-bastnäsite to Ln_2O_3 , LnF_3 and CO_2 yields only one mole of CO_2 gas, while that of hydroxylbastnäsite yields two moles of gases (CO_2 and H_2O). Thus, decomposition of hydroxylbastnäsites is more favorable to occur from an entropic perspective, resulting in relatively lower thermodynamic stabilities.

The enthalpies of mixing (ΔH_{mix}) were directly derived from ΔH_{ds} values (plotted in Fig. 6a) using the thermochemical relations in Table 3. Values of ΔH_{mix} are plotted in Fig. 6b and fitted by the quadratic polynomial function (with an adjusted $R^2 = 0.9989$) assuming a regular solution model:

$$\Delta H_{\text{mix}} = \Omega \cdot x(1 - x) \quad (5)$$

where $\Omega = 12.58 \pm 0.16$ kJ/mol, is the regular solution parameter that quantifies the extent of non-ideality in the mixing of La and Nd in $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$. This small positive value of Ω indicates that the mixing of La and Nd is weakly endothermic, indicating that $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solution is slightly metastable compared to the physical mixture of LaCO_3OH and NdCO_3OH . It also implies a $\text{La}^{3+} - \text{Nd}^{3+}$ miscibility gap within the hydroxylbastnäsite structural matrix at ambient conditions (Glynn, 2000). This finding may be counterintuitive because all naturally occurring hydroxylbastnäsites are found as solid solutions (Maksimović and Pantó, 1985; Williams-Jones and Wood, 1992; Peishan et al., 1995). The positive ΔH_{mix} may be attributed to the lattice effects originated from the near-

random distribution of La and Nd in metal sublattices. Previous and current crystallographic studies demonstrated that the hexagonal LnCO_3OH structure (space group $P\bar{6}$) consists of nine coordinated Ln (tricapped trigonal prisms) forming layers of carbonate linked $2_{\infty}[(\text{OH})\text{Ln}_{3/3}]^{2+}$ ions (Michiba et al., 2011; Shivaramaiah et al., 2016). Substituting La (1.216 Å) by the smaller cation Nd (1.163 Å) can cause a slight reduction in the Ln–O bond length, leading to the contraction of the hexagonal unit cell (non-isotropic reduction in both a and c parameters) and a certain degree of lattice strain contributing to the weakly endothermic enthalpy of mixing (Yi et al., 2018). Such a hypothesis may also be appropriate to explain the origin of the high content of La (and Ce with 1.196 Å as the ionic radii of its trivalent state) in naturally occurring hydroxylbastnäsites. Since trivalent La and Ce are the softer Ln Lewis acids, they are favored by the large nine coordinated crystallographic sites (Michiba et al., 2011; Kim et al., 2018), and can attenuate the lattice strain induced by the minor presence of heavier Ln to attain phase stability.

Similar results have been reported on REE phosphate systems by calorimetric studies. For instance, in the monazite (LnPO_4 , space group $P2_1/n$) solid solutions, Popa et al. determined the interaction parameters $\Omega = 14.0 \pm 4.1$ kJ/mol, 13.9 ± 8.3 kJ/mol and 23.8 ± 8.7 kJ/mol for $\text{La}_{1-x}\text{Nd}_x\text{PO}_4$, $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$, and $\text{La}_{1-x}\text{Gd}_x\text{PO}_4$, respectively (Popa et al., 2007). Neumeier et al. have determined interaction parameters $\Omega = 2.5 \pm 2.6$ kJ/mol and 11.4 ± 3.1 kJ/mol for $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$ and $\text{La}_{1-x}\text{Gd}_x\text{PO}_4$, respectively (Neumeier et al., 2017). Noted that the magnitude of the interaction parameter obtained by Popa et al. for the $\text{La}_{1-x}\text{Nd}_x\text{PO}_4$ is in good agreement with that of the hexagonal $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ determined in this work. This may be

due to the similar elastic lattice strains in the nine-coordinated environment where metal cations mix, which is commonly shared by monazite and hydroxylbastnäsite in spite of their significant crystallographic differences. When higher REE (smaller ionic radii) are incorporated into the 9-coordinated sites of hydroxylbastnäsite or monazite structures, lattice strain accompanied by an enthalpic penalty is induced on the lattice giving rise to unfavorable enthalpies of mixing (Popa et al., 2007; Migdisov et al., 2019). The interaction parameter of monazite has a positive correlation with the difference between the ionic radii of mixed components (Popa et al., 2007; Mogilevsky, 2007; Neumeier et al., 2017; Migdisov et al., 2019), which could also be translated to the hydroxylbastnäsite systems.

Furthermore, the interaction parameter can be empirically related to the molar volume (V_m), the difference in the molar volume of the solid solution endmembers (ΔV_m), and their corresponding Young's moduli (E) (Brice, 1975; Mogilevsky, 2007; Kowalski and Li, 2016). Currently, there are no experimentally measured elastic moduli of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$, which, however, may still be estimated through an empirical relation developed for the monazite system: $E \approx 4.8 + 110.6 \cdot r$, where E is the Young's modulus (GPa) and r denotes the ionic radius (Å) of REE (Mogilevsky, 2007). Using this relation, we estimated the Young's modulus of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ ($x = 0.5$) to be 136.4 GPa (see details in the SI). Using the estimated E , we further calculated the interaction parameter of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ based on an empirical relation: $U_e = \frac{E}{6V_m}(\Delta V_m)^2$, where $U_e \approx \Omega$ is the elastic energy (kJ/mol) associated with cation substitution within a lattice and directly to the interaction parameter (SI) (Brice, 1975;

Kowalski and Li, 2016). The calculated Ω based on the estimated E , 5.4 kJ/mol, only represents the elastic term that originates from the volume of mixing, and thus is lower than our calorimetrically determined value ($\Omega = 12.58 \pm 0.16$ kJ/mol). Although the discrepancy may be also due to *i*) the differences in crystallographic and chemical properties between $\text{CO}_3\text{OH}^{3-}$ (hydroxylbastnäsite) and PO_4^{3-} (monazite, xenotime), which may result in inaccurate predictions using the above model to the hydroxycarbonate systems, and *ii*) the lack of experimental data of Young's moduli that can benchmark the empirically derived values.

To further evaluate the thermodynamics of cationic mixing in $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$, the Gibbs free energy of mixing (ΔG_{mix}) was estimated using the regular solution model, where the configurational entropy of mixing ($\Delta S_{\text{mix,config}}$) of La^{3+} and Nd^{3+} in the metal crystallographic sites was calculated using the Boltzmann entropy formula:

$$\Delta S_{\text{mix,config}} = -R \cdot [(1-x) \cdot \ln(1-x) + x \cdot \ln(x)] \quad (6)$$

The vibration entropy of mixing at room temperature ($\Delta S_{\text{mix,vib}}$) can be estimated by using an empirical relation of standard entropy of formation (S_{298}° K) to the molar volume (V_m) of a compound, and is represented by Eq. (7) (Jenkins and Glasser, 2003):

$$S_{298}^\circ \text{ K} / J \cdot K^{-1} \text{ mol}^{-1} = k \cdot (V_m / \text{formula unit})^3 + c \quad (7)$$

where k and c are the correlation coefficients, 1.262 ± 0.028 / $J \cdot K^{-1} \text{ mol}^{-1}$ and 13 ± 5 / $J \cdot K^{-1} \text{ mol}^{-1}$, respectively, and formula unit volume V_m is obtained from the experimentally obtained unit cell volume (in Å³) (Table 1) of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ divided by the z number (18 formula units per unit cell). This value largely reflects the change

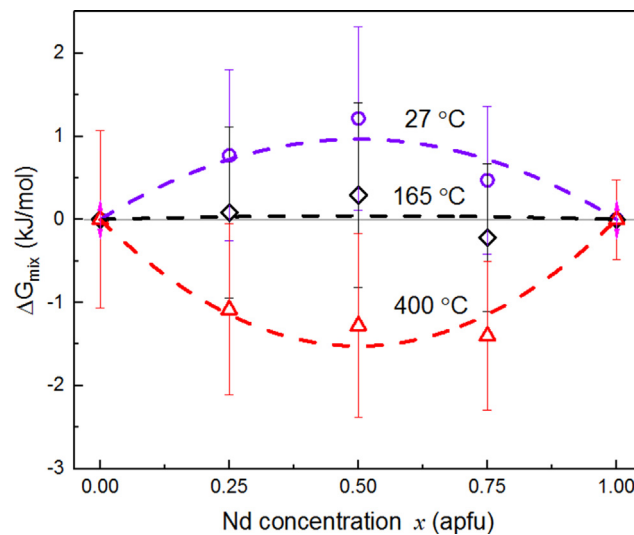


Fig. 8. Estimated trends of Gibbs free energy of mixing (ΔG_{mix}) based on experimentally measured ΔH_{mix} and calculated $\Delta S_{\text{mix,tot}}$ using Eq. (6) and the empirical relation (Eq. (7)) (Jenkins and Glasser, 2003) based on molar volumes (V_m) as obtained from the refinement of XRD results (Table 1). Purple circles represent values calculated at ambient temperature (27 °C) and are fitted by $\Delta G_{\text{mix}} = (4.57 \pm 0.15) \cdot x \cdot (1-x)$ (adjusted $R^2 = 0.9933$). Black rhomboids represent values calculated at synthesis temperature (165 °C) and are fitted by $\Delta G_{\text{mix}} = (0.89 \pm 0.15) \cdot x \cdot (1-x)$ (adjusted $R^2 = 0.8615$). Red triangles represent values calculated at 400 °C, which is relevant for hydrothermal formation (Hou et al., 2009) and are fitted by $\Delta G_{\text{mix}} = -(5.38 \pm 0.14) \cdot x \cdot (1-x)$ (adjusted $R^2 = 0.9960$). All ΔG_{mix} values were calculated assuming ΔH_{mix} and $\Delta S_{\text{mix,tot}}$ values do not change with temperature.

in the vibrational entropy based on the volumetric change of lattice, and has been successfully applied to estimate $S^{\circ}_{298 \text{ °K}}$ for a variety of mineral types (Jenkins and Glasser, 2003). The calculated $S^{\circ}_{298 \text{ °K}}$ for $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ are presented in Table S2. By calculating the difference between $S^{\circ}_{298 \text{ °K}}$ of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ and endmembers (LaCO_3OH and NdCO_3OH), an approximate $\Delta S^{\circ}_{\text{mix,vib}}$ can be extracted and combined with the configurational $\Delta S^{\circ}_{\text{mix,config}}$ to yield an appropriate estimate for the total entropy of mixing, $\Delta S^{\circ}_{\text{mix,tot}}$ (Table S2). Here $\Delta S^{\circ}_{\text{mix,config}}$ values are in general a magnitude larger than those of $\Delta S^{\circ}_{\text{mix,vib}}$, suggesting that configurational entropy is the dominant entropic force facilitating mixing in this system. Thus, only $\Delta S^{\circ}_{\text{mix,config}}$ was considered in the following thermodynamic assessment of Gibbs free energy of mixing. The Gibbs free energies of mixing, $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S^{\circ}_{\text{mix,tot}}$, at 27 °C, 165 °C, and 400 °C were then obtained and plotted in Fig. 8. These temperatures were chosen to evaluate phase equilibria under ambient, synthetic, and high temperature geothermal conditions (German and Von Damm, 2003). At 27 °C, ΔG_{mix} is positive for all compositions of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ with a maximum value of 1.26 ± 1.11 kJ/mol at $x = 0.5$. This suggests that mixing of La and Nd is not spontaneous at ambient temperature, and the formation of exsolution is thermodynamically favorable. When temperature increases to 165 °C, ΔG_{mix} is close to zero for all solid solutions ($\Delta G_{\text{mix}} = 0.08 \pm 1.03$ kJ/mol, 0.29 ± 1.11 kJ/mol, and 0.17 ± 0.89 kJ/mol at $x = 0.25, 0.50$ and 0.75 , respectively). Observations during sample synthesis support this thermodynamic assessment indicating that the equimolar $\text{La}_{0.5}\text{Nd}_{0.5}\text{CO}_3\text{OH}$ composition was the most challenging phase to synthesize (requiring ~ 14 weeks at 165 °C). However, at temperatures above 250 °C (e.g., ~ 400 °C) where natural bastnäsite ores typically form (Hou et al., 2009), ΔG_{mix} of all compositions are negative, suggesting that $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions may form spontaneously from the corresponding hydroxylbastnäsite endmembers in a hypothetical thermodynamic scenario. This implies that stabilization of hexagonal hydroxylbastnäsite solid solutions is driven by entropic effects, in agreement with the onset thermal decomposition temperature trends determined from TGA (Fig. 5). Particularly, $\text{La}_{0.5}\text{Nd}_{0.5}\text{CO}_3\text{OH}$ that maximizes configuration entropy ($x = 0.5$) has the onset of the decomposition of 528 °C, which is higher than the decomposition temperatures of LaCO_3OH and NdCO_3OH endmembers by 66 °C and 88 °C, respectively (Table 2).

4.4. Geochemical implications

The discovery of entropic stabilization of bastnäsite solid solutions at elevated temperatures (>165 °C) has important implications for understanding the mechanisms controlling formation of bastnäsites in natural systems. This is because our calorimetric data suggest a miscibility gap between the La- and Nd-endmembers, while in natural systems, bastnäsites occur exclusively as solid solutions with La, and Nd as typical compositionally dominant components (Gysi and Williams-Jones, 2015; Wang et al., 2020), so entropic contribution must play a major role in stabiliz-

ing the solid solutions at elevated temperatures, which also implies the conditions for natural formation of bastnäsites. Recent modeling work by Liu et al. in 2020 (Liu et al., 2020) has demonstrated that pressure variations have minimal impacts on the paragenesis of LREE minerals (including bastnäsites), with temperature and compositional fluctuations dictating the associated metasomatic processes. Combined with our experimentally determined temperature of hydroxylbastnäsite decomposition (475 ~ 530 °C), this permits to narrow down the temperature interval at which these minerals may be formed in nature. It is therefore tempting to model the formation of hydroxylbastnäsites and to estimate the minimum temperature required for the stabilization of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions under pseudo-natural (La^{3+} and Nd^{3+} are the only REE present) hydrothermal conditions.

To accomplish this, we modelled precipitation of hydroxylbastnäsites triggered by mixing of 10 ml La- and Nd-bearing chloride solution (pH ~ 7) with 1000 ml of carbonate-bearing solution containing NaHCO_3 , to simulate their formations as a function of temperature under relevant natural conditions. The model of aqueous solution involved H^+ , OH^- , O_2 , H_2 , Na^+ , NaOH , NaCl , CO_2 , CO_3^{2-} , HCO_3^- , Cl^- , HCl , NaCO_3 , NaHCO_3 , La^{3+} , LaCO_3^+ , LaHCO_3^{2+} , LaOH^{2+} , LaO^+ , LaOOH , Nd^{3+} , NdOH^{2+} , $\text{Nd}(\text{OH})_3$, $\text{Nd}(\text{OH})_2^+$, NdCO_3^+ , NdHCO_3^{2+} , LaCl^{2+} , NdCl^{2+} , LaCl_2^+ , and NdCl_2^+ . Thermodynamic data were taken from Helgeson et al., 1981; Kestin et al., 1984; Shock and Helgeson, 1988; Oelkers and Helgeson, 1990; Oelkers and Helgeson, 1991; Johnson et al., 1992; Haas et al., 1995; Shock et al., 1997; Sverjensky et al., 1997; Holland and Powell, 1998; Wood et al., 2002; Migdisov et al., 2009. The solid phases accounted for by the model were represented by La- and Nd-enriched hydroxylbastnäsite solid solutions, where the standard enthalpies for pure endmembers and mixing parameters derived in this study were used. It should be noted, that thermodynamic model also requires knowledge of heat capacities (C_p) and standard entropies ($S^{\circ}_{298 \text{ °K}}$, Table S2). However, as a result of the of the experimental data on C_p for these hydroxylbastnäsite phases, we used Neumann-Kopp's rule (Leitner et al., 2013) to estimate the heat capacity functions based on the known C_p of $\text{Ln}(\text{OH})_3$, Ln_2O_3 , and CO_2 , (Chase, 1998; Diakonov et al., 1998; Konings et al., 2014); the details are discussed in SI. Using the Hch/Unitherm code, (Shvarov and Bastrakov, 1999; Shvarov, 2010) and the regular solution model (Eq. (5)) we performed thermodynamic calculations to evaluate changes in compositions of hydroxylbastnäsite solid solutions as a function of temperature from 25 to 450 °C. The thermodynamic parameters used for modeling solid solutions are summarized in Table S3 in SI. Considering the highly approximate nature of both the entropy and heat capacity used in our calculations, we would like to caveat the outcome of the model presented here as preliminary. There are thus a need for experimental refinements of each of these parameters to develop accurate models of hydroxylbastnäsite formation at elevated temperatures.

The compositional temperature dependence of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ under equilibrium with aqueous

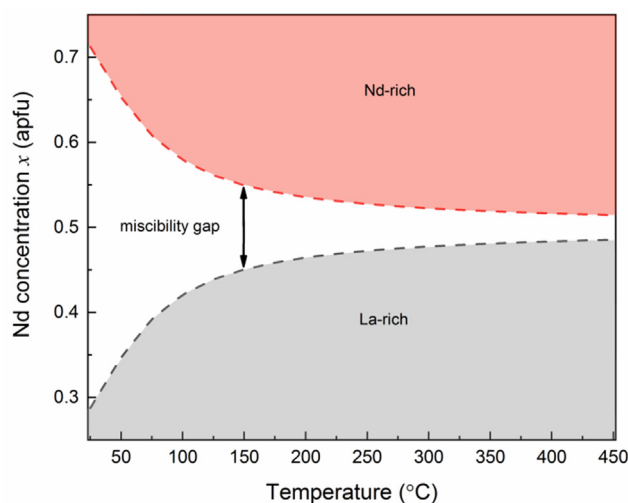


Fig. 9. The concentration of Nd in the Nd- and La-rich hydroxylbastnäsite (initially at 25 °C) as a function of temperature when in equilibrium with NaHCO_3 and $\text{LaCl}_3/\text{NdCl}_3$ solutions, where the regular solution model determined from calorimetric work is used. The reversed but same concentration is reported for La in these two hydroxylbastnäsite solid solutions (initially at 25 °C), which is not shown in this figure. The raw data for plotting this Fig. can be found in SI (Table S4).

NaHCO_3 and La, Nd-chlorides is demonstrated in Fig. 9 (with detailed results presented in Table S4 in SI). The starting solid phases in equilibrium with the solutions at 25 °C are La- and Nd-rich hydroxylbastnäsites, which have 71.2 mol % La and Nd, respectively. With increasing temperature, there is a significant decrease in the miscibility gap between La and Nd within the $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ matrix. At 450 °C, the stabilization of nearly equimolar solid solutions was found to occur (La and Nd are 51.5 and 48.5 mol %, respectively in the La-rich hydroxylbastnäsite, and *vice versa* for Nd-rich counterpart). This conclusion further suggests that temperature variance of ΔG_{mix} (discussed above) dictates the formation of the solid solution above 165 °C (Fig. 8). Note the results are based on the mixing model established at 25 °C, which may change at elevated temperatures.

Using these findings, our results can be utilized to gain an approximate understanding of the formational conditions of a given deposit, based on the effects of temperature on the overall favorability of ΔG_{mix} . An example of which is demonstrate by the rare authigenic Nd-dominant hydroxylbastnäsite found in the bauxites deposit near Nikšić, Montenegro (Zagrad deposit) (Maksimović and Pantó, 1985). The deposit is a red karstic bauxite of the Jurassic period (Maksimović and Pantó, 1985). As the mineral is authigenic, it can be used in order to understand the diagenetic conditions of the deposit. The elemental composition of this Nd-hydroxylbastnäsite was determined to be $(\text{Nd}_{0.41}\text{La}_{0.36}\text{Pr}_{0.11}\text{Sm}_{0.06}\text{Gd}_{0.02}\text{Eu}_{0.02}\text{Ca}_{0.01})_{\Sigma 0.99}(\text{CO}_3)_{1.03}[(\text{OH})_{0.55}\text{F}_{0.38}]_{\Sigma 0.93}$ (Maksimović and Pantó, 1985) and thus, serves as an excellent natural analog to the synthetic $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ system examined in this study. Earlier reports suggest that the majority of bastnäsites within the Zagrad deposit were formed by early diagenetic processes (<90 °C) under alkaline, reductive conditions (Radusinović et al., 2017; Radusinović and Papadopoulos, 2021). However, based

on the results of this study, we would suggest the temperatures were significantly higher. Such assertions are based on that the nearly equal molar composition of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ results are not stabilized until high temperatures are approaching ~ 200 °C (Fig. 8). This would indicate Zagrad deposit had burial depth of ~ 5000 m (Winter, 2013), as there is no other evidence of thermal history in the deposit beside sedimentary diagenesis (Radusinović et al., 2017; Radusinović and Papadopoulos, 2021).

In short, the above thermodynamic investigation suggests a favorable formation of (La, Nd)-bearing hydroxylbastnäsite phases between ~ 150 to 450 °C, which provides additional confirmation to its potential natural occurrence in higher temperatures. Although $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions are only slightly metastable compared to their endmembers at the ambient condition, they can gain entropic stabilization at higher temperatures allowing the initiation of their precipitation out of hydrothermal fluids or their formations through other metasomatic processes (Schoneveld et al., 2015; Anenburg et al., 2018; Anenburg et al., 2020; Wang et al., 2020; Szucs et al., 2021). This explains that although mixing of different REE-binaries in hexagonal hydroxylbastnäsites is not enthalpically favorable, their formation is driven by entropic effects by inclusions of multiple LREEs, in accordance with their corresponding concentrations within the bastnäsite forming REE-bearing fluids (German and Von Damm, 2003; Radusinović and Papadopoulos, 2021).

5. CONCLUSION

In this work, we have studied the thermodynamic properties and phase relations of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions. Thermal decomposition pathways of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ were determined by TGA-DSC-MS, with the solid solutions exhibiting increased thermal stability

compared to their endmembers, while also confirming these hydroxylbastnäsites being low-T mineral phases. High temperature oxide melt drop solution calorimetry was used to determine $\Delta H_{f,ox}$, ΔH°_f , and ΔH_{mix} of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions at room temperature, which indicate the enthalpic metastability of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions with respect to LaCO_3OH and NdCO_3OH . Detailed analysis reveals a regular solution model for the mixing of La and Nd. Furthermore, the unit cell parameters follow nearly linear relations as a function of Nd content, suggesting a random distribution of La and Nd in the metal sites, enabling the estimation of ΔS_{mix} by the Boltzmann entropy formula. Combining entropy and enthalpy leads to the evaluation of ΔG_{mix} at 27, 165, and 400 °C, which reveals that the formation of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ solid solutions may become favorable at temperatures encountered at hydrothermal or late-stage diagenetic conditions. These results suggest that entropy plays an important role in the stabilization of naturally occurring multi-cationic hexagonal hydroxylbastnäsites solid solutions. Further thermodynamic calculations confirm and narrow down the temperature range (~150 to 450 °C), within which the formation of (La, Nd)-bearing hydroxylbastnäsites become favorable.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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RESEARCH DATA

Research Data associated with this article can be accessed at <http://doi.org/10.17632/xmpp8pz8g9.1>.

APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary material to this article can be found online at <https://doi.org/10.1016/j.gca.2022.04.002>.

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