

From hydroxylbastnäsite to bastnäsite: A crystal chemistry perspective of the incomplete solid solution

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ABSTRACT

Bastnäsite ($\text{REECO}_3[\text{F},\text{OH}]$) is a critical mineral in carbonatitic rare earth element (REE) deposits and serves as a primary global source of REEs. Understanding its crystal chemistry and thermodynamic properties is essential for modeling REE mobilization and deposition in various geological processes. Despite the complexity in natural bastnäsite—arising from cationic substitutions among REE species and coupled F-OH substitution—the impacts of F-OH substitution on its crystal structure and thermodynamic properties remain poorly constrained. In this study, we systematically investigate a synthetic bastnäsite-hydroxylbastnäsite (Bsn-Ce–Hbsn-Ce; CeCO_3F – CeCO_3OH) solid-solution series using single-crystal X-ray diffraction and Raman spectroscopy. Notably, this is the first study to reveal: (1) the positions of hydrogen atoms in bastnäsite and hydroxylbastnäsite, as well as the order-disorder transition of hydrogen initiated by F-OH substitution in hydroxylbastnäsite, which explains the discrepancies in Raman spectroscopy between synthetic end-members and natural hydroxylbastnäsite; (2) the phase boundary between bastnäsite and hydroxylbastnäsite, with crystal structural data indicating a phase boundary at $F = 0.41\text{--}0.52$ apfu; and (3) the effect of F-OH substitution on the volume of the Bsn-Ce–Hbsn-Ce solid solution. This study is also the first attempt to establish a quantitative framework for describing the volume-composition behavior of incomplete solid solutions involving F-OH substitution. Furthermore, this study provides a foundational understanding of the crystal chemistry necessary for further investigations into the thermodynamic properties of Bsn-Ce–Hbsn-Ce solid solutions.

Keywords: Bastnäsite, hydroxylbastnäsite, rare earth minerals, hydrogen atoms, incomplete solid solution

INTRODUCTION

Rare earth elements (REEs), owing to their unique electronic configurations, exhibit remarkable physical and chemical properties in areas such as magnetism, optics, and electricity, rendering them indispensable components in emerging high technologies and green industries. For instance, the incorporation of lanthanum (La) and cerium (Ce) in nickel-metal hydride batteries significantly enhances battery performance and effectively extends the battery lifespan (e.g., Vargas et al. 2021; Ahsan et al. 2023). Neodymium (Nd) compounds with iron and boron are also extensively used to manufacture high-power magnets (e.g., Sagawa et al. 1984; Coey 2020; Chen et al. 2024). In addition, yttrium (Y), La, and Ce in superalloys can significantly improve high-temperature oxidation and corrosion resistance (Li et al. 2024). As the application of REEs in various

industries continues to expand and their demand grows steadily, it is imperative to explore and discover new rare earth deposits with mining potential (Zhou et al. 2017).

However, the mechanisms underlying the mineralization of REEs remain poorly understood (Migdisov et al. 2016; Anenburg et al. 2021; Beland and Williams-Jones 2021; Mororó et al. 2024). This knowledge gap hampers our understanding of the formation of various REE deposits and, consequently, the discovery of new REE deposits. The formation of REE deposits is predominantly controlled by the transport and deposition of REEs during various geological processes, such as magmatic and hydrothermal activities. The transport and deposition of REEs are significantly controlled by the thermodynamic properties of REE minerals and aqueous species (Migdisov et al. 2016). However, the lack of thermodynamic data, particularly for REE minerals (even for the most important and common minerals like bastnäsite), severely impedes our ability to model the transport and deposition of REEs and, consequently, the formation of REE deposits (Gysi and Williams-Jones 2015; Gysi et al. 2015, 2016; Migdisov et al. 2016; Anenburg et al. 2021; Goncharov et al. 2022).

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Bastnäsite is the most commonly occurring REE mineral and serves as the primary ore mineral in carbonatite REE deposits, such as those found at Mountain Pass and Bayan Obo (Zhou et al. 2017; Goncharov et al. 2022). Natural bastnäsite, with the formula $\text{REECO}_3[\text{F},\text{OH}]$, exhibits a complex solid solution involving cationic substitution among REE species and substitution of F-OH (Donnay and Donnay 1953; Chakhmouradian and Wall 2012). Hydroxylbastnäsite forms when a significant proportion of F is replaced by OH, probably when $\text{OH} > \text{F}$. For naturally occurring bastnäsites, the F content exceeds 0.5 atoms per formula unit (apfu), with the minimum reported value being 0.58 apfu (Zambezi et al. 1997). In contrast, for naturally occurring hydroxylbastnäsites, the F contents remain below 0.5 apfu, the maximum observed value being 0.38 apfu (Song et al. 2019).

Given its significance for REE deposits, the fundamental thermodynamic data (e.g., heat capacity, enthalpy, entropy) of bastnäsite are crucial for understanding the transport and deposition of REEs in various geological processes. However, such data for bastnäsite remains limited. For example, only Gysi and Williams-Jones (2015) experimentally measured the heat capacity of a natural bastnäsite ($\text{Ce}_{0.50}\text{La}_{0.25}\text{Nd}_{0.20}\text{Pr}_{0.05}\text{CO}_3\text{F}$) using differential scanning calorimetry (DSC). Additionally, the enthalpies of formation of only synthetic end-member bastnäsite-(La) and -(Ce) have been experimentally determined by high-temperature oxide melt solution calorimetry (Shivaramaiah et al. 2016). Furthermore, Al-Nafai et al. (2019) estimated the standard Gibbs free energy of formation for the end-members bastnäsite-(La), -(Ce), -(Pr), and -(Nd) through theoretical calculations; however, these results remain unverified by experimental data. Moreover, there are no standard entropy data for bastnäsite.

More importantly, due to the complex chemical composition of bastnäsite, very little is known about the effects of REE cationic substitution and F-OH substitution on the thermodynamic properties of bastnäsite-hydroxylbastnäsite, with the exception of $\text{La}_{1-x}\text{Nd}_x\text{CO}_3\text{OH}$ (Goncharov et al. 2022). The lack of such data complicates the accurate simulation of the mobilization, concentration, and mineralization of REEs within natural hydrothermal carbonatite systems.

In this study, a series of Bsn-Ce (CeCO_3F)-Hbsn-Ce (CeCO_3OH) solid solutions was synthesized, in which all REE sites were occupied by Ce. The crystal structures were characterized through single-crystal X-ray diffraction (SCXRD) and Raman spectroscopy to establish a structural foundation for subsequent thermodynamic property studies. We aim to address the following unresolved issues: (1) Hydrogen position. The hydrogen coordination geometry remains ambiguous, although the

fundamental structures of bastnäsite and hydroxylbastnäsite have been well documented decades ago (e.g., Donnay and Donnay 1953; Yang et al. 2008; Michiba et al. 2011; Liu et al. 2019). This ambiguity impedes the interpretation of Raman spectral discrepancies between synthetic and natural hydroxylbastnäsite. Specifically, synthetic end-member hydroxylbastnäsite displays three O-H vibrational modes at $\sim 3500\text{ cm}^{-1}$ and two modes at $\sim 3650\text{ cm}^{-1}$ (Michiba et al. 2011), whereas natural hydroxylbastnäsite exhibits additional O-H bands within the range of $3500\text{--}3650\text{ cm}^{-1}$ (Yang et al. 2008; Michiba et al. 2013). Our hydrogen position refinement provides a crystallographic explanation for these spectroscopic variations. (2) Phase boundary between bastnäsite and hydroxylbastnäsite. Available chemical compositions of natural bastnäsite and hydroxylbastnäsite indicate a phase boundary around $\text{F} = 0.50$ apfu; however, there remains a lack of reliable crystal structure validation. (3) The impact of F-OH substitution on the volume and structure of the Bsn-Ce-Hbsn-Ce solid solutions. Establishing the volume-composition equation is helpful for future construction of thermodynamic properties of the Bsn-Ce-Hbsn-Ce solid-solution series.

SAMPLES AND EXPERIMENTS

Sample Synthesis

The synthesis experiments of the Bsn-Ce-Hbsn-Ce solid solutions were performed using the DS-6 $\times$ 1400t cubic-anvil-type apparatus at the Key Laboratory of High Temperature and High Pressure Study of the Earth's Interior, Institute of Geochemistry, Chinese Academy of Sciences (IGCAS), Guiyang. The synthetic procedure was similar to the previous studies (Zhou et al. 2001; Xu et al. 2018). The starting materials were high-purity $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), NaF (99.9%), NaHCO_3 (99.9%), Na_2CO_3 (99.9%), and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (99.9%), mixed in various proportions (see Table 1). The materials were finely ground with ethanol in an agate mortar to ensure homogeneous mixing. After drying, the sample mixture was enclosed in a copper capsule, with an inner diameter of 8 mm, an outer diameter of 9.5 mm, and a length of 7.5 mm. The experimental pressure and temperature conditions were 0.5 to 1.8 GPa and 685 to 705 °C, respectively. After a run duration of 33–48 h, the sample assemblies were rapidly quenched to room pressure and temperature within 2 min. Then, the run products were extracted from the sample chamber and were washed 5 times with deionized water and anhydrous ethanol. Finally, the crystals were obtained by drying the products at 60 °C for at least 24 h. Ten solid solutions with different compositions ($\text{Bsn}_{0-86}\text{Hbsn}_{100-14}$) were synthesized (Tables 1–2).

Chemical Composition Analysis

A scanning electron microscope was used to study the morphological characteristics of each run product (Figs. 1; Online Materials¹ Fig. S1). Subsequently, selected crystals were used for electron microprobe analysis (EMPA). The EMPA analyses were performed with a JXA8230 tungsten filament electron microscope at IGCAS. The microscope was operated at an acceleration voltage of 25 kV, with a beam current of 10 nA, and a beam diameter of 10 μm . Counting times were 30 s on

TABLE 1. Details of the synthesis experiments for Bsn-Ce-Hbsn-Ce solid solutions

Composition	Starting materials	P (GPa)	T (°C)	Duration (h)
Hbsn ₁₀₀	$\text{CeCl}_3 \cdot 6\text{H}_2\text{O} + 3\text{NaHCO}_3 + \text{C}(1.1\%)$	1.8	685	36
Bsn ₂₃ Hbsn ₇₇	$\text{CeCl}_3 \cdot 6\text{H}_2\text{O} + 0.2\text{NaF} + 2.4\text{NaHCO}_3 + 0.2\text{Na}_2\text{CO}_3 + \text{C}(1.5\%)$	1.8	685	36
Bsn ₃₅ Hbsn ₆₅	$\text{CeCl}_3 \cdot 6\text{H}_2\text{O} + 0.3\text{NaF} + 2.1\text{NaHCO}_3 + 0.3\text{Na}_2\text{CO}_3 + \text{C}(1.5\%)$	1.5	685	36
Bsn ₄₁ Hbsn ₅₉	$\text{CeCl}_3 \cdot 6\text{H}_2\text{O} + 0.4\text{NaF} + 1.8\text{NaHCO}_3 + 0.4\text{Na}_2\text{CO}_3 + \text{C}(1.5\%)$	1.8	705	33
Bsn ₅₂ Hbsn ₄₈	$\text{CeCl}_3 \cdot 6\text{H}_2\text{O} + 0.5\text{NaF} + 1.5\text{NaHCO}_3 + 0.5\text{Na}_2\text{CO}_3 + \text{C}(1.5\%)$	1.8	705	33
Bsn ₅₅ Hbsn ₄₅	$\text{CeCl}_3 \cdot 6\text{H}_2\text{O} + 0.6\text{NaF} + 1.2\text{NaHCO}_3 + 0.6\text{Na}_2\text{CO}_3 + \text{C}(1.5\%)$	1.8	705	33
Bsn ₆₂ Hbsn ₃₈	$\text{CeCl}_3 \cdot 6\text{H}_2\text{O} + 0.7\text{NaF} + 0.9\text{NaHCO}_3 + 0.7\text{Na}_2\text{CO}_3 + \text{C}(1.5\%)$	1.5	685	36
Bsn ₇₁ Hbsn ₂₉	$\text{CeCl}_3 \cdot 6\text{H}_2\text{O} + 0.9\text{NaF} + 0.3\text{NaHCO}_3 + 0.9\text{Na}_2\text{CO}_3 + \text{C}(1.5\%)$	1.8	685	36
Bsn ₈₁ Hbsn ₁₉	$\text{CeCl}_3 \cdot 6\text{H}_2\text{O} + \text{NaF} + 2\text{NaHCO}_3 + \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}(1.5\%)$	0.5	700	48
Bsn ₈₆ Hbsn ₁₄	$\text{CeCl}_3 \cdot 6\text{H}_2\text{O} + \text{NaF} + 2\text{NaHCO}_3 + \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}(1.5\%)$	0.5	700	48

Note: Bsn = CeCO_3F and Hbsn = CeCO_3OH .

TABLE 2. Chemical compositions (wt%) of Bsn-Ce-Hbsn-Ce solid solutions

Composition	Point	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Na ₂ O	CuO	F	Cl	CaO	Total
Bsn ₂₃ Hbsn ₇₇	9	0.02(3)	BDL	68.64(43)	BDL	BDL	BDL	0.01(1)	1.73(18)	0.13(5)	BDL	69.78(41)
Bsn ₃₅ Hbsn ₆₅	9	0.01(1)	BDL	68.34(48)	BDL	BDL	0.01(3)	0.02(2)	2.71(24)	0.06(3)	0.01(1)	70.00(60)
Bsn ₄₁ Hbsn ₅₉	12	0.03(4)	BDL	68.60(42)	0.00(1)	BDL	0.00(1)	0.01(1)	3.28(23)	0.06(3)	0.01(1)	70.59(41)
Bsn ₅₂ Hbsn ₄₈	6	0.01(3)	BDL	68.69(34)	0.00(1)	BDL	BDL	0.01(2)	4.07(15)	0.05(2)	BDL	71.12(37)
Bsn ₅₅ Hbsn ₄₅	6	0.00(0)	BDL	68.73(27)	BDL	BDL	BDL	BDL	4.38(8)	0.04(1)	0.00(1)	71.30(28)
Bsn ₆₂ Hbsn ₃₈	6	0.01(1)	0.01(2)	68.67(50)	0.00(1)	BDL	0.00(1)	BDL	4.94(9)	0.03(1)	0.01(1)	71.58(54)
Bsn ₇₁ Hbsn ₂₉	8	0.01(2)	BDL	68.76(74)	BDL	BDL	0.01(3)	0.02(2)	5.67(4)	0.03(1)	0.01(1)	72.10(74)
Bsn ₈₁ Hbsn ₁₉	6	0.00(1)	BDL	69.16(48)	0.00(1)	BDL	BDL	0.02(3)	6.44(20)	0.03(0)	0.01(0)	72.94(58)
Bsn ₈₆ Hbsn ₁₄	7	0.01(2)	0.02(2)	69.61(57)	0.01(2)	BDL	0.01(1)	0.01(1)	6.94(23)	0.03(1)	BDL	73.71(64)
Standard deviation for standards		0.07	0.14	0.13	0.16	0.14	0.41	0.08	0.17	0.27	0.11	
Probe standards		Y	LaF ₃	CeF ₃	PrF ₃	NdF ₃	Tugtupite	Cuprite	CeF ₃	Tugtupite	Chrome-Diopside	

Note: Numbers in parentheses represent standard deviations to the last significant digit. BDL = Below detection limit.

the peak and 15 s on the background for La, Ce, Pr, Nd, and Y; 10 s on the peak, and 5 s on the background for Cl, Cu, Na, Ca, and F. The rare earth fluoride was used as the standard for La, Ce, Pr, Nd; yttrium metal for Y; CeF₃ for F; tugtupite for Cl and Na; diopside for Ca; and cuprite for Cu. The crystals analyzed for these elements were as follows: LIFL for REEs; TAP for Na and Y; PETH for Cl and Ca; LIFH for Cu; and LDE1 for F. The composition of each sample was determined by the average of the compositions of different shapes, with each shape analyzed based on 3 to 6 points.

Fluorine content in the end-member hydroxylbastnäsite (Hbsn100) was analyzed using an ion microprobe Sensitive High Resolution Ion Microprobe for Stable Isotopes (SHRIMP-SI) at the Research School of Earth Sciences, Australian National University, Canberra. Both ¹⁹F and ¹⁶O were measured simultaneously using Faraday cups, and electrometers were operated in the current mode (Ireland et al. 2014). The Bsn₆₂Hbsn₃₈ sample (F = 4.94 wt%) was used as an in-house primary standard to calibrate the unknowns. The results demonstrate that there were negligible F signals in the Hbsn₁₀₀, which should be pure (≤ 3 ppm).

Single-Crystal X-ray Diffraction

To obtain the structural information of each solid solution, we selected crystals with well-defined shapes and sizes of 100–200 μm , primarily hexagonal column

shape, for SCXRD experiments at room temperature. The experiments were performed using a Bruker D8 Advance diffractometer at the Roentgen Laboratory in the Shulun (Shanghai) Technical Service Co., Ltd. The light source was graphite-monochromatized MoK α radiation, with a tube voltage of 50 kV and a tube current of 1.4 mA. Data collection was performed using the strategy recommended by the Bruker system. The frame width was 0.5° and the counting time was 10 s per frame. The APEX 4.0 software suite was employed to reduce experimental data and determine the unit-cell parameters and volumes. The crystal structures were solved using the SHELX software package (Sheldrick 2008), facilitated by the Olex 2 user interface (Dolomanov et al. 2009). The crystal structure of each sample was further refined using the SHELXL software. The occupancy of each OH/F site was refined with the constraint that O + F = 1, and H = O, and the overall F content was constrained using the EMPA results. We also located the H atoms in the structure using the NoSpherA2 (Kleemann et al. 2021) module implemented on the Olex 2 user interface. Interatomic distances and polyhedral parameters were calculated using the VESTA software (Momma and Izumi 2008).

Raman Spectroscopy

The Raman spectra were collected in the frequency ranges of 100–1500 and 3200–3800 cm^{-1} , using a Renishaw in Via Reflex system at the Key Laboratory of

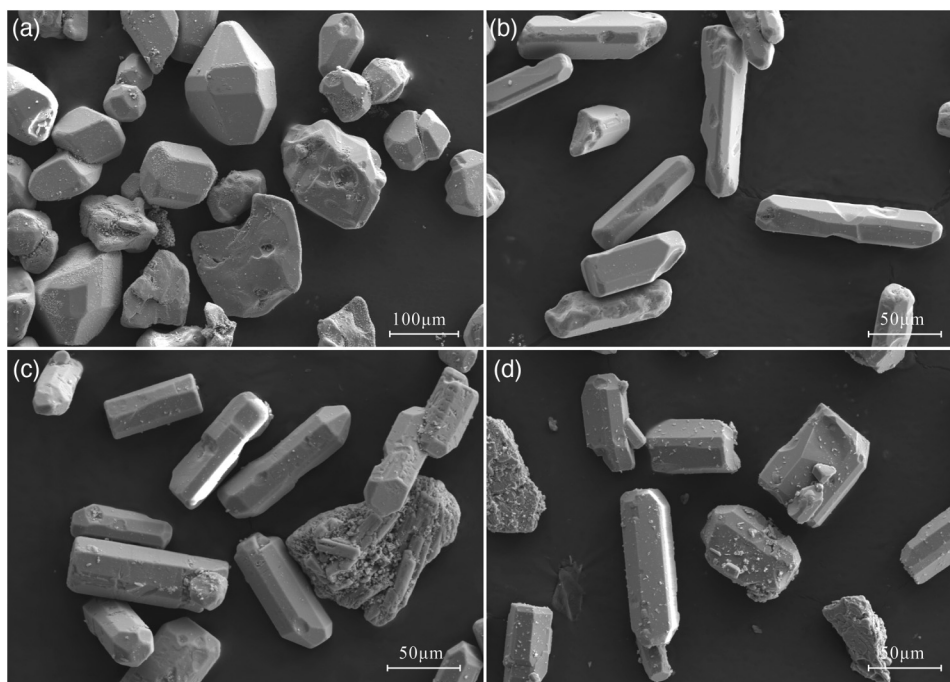


FIGURE 1. Backscattered electron images of crystals of selected Bsn-Ce-Hbsn-Ce solid solutions (for other samples, see the Online Materials¹). (a) Hbsn₁₀₀, (b) Bsn₄₁Hbsn₅₉, (c) Bsn₅₅Hbsn₄₅, and (d) Bsn₇₁Hbsn₂₉. Bsn-Ce and Hbsn-Ce are abbreviated as Bsn and Hbsn, respectively, when referring to the compositions of the solid solutions.

High Temperature and High Pressure Study of the Earth's Interior, IGCAS. The laser had a wavelength of 514 nm. The system had a resolution of 0.2 cm^{-1} using a 2400 grooves/mm grating. Before the measurement, the Raman shift was calibrated using the silicon standard. During the measurement, a $1.6\text{ }\mu\text{m}$ incident laser spot was focused on the sample with a $50\times$ Leica microscope objective, and the Raman spectrum of each sample was obtained with an integration time of 20 s. Finally, the raw Raman spectrum data were processed using the deconvolution method to obtain the mode frequency.

RESULTS

Chemical Composition

We successfully synthesized 10 solid solutions with different F contents, ranging from 0 to 6.94(23) wt% or from 0 to 0.86(2) apfu in the formula. Table 2 presents the chemical composition data of each sample. In addition, other elements such as Ca, Na, Cl, Cu, Y, La, Pr, and Nd only occur in negligible amounts (Table 2). The backscattered electron (BSE) images of the 10 samples were obtained without post-processing under the same conditions as shown in Figure 1 and Online Materials¹ Figure S1. The shapes of the single-crystal samples were primarily hexagonal columns and granules, with a smaller amount of irregular plates present. The granular crystals have sizes of up to $200\text{ }\mu\text{m}$, and columnar crystals exhibit lengths of up to $100\text{ }\mu\text{m}$.

Unit-Cell Parameters and Volumes

Structure analysis and refinement of the synthesized samples were conducted based on SCXRD data (Fig. 2; Online Materials¹ Fig. S2). Online Materials¹ Table S1 presents the details of structural refinements, indicating that all the samples belong to

the hexagonal system. Crystals with F content below 0.41 apfu belong to a $P6\bar{6}$ space group and have a hydroxylbastnäsite structure. In contrast, crystals with $F > 0.52$ apfu have a $P62c$ space group and a bastnäsite structure.

Table 3 and Figure 3 present the unit-cell parameters (a and c), volume (V), and molar volume (V_m) of the solid solution as a function of F content. The unit-cell parameters (a and c) and molar volumes (V_m) decrease with increasing F content. Given that bastnäsite and hydroxylbastnäsite possess different space groups, we employed a piecewise quadratic function to derive polynomial expressions of the a -F and c -F relationships within both stability regions (Figs. 3a and 3b).

For hydroxylbastnäsite, the derived equations are:

$$a = 12.488(3) - 0.02(5)F - 0.31(13)F^2, R^2 = 0.99 \quad (1)$$

$$c = 9.974(3) - 0.16(4)F - 0.30(9)F^2, R^2 = 0.99 \quad (2)$$

For bastnäsite:

$$a = 7.46(5) - 0.82(15)F + 0.47(11)F^2, R^2 = 0.99 \quad (3)$$

$$c = 10.14(7) - 0.88(22)F + 0.48(16)F^2, R^2 = 0.99 \quad (4)$$

We performed a linear regression analysis on the volume data, excluding the data point at $F = 0$ apfu, and the results are shown in Figure 3c: $V_m = 45.51(5) - 3.53(9)F$, $R^2 = 0.99$. This analysis indicates that there is a nearly perfect linear correlation between F content and volume in the F-bearing samples. However, extrapolating this linear fit to $F = 0$ apfu yields a molar volume of $45.51(5)\text{ cm}^3/\text{mol}$, which deviates by 10.1% from the experimentally measured value of

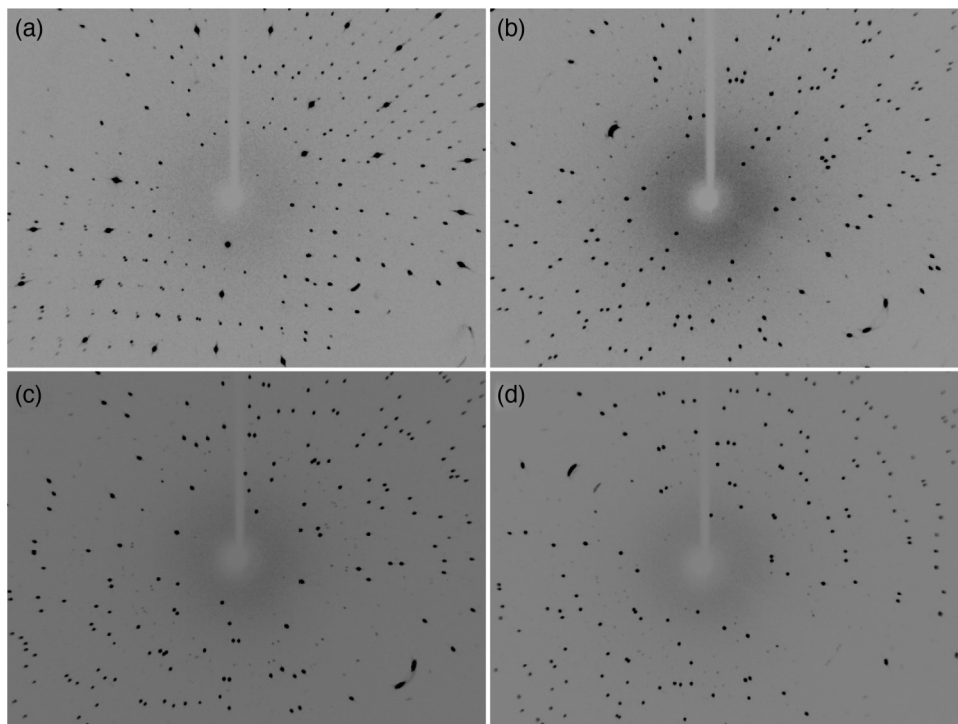


FIGURE 2. Representative diffraction images of the selected Bsn-Ce-Hbsn-Ce solid solutions (for other samples, see the Online Materials¹). (a) Hbsn₁₀₀, (b) Bsn₄₁Hbsn₅₉, (c) Bsn₅₅Hbsn₄₅, and (d) Bsn₇₁Hbsn₂₉.

TABLE 3. Unit-cell parameters (*a* and *c*) and volume (*V*) and molar volume (*V_m*) for Bsn-Ce-Hbsn-Ce solid solutions

Composition	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>V_m</i> (cm ³ /mol)	<i>V_{m,ex}</i>
Hbsn ₁₀₀	12.4882(2)	9.9735(3)	1347.03(5)	45.051(2)	0(0)
Bsn ₂₃ Hbsn ₇₇	12.4687(3)	9.9219(4)	1335.88(7)	44.678(2)	0.24(5)
Bsn ₃₅ Hbsn ₆₅	12.4391(4)	9.8779(6)	1323.65(10)	44.269(3)	0.13(5)
Bsn ₄₁ Hbsn ₅₉	12.4299(3)	9.8589(3)	1319.10(6)	44.117(2)	0.15(6)
Bsn ₅₂ Hbsn ₄₈	7.1583(2)	9.8170(7)	435.64(4)	43.709(4)	0.01(6)
Bsn ₅₅ Hbsn ₄₅	7.1492(3)	9.8010(6)	433.83(4)	43.528(4)	-0.08(6)
Bsn ₆₂ Hbsn ₃₈	7.1264(3)	9.7854(8)	430.38(4)	43.181(4)	-0.24(7)
Bsn ₇₁ Hbsn ₂₉	7.1130(3)	9.7610(8)	427.69(4)	42.912(4)	-0.27(7)
Bsn ₈₁ Hbsn ₁₉	7.1018(1)	9.7444(3)	425.62(2)	42.704(2)	-0.24(9)
Bsn ₈₆ Hbsn ₁₄	7.0993(3)	9.7454(8)	425.37(3)	42.679(3)	-0.12(11)
Bsn ₁₀₀	—	—	—	42.45(11)	0.00(15)

Note: Numbers in parentheses represent standard deviations to the last significant digit.

45.051(2) cm³/mol. This discrepancy suggests that the linear model is inadequate to describe the entire data set. In contrast, a cubic function provides a significantly better fit to the *V_m*-*F* data across the full compositional range, as illustrated in Figure 3c. The boundary conditions for the fitting were set such that *V_m* reaches its minimum at *F* = 1 apfu and maximum at *F* = 0 apfu. The resulting equation is:

$$V_m = 45.04(2) - 7.77(9)F^2 + 5.18(6)F^3, R^2 = 0.99 \quad (5)$$

The goodness of fit is evaluated using the coefficient of determination, *R*². Values close to 1 indicate that our fitting formula closely matches the observed values (Fig. 3).

Polyhedral Behaviors

In this study, O atoms bonded to H atoms are designated as OH to unambiguously identify those sites that may be substituted by F atoms. When referring to O-H bonds or O-H vibrations, “O-H” is used unless the specific O-H bonds or O-H vibrations in the crystal structure are involved. In contrast, when referring to specific O-H bonds or O-H vibrations, or to O atoms bonded to H atoms and potentially replaced by F atoms, “OH” is used instead of “O”, for example, OH1-H1, OH5-H5, OH1/F1, OH5/F5.

The structure of bastnäsite consists of a crystallographically unique [CO₃] unit, one Ce, and two different F positions, commonly with F-OH substitution (F1/OH1 and F2/OH2). In contrast, the structure of hydroxylbastnäsite contains six symmetrically independent [CO₃] units, three Ce (Ce1, Ce2, and Ce3), and five F/OH (F1/OH1-F5/OH5). The occupancy of F/OH for the samples, except for Hbsn₁₀₀, was refined. The results indicate that, for all but Hbsn₁₀₀, F-OH substitution exists for all F/OH positions (Online Materials¹ Fig. S3).

As illustrated in Online Materials¹ Figure S4 and Tables S2–S3, the 9-coordination polyhedron of Ce [CeO₆(F/OH)₃] comprises three Ce-(F/OH) bonds and six Ce-O bonds. As the *F* content increases, the distance between Ce and F/OH [*d*_{Ce-(F/OH)}] shows a decreasing trend for both hydroxylbastnäsite and bastnäsite (Online Materials¹ Figs. S4a–S4c and Tables S2–S3). However, the distances *d*_{Ce-O} do not follow a consistent pattern with increasing *F* content (Online Materials¹ Figs. S4d–S4f and Tables S2–S3). In the hydroxylbastnäsite region, some of the *d*_{Ce-O} decreases as the *F* content increases. For example, *d*_{Ce1-O3} decreases from 2.6500(40) Å (*F* = 0 apfu) to 2.5870(40) Å (*F* = 0.41 apfu), a decrease of 2.38%. However, *d*_{Ce1-O4}, *d*_{Ce1-O11}, *d*_{Ce2-O1}, and *d*_{Ce2-O4}

(Online Materials¹ Figs. S4d–S4f) show an increasing trend with increasing *F* content. In contrast, in the bastnäsite region, the distance *d*_{Ce1-O1} initially increases from *F* = 0.52 to 0.55 apfu and then decreases, while the distances between other Ce and O atoms tend to increase over the whole data range. As the *F* content increases, the averages of *d*_{Ce1-F/OH}, *d*_{Ce2-F/OH}, and *d*_{Ce3-F/OH} display a consistent decrease trend through hydroxylbastnäsite region and the average of *d*_{Ce1-F/OH} also shows a consistent decrease in bastnäsite region (Fig. 4a). However, the averages of *d*_{Ce1-O}, *d*_{Ce2-O}, and *d*_{Ce3-O} display a decreasing trend in hydroxylbastnäsite region as the *F* content increases and then exhibit discontinuities at approximately *F* = 0.5 apfu (Fig. 4b). The average value of *d*_{Ce1-O} increases from 2.5597(13) Å at *F* = 0.52 apfu to 2.5700(13) Å at *F* = 0.55 apfu and then does not change significantly until *F* = 0.86 apfu (Fig. 4b). The three polyhedral volumes of CeO₆(F/OH)₃ (*V*_{Ce1}, *V*_{Ce2}, *V*_{Ce3}) in the hydroxylbastnäsite region gradually decreases with increasing *F* content, decreasing by 1.19%, 2.43%, and 2.36%, respectively (Fig. 4c). Notably, there is a significant increase in *V*_{Ce} across the Bsn-Ce-Hbsn-Ce boundary, as shown in Figure 4c and Online Materials¹ Tables S2–S3. In the bastnäsite region, *V*_{Ce} increases from 31.79 Å³ at *F* = 0.52 apfu to 32.21 Å³ at *F* = 0.55 apfu, and then it gradually decreases with increasing *F* content. At *F* = 0.86 apfu, *V*_{Ce} decreases to 31.57 Å³ (Fig. 4c).

In the [CO₃] unit, the *d*_{C-O} does not show regular changes with increasing *F* content (Online Materials¹ Fig. S5 and Tables S2–S4). For example, in hydroxylbastnäsite *d*_{C2-O4}, *d*_{C3-O6}, and *d*_{C5-O9} show a decreasing trend with increasing *F* content, decreasing by 2.03%, 2.51%, and 2.73%, respectively (Online Materials¹ Figs. S5b–S5c and S5e, and Table S4). By contrast, *d*_{C2-O3} and *d*_{C3-O5} show an increasing trend with increasing *F* content, increasing by 9.09% and 10.40%, respectively (Online Materials¹ Figs. S5b–S5c and Table S4). Notably, *d*_{C1-O1} in the bastnäsite near the Bsn-Ce-Hbsn-Ce boundary is significantly larger than other *d*_{C1-O}. However, it is notable that in the bastnäsite region, the *d*_{C1-O1} decreases rapidly from 1.530(30) to 1.326(17) Å as the *F* content increases from 0.52 to 0.55 apfu, resulting in a reduction of 13.33% (Online Materials¹ Fig. S5 and Table S2). In contrast, when *F* increases from 0.55 to 0.86 apfu, *d*_{C1-O1} decreases by only 2.94%. On the other hand, the distance *d*_{C1-O2} shows a slight increase by 2.44%, from 1.269(10) to 1.300(9) Å as *F* content increases from 0.52 to 0.55 apfu. Subsequently, *d*_{C1-O2} decreases with a further increase in *F* content. At the maximum value of *F* = 0.86 apfu, the *d*_{C1-O2} decreases to

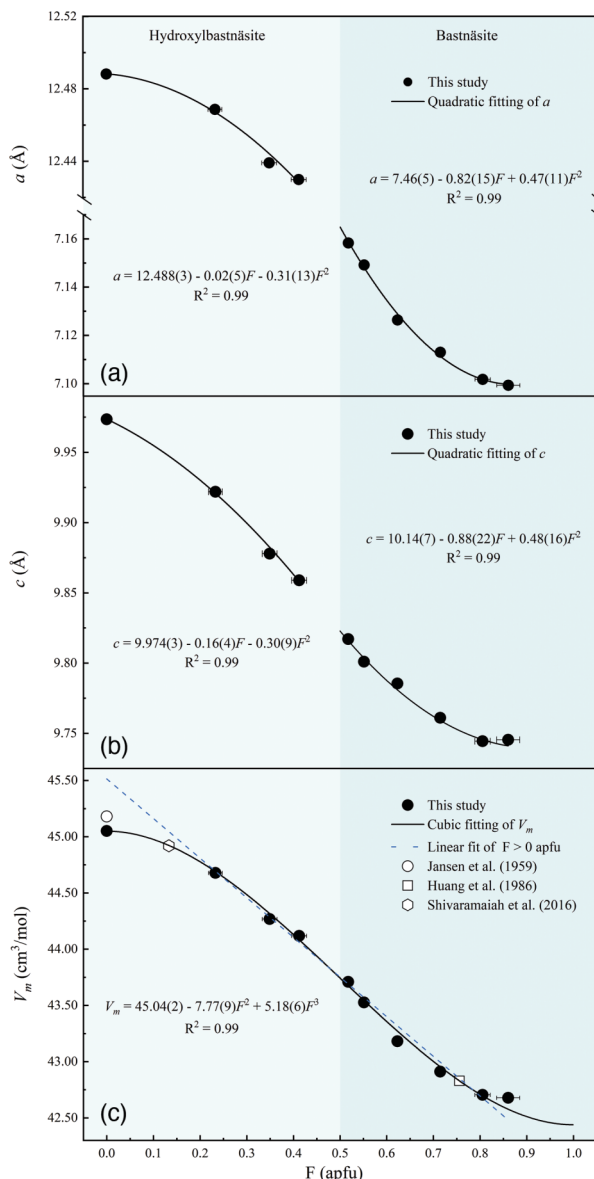


FIGURE 3. Illustration of the relationships between F content and various parameters: unit-cell parameters a (a) and c (b), and molar volume V_m (c). Black lines in (a–b) represent quadratic fits to the data from this study, limited to the hydroxylbastnäsite (light-shaded) and bastnäsite (dark-shaded) regions, with the corresponding equations shown nearby. Black line in (c) represents a cubic fit to the whole data set from this study. Blue dotted line represents a linear fit to the molar volume data from this study only, excluding the point at F = 0 apfu. (Color online.)

1.282(2) Å, indicating a total reduction of 1.38%, as shown in Online Materials¹ Figure S5 and Table S2.

F-OH Substitution and O-H Bond Lengths

The refinement of the site occupancies of F indicates that F atoms are not evenly distributed among the various F/OH sites within both the hydroxylbastnäsite and bastnäsite regions (Online Materials¹ Fig. S3). In the case of hydroxylbastnäsite,

as the F content increases to 0.23 apfu, the occupancies at the F1/OH1, F2/OH2, and F3/OH3 sites significantly rise, continuing to increase steadily with further increases in F content up to 0.42 apfu. The F occupancy at the F1/OH1 site increases approximately up to ~0.4 as the F content rises from 0.23 to 0.35 apfu, before decreasing to ~0.3 when the F content reaches 0.41 apfu. For the F5/OH5 site, substantial F-OH substitution occurs only when the F content increases to 0.35 apfu (with an occupancy of ~0.02), after which its occupancy significantly increases to ~0.3 at an F content of 0.41 apfu. The F occupancy at the F4/OH4 site increases linearly with increasing F content up to F = 0.41 apfu.

In contrast, for bastnäsite, the occupancy of the F2/OH2 site decreases linearly with decreasing F content, from 0.86 to 0.55 apfu, with an inflection point at 0.52 apfu. Meanwhile, the occupancy of the F1/OH1 site decreases nonlinearly with decreasing fluorine content, with a significantly slower rate until it reaches 0.55 apfu, where a similar inflection point is observed.

The O-H bond lengths exhibit relatively large uncertainties (Online Materials¹ Fig. S6). In the hydroxylbastnäsite region, the O-H bond lengths (d_{O-H}) vary within their uncertainties; a similar phenomenon is observed in the bastnäsite region. However, it is noteworthy that the d_{O-H} values in the bastnäsite region are generally smaller than those in the hydroxylbastnäsite region.

Raman Spectroscopy

Raman spectra are shown in Figure 5 and Online Materials¹ Figure S7. In this study, more than 30 Raman peaks were identified across the ranges of 100–1500 cm⁻¹ and 3200–3800 cm⁻¹. Based on previous studies on the vibrational spectroscopies of bastnäsite and hydroxylbastnäsite (Yang et al. 2008; Song et al. 2019), the Raman peaks below 500 cm⁻¹ are attributed to hydroxyl deformation and Ce-(F/OH) stretching vibration modes. Within the range of 500–1000 cm⁻¹, two distinct groups of vibrational modes are observed for the [CO₃] units, corresponding to their in-plane and out-of-plane bending modes. The symmetric stretching modes of the [CO₃] units (ν_1 – ν_3) are located between 1000 and 1200 cm⁻¹ and exhibit three strong bands when F = 0 to 0.55 apfu (Fig. 5a). The asymmetric stretching modes of the [CO₃] unit are observed between 1300 and 1500 cm⁻¹.

Additionally, O-H stretching vibrations (ν_4 – ν_{11}) appear in the range of 3200–3800 cm⁻¹. At F = 0 apfu, five Raman peaks are clearly observable (Figs. 5b and 6b). Notably, two new Raman peaks (ν_7 and ν_8) emerge at F = 0.23 apfu, while another peak (ν_9) appears at F = 0.52 apfu. As the F content increases, ν_7 disappears at F > 0.41 apfu, and ν_4 , ν_5 , ν_8 , ν_{10} , and ν_{11} disappear at F > 0.71 apfu. Apart from the symmetric vibrational modes of the [CO₃] units and the O-H stretching modes, other Raman peaks are either too weak or too broad to reliably identify or determine their positions through peak fitting. Therefore, only the Raman peaks corresponding to ν_1 – ν_{11} were deconvolved to investigate their Raman shift evolution with varying F content (Online Materials¹ Figs. S8–S9). As shown in Figure 6, the Raman shifts of ν_1 and ν_2 increase with increasing F content, while that of ν_3 exhibits a nonlinear decrease when F > 0.23 apfu. At F > 0.55 apfu, only one peak (ν_2) remains observable,

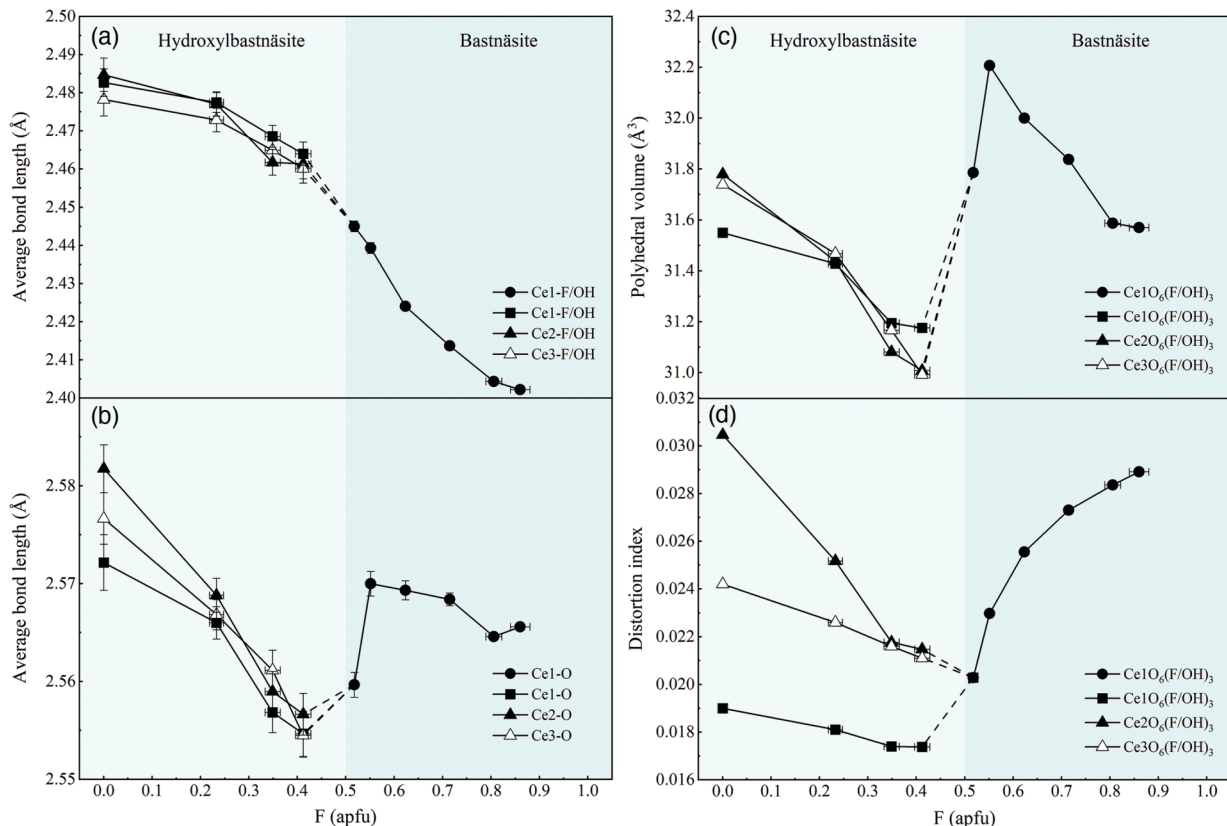


FIGURE 4. Average bond length of Ce-F/OH (a) and Ce-O (b), CeO₆(F/OH)₃ polyhedral volume (c), and distortion index (d) as functions of F content within the hydroxylbastnäsite (light-shaded) and bastnäsite (dark-shaded) regions. (Color online.)

with its Raman shift continuing to increase as the F content rises. Within the range of 3200–3800 cm⁻¹, all peaks display nonlinear relationships with increasing F content; however, ν_7 shows no significant changes across the data range.

DISCUSSION

Crystal Structural Variations Across the Bsn-Ce-Hbsn-Ce Solid Solution

Hydroxylbastnäsite-Bastnäsite Transition Boundary

The mutual substitution between F and OH is commonly observed in natural minerals, including apatite (Hovis et al. 2014; Bulina et al. 2020; Sordyl et al. 2020), topaz (Ulman and Valdrè 2017), humite (Ribbe et al. 1968), iranite (Yang et al. 2007), amblygonite (Groat et al. 1990), mica (Petersen et al. 1982; Robert et al. 1993; Papin et al. 1997; Sallet et al. 2018; Zhang et al. 2022), hambergite (Burns et al. 1995), and amphibole (Troll and Gilbert 1972; Holloway and Ford 1975; Robert et al. 1989; Della Ventura et al. 1993, 2019). In some cases, such as amphibole and mica, complete F-OH substitution can occur without altering the crystal structure (e.g., Robert et al. 1993; Della Ventura et al. 2019). However, for other minerals like hambergite, only incomplete F-OH substitution is possible, with a maximum observed substitution of 48% in natural specimens; the synthetic F-end-member exhibits a different crystal structure (Burns et al. 1995). The F content is limited to a maximum of

0.50 apfu due to the strong hydrogen bonding effects (Burns et al. 1995; Hawthorne 2023).

Regarding Bsn-Ce-Hbsn-Ce, there exists only an incomplete solid solution of OH and F (Fig. 3; Online Materials¹ Table S1). This is supported by crystal structural refinement, which indicates that the transition from hydroxylbastnäsite to bastnäsite occurs at F = 0.41–0.52 apfu. For natural bastnäsite, to the best of our knowledge, the minimum F content is recorded at 0.58 apfu (Zambezi et al. 1997), whereas the maximum F content in hydroxylbastnäsite is noted to be 0.38 apfu (Song et al. 2019). Although data closer to F = 0.50 apfu were not available, it is reasonable to infer that the phase boundary lies at this value.

Furthermore, as illustrated in Online Materials¹ Figure S3, among the five OH/F sites in hydroxylbastnäsite, only OH4/F4 has F → OH replacement exceeding 50% as F content increases. Notably, the OH4-H4 bond length is relatively shorter than those of other O-H bonds (Online Materials¹ Fig. S6), indicating a comparatively weaker hydrogen bonding effect. This weaker bonding may allow OH4 to be replaced by F by more than 50% without altering crystal symmetry.

Volume Behaviors Across the Phase Boundary

The V_m -F relationship is distinctly nonlinear within both the hydroxylbastnäsite and bastnäsite regions (Fig. 3c), indicating that the Bsn-Ce-Hbsn-Ce system is not only incomplete but also a non-ideal solid solution. It is particularly noteworthy that,

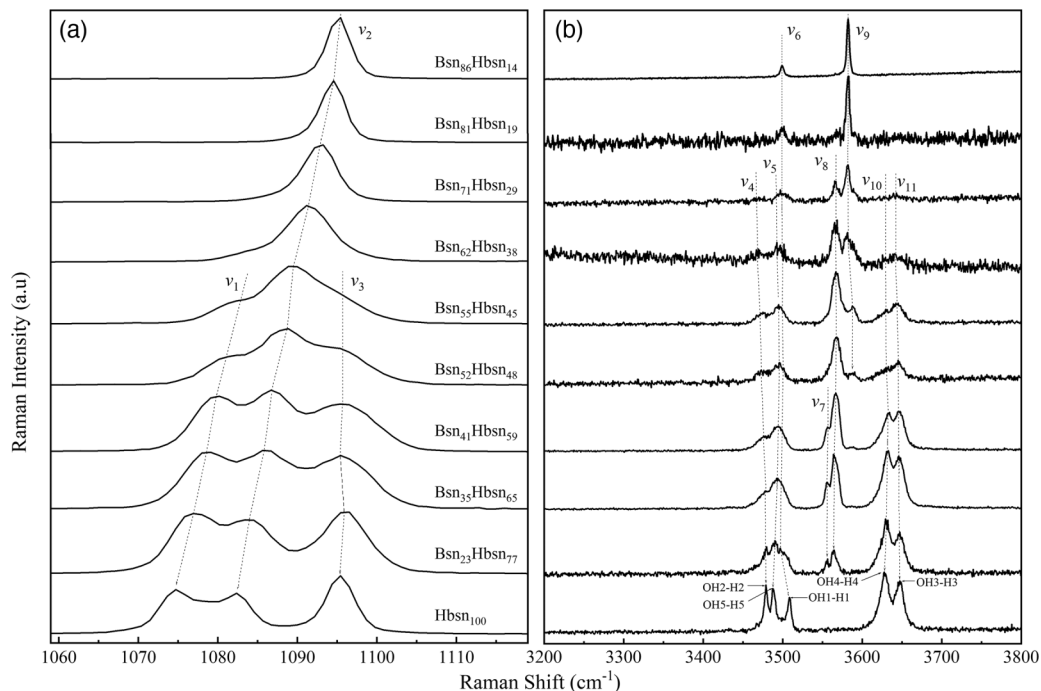


FIGURE 5. Raman spectra of the synthetic Bsn-Ce-Hbsn-Ce solid solutions. (a) symmetric stretching modes of the $[\text{CO}_3]$ units (ν_1 – ν_3); (b) O-H stretching vibrations (ν_4 – ν_{11}). ν_i denotes the different Raman vibration peaks.

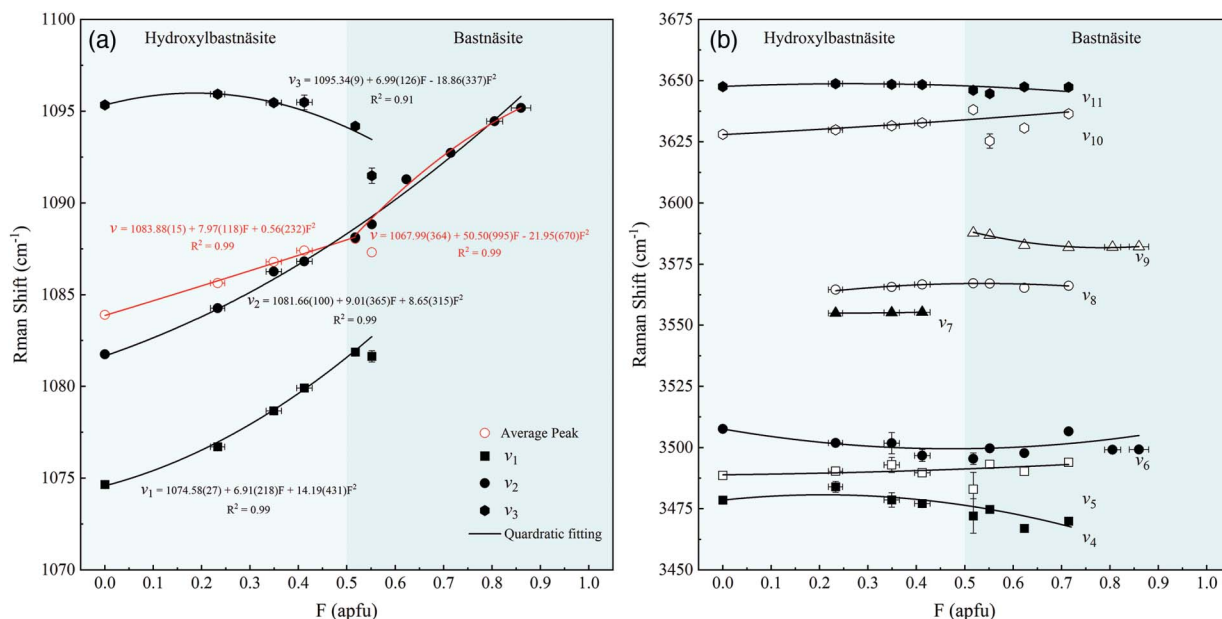


FIGURE 6. Raman Shifts of the symmetric stretching modes of the $[\text{CO}_3]$ units (a) (ν_1 – ν_3) and O-H stretching modes (b) (ν_4 – ν_{11}) in the Bsn-Ce-Hbsn-Ce solid solutions. Red spheres represent the average Raman shifts of ν_1 , ν_2 , and ν_3 for F contents from 0 to 0.41 apfu. Black lines show the quadratic fits to the Raman shift data, with the corresponding equations displayed nearby. Within the bastnäsite (dark-shaded) and hydroxylbastnäsite (light-shaded) regions, the quadratic fits are applied piecewise. (Color online.)

although the Bsn-Ce-Hbsn-Ce system does not form a complete solid solution, the molar volumes vary continuously across the phase boundary. This phenomenon is attributable to the structural similarity between the two phases, both of which crystallize

in the hexagonal system. Their structures are characterized by alternating layers of $[\text{CO}_3]$ and Ce-(OH/F) polyhedra stacked along the c -axis (Online Materials¹ Fig. S10). Notably, both phases exhibit the same cationic coordination environments,

with Ce adopting a ninefold coordination. Furthermore, their Raman spectra reveal substantial overall similarity, especially when the F content is below 0.55 apfu (see the following section). Thus, although the progressive substitution of F by OH reduces the overall symmetry of Hbsn-Ce relative to Bsn-Ce, the basic connectivity of atoms remains essentially unchanged in both structures, as illustrated in Online Materials¹ Figure S10.

Polyhedral Behaviors Across the Phase Boundary

Significant discontinuities occur in bond lengths, polyhedral volumes, and the distortion indices of the $\text{CeO}_6(\text{OH}/\text{F})_3$ polyhedra near the phase transition boundary. For instance, a sudden increase in $d_{\text{C-O1}}$ is noted at the phase boundary, particularly with $d_{\text{C1-O1}}$ increasing from 1.326(17) to 1.530(30) Å as the F content decreases from 0.55 to 0.52 apfu (Online Materials¹ Fig. S5). A similar phenomenon is observed in the volume of the $\text{CeO}_6(\text{OH}/\text{F})_3$ polyhedron, which steadily increases from 31.57 to 32.21 Å³ as F decreases from 0.86 to 0.55 apfu, but then abruptly decreases from 32.21 to 31.79 Å³ when F further decreases to 0.52 apfu (Fig. 4c).

Moreover, the distortion indices of the $\text{CeO}_6(\text{OH}/\text{F})_3$ polyhedra show a strong correlation with increasing F content within both the hydroxylbastnäsite and bastnäsite ranges (Fig. 4d). In hydroxylbastnäsite, the distortion indices of the three $\text{CeO}_6(\text{OH}/\text{F})_3$ polyhedra decrease as the F content increases; however, this relationship changes significantly at the phase transition boundary. Within the bastnäsite range, the distortion index of the $\text{CeO}_6(\text{OH}/\text{F})_3$ increases with increasing F content, suggesting that the polyhedral distortion minimizes as F approaches 0.5 apfu (Fig. 4d).

Furthermore, within the bastnäsite region, as the F content decreases, the F occupancies at F1/OH1 and F2/OH2 sites consistently decrease. However, near the phase boundary, occupancy at F2/OH2 suddenly increases while occupancy at F1/OH1 experiences a more significant decrease (Online Materials¹ Fig. S3).

Raman Spectroscopy Across the Phase Boundary

Raman spectra of Bsn-Ce–Hbsn-Ce solid solutions exhibit overall similarity but also notable changes as the F content varies. The most significant differences in the Raman spectra between hydroxylbastnäsite and bastnäsite are observed in the symmetric stretching vibration modes of the $[\text{CO}_3]$ units, which occur in the range of 1000–1200 cm^{−1}, as well as in the O–H stretching vibration modes, which are in the range of 3400–3800 cm^{−1} (Fig. 5). In bastnäsite with an F content of 0.86 apfu, a prominent peak corresponding to the symmetric stretching mode of the $[\text{CO}_3]$ unit is observed at 1095.19(1) cm^{−1}. This finding is consistent with crystal structural refinement results indicating that only one crystallographically unique $[\text{CO}_3]$ unit exists in its structure (Online Materials¹ Fig. S5 and Tables S2). In hydroxylbastnäsite, although six crystallographically distinct $[\text{CO}_3]$ units are present, only three symmetric stretching vibration peaks (ν_1 , ν_2 , ν_3) are discernible in its Raman spectrum (Fig. 5a). This observation implies a pronounced vibrational degeneracy. A contributing factor to this degeneracy is the near equivalence of C–O bond lengths. For example, at F = 0 apfu, the bond lengths of C2–O [1.294(12) Å] and C4–O [1.293(8) Å] are virtually indistinguishable within

uncertainties; similarly close are the values for C5–O [1.313(11) Å] and C6–O [1.305(12) Å], as well as for C1–O [1.275(7) Å] and C3–O [1.266(11) Å]. Such similarity likely leads to the overlap of symmetric stretching vibrational modes corresponding to $[\text{C2O}_3]$ and $[\text{C4O}_3]$; $[\text{C5O}_3]$ and $[\text{C6O}_3]$; and $[\text{C1O}_3]$ and $[\text{C3O}_3]$. Consequently, despite the presence of six distinct crystallographic $[\text{CO}_3]$ units, only three symmetric stretching vibration peaks are observed in the Raman spectrum of hydroxylbastnäsite.

As the F content decreases, a notable splitting trend is observed in the symmetric stretching peak (Figs. 5a and 6a). For F contents ranging from 0 to 0.55 apfu, at least three Raman peaks can be identified within the Raman shift range associated with the symmetric stretching mode of the $[\text{CO}_3]$ units (Figs. 5a and 6a). In the range of 3400–3800 cm^{−1}, Bsn₈₆Hbsn₁₄ displays two Raman peaks corresponding to two O–H stretching modes, while Hbsn₁₀₀ shows five Raman peaks corresponding to five O–H stretching modes. This observation aligns with crystal structural refinement results that indicate the presence of two and five crystallographically distinct OH/F sites in bastnäsite and hydroxylbastnäsite, respectively.

The Raman spectra within this frequency range are very similar at F < 0.86 apfu except for F = 0 apfu (see the next section). This suggests that the crystal structure of bastnäsite evolves toward that of hydroxylbastnäsite as F content decreases, resulting in very similar Raman spectra for bastnäsite-dominant and hydroxylbastnäsite-dominant Bsn-Ce–Hbsn-Ce solid solutions within a specific range of F content (0.23–0.55 apfu; Fig. 5; Online Materials¹ Fig. S7). However, our SCXRD analysis identified the hydroxylbastnäsite structure only at F contents lower than 0.50 apfu, indicating that Raman spectroscopy is more sensitive than XRD in detecting subtle structural changes during the Bsn-Ce–Hbsn-Ce phase transition.

Additionally, we examined the relationship between Raman shifts of the $[\text{CO}_3]$ symmetric stretching modes (1000–1200 cm^{−1}) and varying F content. For F = 0–0.55 apfu, the average Raman shift is calculated by taking the mean value of the three deconvoluted peaks (ν_1 – ν_3); for F = 0.62–0.86 apfu, we only used ν_2 . The results indicate that Raman shifts vary systematically with changing F content within both hydroxylbastnäsite and bastnäsite regions (Fig. 6a), and a quadratic function fits the data well.

For hydroxylbastnäsite, we obtain the following equation:

$$\nu = 1083.88(15) + 7.97(118)F + 0.56(232)F^2, \\ R^2 = 0.99$$

For bastnäsite:

$$\nu = 1067.99(364) + 50.50(995)F - 21.95(670)F^2, \\ R^2 = 0.99$$

These functions could potentially serve as a method for identifying F contents in natural and synthetic Bsn-Ce–Hbsn-Ce solid solutions; however, it is essential to consider the effects of cationic substitution on the Raman shifts.

Order-disorder Transition of H Atoms Across the Bsn-Ce–Hbsn-Ce Solid Solution

Although the crystal structures of bastnäsite and hydroxylbastnäsite have been established for several decades

(e.g., Donnay and Donnay 1953; Yang et al. 2008; Michiba et al. 2011; Liu et al. 2019), the positions of hydrogen atoms within these structures remain ambiguous. This study represents the first attempt to locate the hydrogen atoms in both bastnäsite and hydroxylbastnäsite structures using SCXRD data. At $F = 0$ apfu, five distinct OH/F sites are each associated with a hydrogen atom (H1 to H5). Notably, H1, H2, and H3 occupy special crystallographic sites, and the OH-H1, OH2-H2, and OH3-H3 bonds are parallel to the c -axis, while H4 and H5 occupy general positions. All hydrogen atoms for the five OH/F sites are in an ordered state (Fig. 7a).

As the F content increases to 0.23 apfu, the F occupancy at the OH2/F2 site rises to 36%. Structural refinement results indicate that at this point, the H2 atom enters a disordered state (Fig. 7b), with three possible positions around the OH2/F2 site. Furthermore, Raman spectroscopy analysis reveals the emergence of two new peaks within the range of $3500\text{--}3600\text{ cm}^{-1}$ (Fig. 5b; Online Materials¹ Fig. S9) at $F = 0.23$ apfu, which aligns well with the order-disorder transition of the H2 atom.

The transition of hydrogen atoms from an ordered to a disordered state is a common phenomenon in various hydrous phases, with Raman spectroscopy serving as a critical analytical technique for its detection. For example, Salzmann et al. (2006) demonstrated the phase transition between hydrogen-ordered ice XIII and disordered ice V. This transition manifests in the Raman spectra by a decrease in peak intensity and broadening of the peaks within the O-H stretching region, indicating the order-to-disorder transition of hydrogen atoms. Similar phenomena have been documented in other compounds, such as pentaerythritol $[\text{C}(\text{CH}_2\text{OH})_4]$ (Jain and Deb 2020) and 1-adamantane-methanol ($\text{C}_{11}\text{H}_{18}\text{O}$, Ben Hassine et al. 2021). Additionally, Comodi et al. (2007) reported an order-disorder transition of hydrogen atoms in the 10-Å phase $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot\text{H}_2\text{O}]$ under high-pressure conditions using Raman spectroscopy. This transition is evidenced by the broadening of the O-H stretching vibration peak at 3597 cm^{-1} . A comparable phenomenon has also been observed in the 3.65 Å phase $[\text{MgSi}(\text{OH})_6]$, as reported by Basu et al. (2023).

In this study, however, the ordered-disorder transition of hydrogen atoms is manifested in the Raman spectrum by the appearance of new Raman peaks, which may be related to the specific nature of hydrogen-atom disorder. As shown in Figure 7b, H2 disorder results in the formation of a pseudo $[\text{O}(\text{H}_{1/3})_3]$ unit, similar to the $[\text{CO}_3]$ unit. These newly observed Raman peaks may correspond to certain vibrational modes of the pseudo $[\text{O}(\text{H}_{1/3})_3]$ unit, such as corresponding to the asymmetric stretching vibrational modes of the $[\text{CO}_3]$ unit.

As the F content increases, H2 atoms within hydroxylbastnäsite remain disordered. Furthermore, within the Raman spectrum range of $3400\text{--}3800\text{ cm}^{-1}$, no new peaks are observed, nor do any existing peaks disappear until F content reaches 0.52 apfu. Within the stable range of bastnäsite ($F = 0.52$ to 0.86 apfu), structural refinement results indicate that H1 atoms also exhibit disorder by occupying two possible positions while H2 atoms are ordered (Fig. 7c).

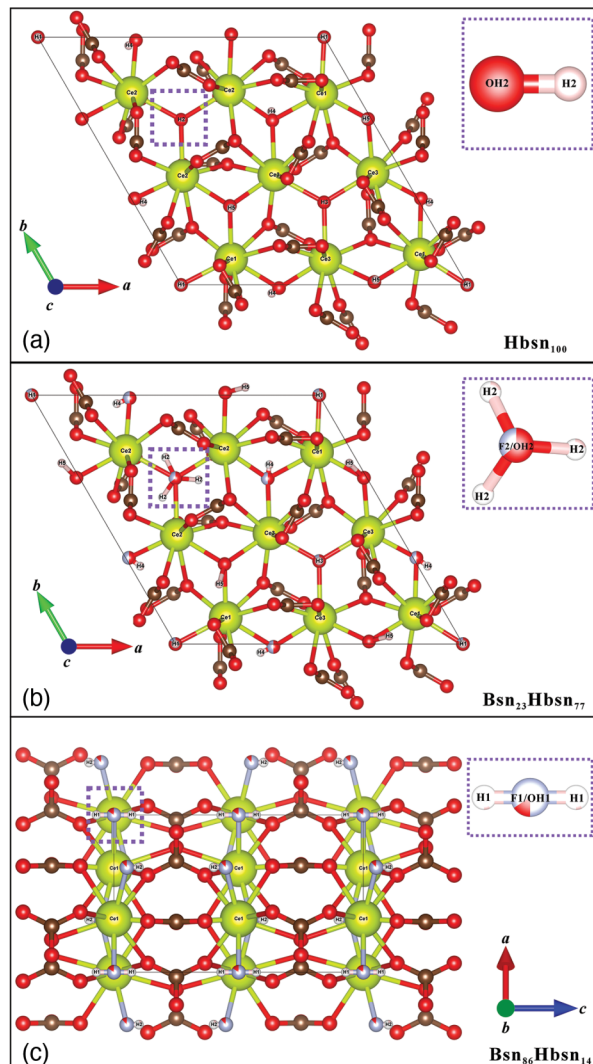


FIGURE 7. Crystal structure and hydrogen bonding in the synthetic Bsn-Ce-Hbsn-Ce solid solutions. (a) Hbsn_{100} , (b) $\text{Bsn}_{23}\text{Hbsn}_{77}$, and (c) $\text{Bsn}_{86}\text{Hbsn}_{14}$. The content within the blue square at the upper right corner illustrates the hydrogen bond, providing an enlarged view of the hydrogen bonding details from the corresponding region in the crystal structure. (Color online.)

Comparisons with Literature Studies

Unit-cell Parameters and Volumes

Since the last century, extensive research has focused on synthesizing end-member hydroxylbastnäsite (e.g., Haschke 1975; Hsu 1992; Michiba et al. 2011; Shivaramaiah et al. 2016; Hämmer and Höpfe 2019; Li et al. 2021) and end-member bastnäsite (e.g., Jansen et al. 1959; Huang et al. 1986; Hsu 1992; Pradip et al. 2013; Shivaramaiah et al. 2016; Buyer et al. 2022). However, for hydroxylbastnäsite-(Ce) and bastnäsite-(Ce), there has been no detailed characterization of the composition of the synthesized samples. Currently, three studies have reported the synthesis of bastnäsite-(Ce); however, none of these studies measured the F content in the samples. Furthermore, the unit-cell

parameters reported in these three studies vary significantly. Jansen et al. (1959) reported unit-cell parameters of $a = 7.2400$ Å and $c = 9.9200$ Å, while Shivaramaiah et al. (2016) obtained $a = 7.2010(10)$ Å and $c = 9.9700(20)$ Å. In contrast, Huang et al. (1986) reported $a = 7.1140$ Å and $c = 9.7400$ Å. The discrepancies among these values are likely attributable to varying F content in the samples among these three studies.

To the best of our knowledge, only Han et al. (2004) reported synthesizing hexagonal CeCO_3OH for hydroxylbastnäsite-(Ce), but they also did not measure the F content in their samples. This study is the first attempt to synthesize Bsn-Ce-Hbsn-Ce solid solutions, and we analyzed the F contents. However, we only synthesized pure end-member hydroxylbastnäsite-(Ce) (CeCO_3OH) and were unable to synthesize pure end-member bastnäsite-(Ce) (CeCO_3F). Given that we used $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ as the source of Ce, the presence of water in the system is unavoidable, making it possible that pure CeCO_3F could not be synthesized.

Nonetheless, the established V_m -F relationship depicted in Figure 3c offers a means to estimate the F contents in previously reported bastnäsite-(Ce) samples. We calculated the molar volumes of samples from previous studies (Jansen et al. 1959; Huang et al. 1986; Shivaramaiah et al. 2016) and plotted these values on our V_m -F curve (Fig. 3c). The results show that the F content of the sample synthesized by Huang et al. (1986) is ~ 0.76 apfu. Conversely, the F content of the sample synthesized by Shivaramaiah et al. (2016) is ~ 0.13 apfu. This latter value lies within the stability field of hydroxylbastnäsite, suggesting that the material reported by Shivaramaiah et al. (2016) is more properly classified as hydroxylbastnäsite rather than bastnäsite. A similar case is observed for the sample synthesized by Jansen et al. (1959), with a molar volume even greater than that of our end-member hydroxylbastnäsite (Fig. 3c). However, it is important to note that instrumental errors intrinsic to different XRD techniques may produce variations in measured volumes, thereby rendering exclusive compositional inference from volume data uncertain.

Raman Spectroscopy

Similarly, in-depth Raman spectroscopic analyses of hydroxylbastnäsite and bastnäsite have been reported (e.g., Yang et al. 2008; Michiba et al. 2011, 2013; Liu et al. 2019; Song et al. 2019; Vennari and Williams 2019; Li et al. 2020; Yuan et al. 2024). For hydroxylbastnäsite, its Raman peaks in the range of 100 – 1500 cm^{-1} do not exhibit significant differences between these studies, with shifts in peak positions primarily attributed to varying substitutions of F-OH and different REE cations (Online Materials¹ Fig. S7). The main differences are concentrated in the high-frequency region associated with OH vibrations. As shown in Figure 8, the Raman spectrum of the synthetic end-member hydroxylbastnäsite-(Ce) (Hbsn₁₀₀) from this study is very similar to that of the synthetic end-member hydroxylbastnäsite-(La), as both have two O-H vibration groups around 3500 and 3650 cm^{-1} . The synthetic hydroxylbastnäsite-(Sm) reported by Liu et al. (2019) exhibits similar characteristics to our Hbsn₁₀₀ and hydroxylbastnäsite-(La) within the range of 3400 – 3700 cm^{-1} . However, this sample has very broad Raman peaks within the

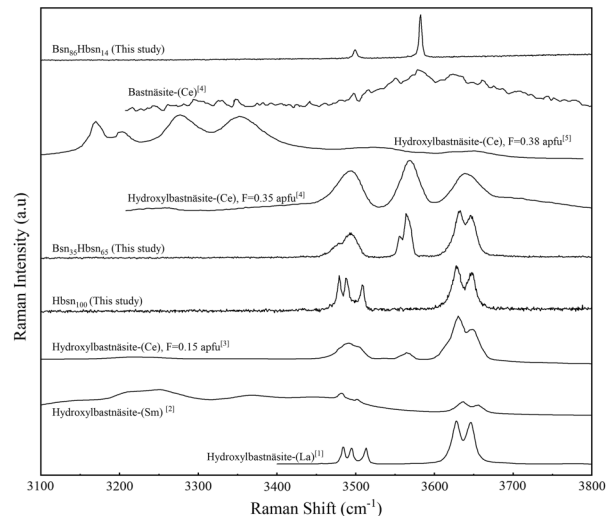


FIGURE 8. Raman spectra of the synthetic Bsn-Ce-Hbsn-Ce solid solutions in the O-H stretching vibration region are presented and compared with previous studies. References: [1] Michiba et al. (2011); [2] Liu et al. (2019); [3] Michiba et al. (2013); [4] Yang et al. (2008); [5] Song et al. (2019).

range of 3100 – 3400 cm^{-1} (Fig. 8). Similar phenomena are also observed in natural hydroxylbastnäsite (Yang et al. 2008; Michiba et al. 2013; Song et al. 2019). In some cases (Yang et al. 2008; Michiba et al. 2013), these peaks are very weak compared to those within the range of 3400 – 3800 cm^{-1} . Due to their broadening, these peaks may be attributed to the effects of fluorescence interference. For natural hydroxylbastnäsite ($F = 0.15$ – 0.38 apfu) (Yang et al. 2008; Michiba et al. 2013; Song et al. 2019), all samples exhibit Raman peaks around 3550 cm^{-1} in addition to those around 3500 and 3650 cm^{-1} (Fig. 8), which are similar to our synthetic hydroxylbastnäsite ($F = 0.23$ – 0.41 apfu). This indicates the presence of disordered hydrogen atoms in the structures of these natural hydroxylbastnäsite.

Previous Raman spectra of bastnäsite have primarily focused on the range of 100 – 1500 cm^{-1} ; only a limited number of studies examined the O-H vibrations (e.g., Yang et al. 2008). Findings from studies on bastnäsite also suggest that the Raman peaks within the 100 – 1500 cm^{-1} range do not show significant differences (Online Materials¹ Fig. S7). The key distinction between this work and previous studies is that the symmetric stretching vibrations of the $[\text{CO}_3]$ unit reveal three splitting peaks when F is between 0.52 and 0.55 . Furthermore, the natural bastnäsite reported by Yang et al. (2008) only exhibits a very broad Raman peak in the region of 3500 – 3800 cm^{-1} (Fig. 8), in contrast to at least two identifiable Raman peaks of our synthetic bastnäsite. A possible reason may be that their bastnäsite sample contains a very minor amount of OH, which results in very weak Raman peaks, making it difficult to identify separable peaks within this frequency region.

IMPLICATIONS

REE minerals are essential for understanding REE cycling in the deep Earth and the genesis of REE deposits (Gysi and

Williams-Jones 2015; Gysi et al. 2015, 2016; Migdisov et al. 2016). Currently, research on the thermodynamic properties of many REE minerals remains limited, leading to the lack of thermodynamic data even for bastnäsite, a key mineral in carbonate REE deposits (Migdisov et al. 2016). Despite natural bastnäsite and hydroxylbastnäsite exhibiting significant substitution of F by OH, little is known about the impact of F-OH substitution on their thermodynamic behaviors (e.g., Yang et al. 2008; Michiba et al. 2013; Song et al. 2019). This study presents crystal chemistry data for a synthetic Bsn-Ce-Hbsn-Ce solid-solution series, which reveals nonideal volume mixing behavior. Establishing a solution model to describe the volume-composition relationship could provide valuable insights into mixing behaviors of other thermodynamic properties.

Although the Bsn-Ce-Hbsn-Ce series is an incomplete solid solution, its volume decreases continuously with increasing F content (Fig. 3; Online Materials¹ Table S1). This enabled the modeling of the V_m -F relationship using a single cubic function (Eq. 5). At F = 1 apfu, Equation 5 predicts $V_m = 42.45(11)$ cm³/mol. Using this value and measurements from 10 samples, we calculated the excess volume ($V_{m,ex}$) across the series. Figure 9 shows positive $V_{m,ex}$ in the hydroxylbastnäsite region and negative values in the bastnäsite region. We applied an asymmetric solution model (White 2013) to describe the $V_{m,ex}$ -F relationship: $V_{m,ex} = [W_{V_1}F + W_{V_2}(1-F)](1-F)F$, where W_{V_1} and W_{V_2} are interaction parameters. Fitting the data yields $W_{V_1} = -2.66(34)$ cm³/mol and $W_{V_2} = 2.55(31)$ cm³/mol, and $R^2 = 0.91$.

However, the Bsn-Ce-Hbsn-Ce solid-solution system comprises two distinct crystal structures, which structurally prevent the formation of a strictly continuous solid solution. Although a single cubic function can mathematically describe the molar volume across the entire compositional range, this approach risks obscuring discontinuities associated with the symmetry transition. Moreover, while the derived excess volume function is mathematically continuous, it may partially reflect structural

reorganization or phase boundary effects rather than accurately capturing true lattice strain behavior. Although empirically useful, the fitting results lack a robust physical basis, providing only an empirical mathematical relation to describe volume as a function of F content across the Hbsn-Ce-Bsn-Ce solid-solution series. Consequently, its practical application requires careful consideration of specific thermodynamic properties, such as the entropy of the solid-solution system. This study represents a foundational step toward the thermodynamic characterization of the Bsn-Ce-Hbsn-Ce solid solutions. Future work will involve systematic measurement of the thermodynamic properties of this solid-solution system.

In addition, F commonly substitutes for OH in rock-forming hydrated minerals such as micas, amphiboles, and apatites, reaching major-element concentrations of several weight percent (Edgar et al. 1996; Mi and Pan 2018). However, systematic experimental studies on F-OH mixing thermodynamics in these minerals remain scarce. In the aforementioned minerals, the substitution of F and OH exhibits different solid-solution behaviors in volume across different mineral groups. For instance, Hovis et al. (2014) and Bulina et al. (2020) examined the fluorapatite-hydroxylapatite solid-solution series, revealing ideal volumetric mixing but negative excess enthalpy in OH-rich compositions (Hovis et al. 2014). In contrast, within the mica groups, both ideal and non-ideal solid-solution behaviors are observed. For example, Robert et al. (1993) found that the volume of the tetrasilicic magnesium mica (TMM) decreases with increasing X_F [$F/(F+OH)$] when $X_F < 0.5$, whereas it remains nearly constant when $X_F > 0.5$, exhibiting non-ideal behavior. Conversely, phlogopite exhibits an ideal solid-solution behavior over the X_F range of 0 to 0.7 (Papin et al. 1997). Moreover, amphibole groups display significant composition-dependence in solid-solution behavior, with pargasite (Holloway and Ford 1975) and Rb-bearing richterites (Della Ventura et al. 2019) exhibiting non-ideal solid solutions, whereas Na/K/Ti-bearing richterites (Robert et al. 1989; Della Ventura et al. 1993) form ideal solid solutions. Notably, the substitution of F and OH in apatite, mica, and amphibole typically results in complete solid solutions.

The results of this study also highlight the need to evaluate F-OH substitution effects in other important F-bearing rock-forming minerals and to develop robust solid-solution models to accurately describe the thermodynamic behaviors of their solid solutions. Such works are important because F-bearing phases like amphibole and biotite are essential to widely used geothermobarometers. Examples include amphibole-plagioclase (Holland and Blundy 1994) and garnet-biotite (Ferry and Spear 1978) geothermobarometers. In addition, these phases also control phase equilibria in petrological simulations, as they commonly occur as major minerals in a rock. Despite their importance, some important thermodynamic databases (e.g., Holland and Powell 2011) lack F-end-member properties for micas and amphiboles, relying solely on OH-end-member data. Closing this gap will substantially improve the accuracy of geothermobarometry and petrological modeling in F-bearing systems.

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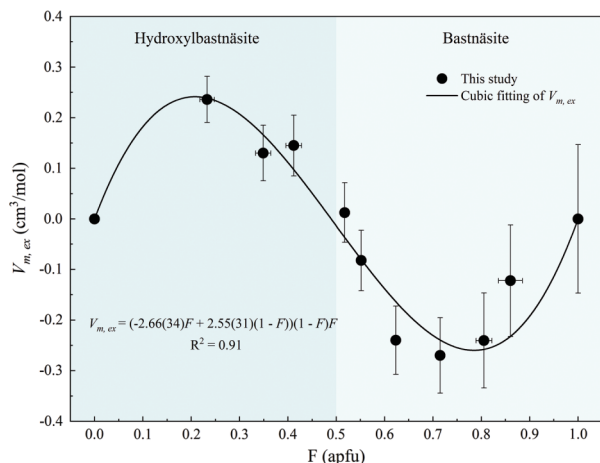


FIGURE 9. Illustration of the relationship between F content and excess molar volume ($V_{m,ex}$) in the Bsn-Ce-Hbsn-Ce solid solutions. Black spheres represent the calculated excess molar volume. Black lines show the cubic fit to the excess molar volume data. (Color online.)

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