

Crystal structure of hydroxylbastnäsite-(Ce) from Kamihour, Miyazaki Prefecture, Japan

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The crystal structure of hydroxylbastnäsite-(Ce), $(\text{Ce}_{0.49}\text{La}_{0.21}\text{Nd}_{0.16}\text{Pr}_{0.06}\text{Y}_{0.03}\text{Sm}_{0.02}\text{Gd}_{0.01}\text{Th}_{0.01}\text{Eu}_{0.01})(\text{CO}_3)(\text{OH}_{0.85}\text{F}_{0.15})$, was solved and refined $R1 = 0.0363$, $wR2 = 0.0871$ using single crystal CCD-XRD data. The hexagonal unit cell of space group $P\bar{6}$ is identical to those of synthetic $\text{RE}(\text{CO}_3)\text{OH}$, but is different from that of bastnäsite-(Ce), $P\bar{6}2c$. The refined dimensions are: $a = 12.4730(9)$, $c = 9.9607(14)$ Å, $V = 1342.0(2)$ Å³, and $Z = 18$ for $\text{Ce}(\text{CO}_3)(\text{OH})$. Each of the three crystallographically independent 9-fold RE cations is coordinated by three $[(\text{OH}), \text{F}]^-$, four monodentate $(\text{CO}_3)^{2-}$, and one bidentate $(\text{CO}_3)^{2-}$ ions in hydroxylbastnäsite-(Ce), in contrast to the 9-fold RE cation coordinated to three F^- and six monodentate $(\text{CO}_3)^{2-}$ ions in bastnäsite-(Ce). The replacement of OH for F modifies the coordination of RE polyhedra, thereby lowering the symmetry and enlarging the unit cell in the crystal structure of hydroxylbastnäsite-(Ce).

Keywords: Hydroxylbastnäsite-(Ce), Rare-earth carbonate hydroxides, Crystal structure analysis

INTRODUCTION

Hydroxylbastnäsite-(Ce) $[\text{Ce}(\text{CO}_3)\text{OH}]$ is a hexagonal rare-earth carbonate hydroxide, and is a polymorph of orthorhombic $\text{Ce}(\text{CO}_3)\text{OH}$, which is isostructural with kozoite-(Nd) $[\text{Nd}(\text{CO}_3)\text{OH}]$ (Miyawaki et al., 2000) and kozoite-(La) $[\text{La}(\text{CO}_3)\text{OH}]$ (Miyawaki et al., 2003). Hydroxylbastnäsite-(Ce) was originally described as a (OH)-analogue of bastnäsite-(Ce) (Kirillov, 1964). Later, the La-dominant analogue (Maksimović and Pantó, 1983) and hydroxylbastnäsite-(Nd) (Maksimović and Pantó, 1985; Farkas et al., 1985; Podporina and Burkov, 1986) were reported. Kirillov (1964) proposed a unit cell and a $P\bar{6}2c$ space group for hydroxylbastnäsite-(Ce) that were identical to those for bastnäsite-(Ce) because of their similar XRD patterns. Haschke (1975) reported that synthetic $\text{La}(\text{CO}_3)\text{OH}$ and $\text{La}(\text{CO}_3)\text{F}$ form a series of continuous solid solutions. Neither the crystal structure nor crystallo-

graphic data based on single-crystal diffraction have been reported for the natural specimens of hydroxylbastnäsite-(Ce), hydroxylbastnäsite-(Nd), and the La-analogue, so-called hydroxylbastnäsite-(La).

The crystal structures of hexagonal $\text{RE}(\text{CO}_3)\text{OH}$ have been determined using some synthetic materials (Christensen, 1973 for RE = Nd; Kutlu and Meyer, 1999 for RE = Dy; Michiba et al., 2011 for RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er). These crystal structure analyses revealed the dimensions of the unit cell to be $a \approx 12$, $c \approx 10$ Å, $Z = 18$, which are different from those of bastnäsite-(Ce); $a \approx 7$, $c \approx 10$ Å, $Z = 6$. The space group, adopted for all hexagonal $\text{RE}(\text{CO}_3)\text{OH}$, $P\bar{6}$, has lower symmetry than $P\bar{6}2c$, the space group of bastnäsite-(Ce). Michiba et al. (2011) cast doubt upon $P\bar{6}2c$ previously reported for hydroxylbastnäsite-(Ce), because they believed hydroxylbastnäsite-(Ce) to be the natural hexagonal phase of $\text{Ce}(\text{CO}_3)\text{OH}$. Discrepancies in the settings of the unit cell and space groups between natural minerals and synthetic compounds have been presented, in spite of similarities in their powder X-ray diffraction patterns. In the



Figure 1. A photomicrograph of hydroxylbastnäsite-(Ce) from Kami-houri, Miyazaki Prefecture, Japan (NSM-M29287), showing a hexagonal short prismatic crystal with yellowish light brown color.

present study, the crystal structure of hydroxylbastnäsite-(Ce) was determined using a natural specimen to clarify the doubt.

The sample of hydroxylbastnäsite-(Ce) used in the present study is from Kami-houri, Kitagawa, Nobeoka, Miyazaki Prefecture, Japan (Minakawa et al., 1992), and is registered in the mineral collection of the National Museum of Nature and Science (NSM-M29287). It occurs in the Miocene-granitic-pegmatite-intruding Shimanto supergroup associated with beryl, zircon, xenotime-(Y), allanite-(Ce), gadolinite-(Y), and ilmenite. The crystals of hydroxylbastnäsite-(Ce) have granular to hexagonal short prismatic habit, and are yellow to yellowish light brown in color (Fig. 1). The size of these crystals usually ranges from hundred to several hundred micrometers.

CHEMICAL COMPOSITION

A quantitative chemical analysis was carried out using a JEOL JXA-8800M WDS electron microprobe analyzer by utilizing the ZAF corrections for data obtained under the following conditions; 15 kV, 10 nA, and 5 μm beam diameter. The following analytical standard materials were used: RE_2O_3 (RE = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb), wollastonite (Ca), SrSO_4 (Sr), ThO_2 (Th), and CaF_2 (F). The compositional homogeneity of each grain was checked at a minimum of six analytical points.

The results of this chemical analysis are listed in Table 1. No elements with an atomic number greater than eight were detected. The presence of OH and CO_3 was confirmed by Raman spectroscopy as described below. The amounts of H_2O (3.44 wt%) and CO_2 (19.63 wt%)

Table 1. Chemical composition of hydroxylbastnäsite-(Ce)

n = 6	wt% (Average)	Range*		apfu
La_2O_3	14.94	14.77-15.32	La	0.206
Ce_2O_3	35.87	35.25-36.47	Ce	0.490
Pr_2O_3	4.15	3.95-4.46	Pr	0.056
Nd_2O_3	12.14	11.41-12.59	Nd	0.162
Sm_2O_3	1.50	1.29-1.67	Sm	0.019
Eu_2O_3	0.63	0.49-0.72	Eu	0.008
Gd_2O_3	0.84	0.50-1.27	Gd	0.010
Dy_2O_3	0.27	0.12-0.41	Dy	0.003
Ho_2O_3	0.08	0.01-0.18	Ho	0.001
Yb_2O_3	0.06	0.00-0.18	Yb	0.001
Y_2O_3	1.61	1.37-1.96	Y	0.032
CaO	0.02	0.00-0.05	Ca	0.001
SrO	0.03	0.00-0.11	Sr	0.001
ThO_2	1.21	0.78-1.46	Th	0.010
$\text{CO}_2^\S$	19.63	19.37-19.84	C §	1.000
$\text{H}_2\text{O}^\S$	3.44	3.37-3.50	H §	0.855
F	1.23	1.13-1.41	F	0.145
- O = F $_2$	-0.52			
Total	97.13			

§ CO_2 , H_2O are calculated assuming ideal stoichiometry.

* The compositional range of six analytical points.

were calculated using the stoichiometry based on the ideal formula $(\text{RE}, \text{Th}, \text{Ca}, \text{Sr})(\text{CO}_3)(\text{OH}, \text{F})$. The empirical formula obtained on the basis of total cations = 1 apfu is $(\text{Ce}_{0.49}\text{La}_{0.21}\text{Nd}_{0.16}\text{Pr}_{0.06}\text{Y}_{0.03}\text{Sm}_{0.02}\text{Gd}_{0.01}\text{Th}_{0.01}\text{Eu}_{0.01})(\text{CO}_3)(\text{OH}_{0.85}\text{F}_{0.15})$.

RAMAN SPECTROSCOPY

The Raman spectrum of hydroxylbastnäsite-(Ce) was measured using a JASCO NRS-3200 spectrometer employing a charge-coupled device as a detector, in the range 400–4000 cm^{-1} with a resolution of 1 cm^{-1} . The sample was excited by irradiating its surface with green laser (523 nm) having a beam size of 1 μm and power of 3.0 mW. The elastic Rayleigh line was attenuated by a holographic notch filter before reaching the detector. Five scans with a typical acquisition time of about 10 s were accumulated. The spectrum was calibrated using lines for polypropylene.

The Raman spectrum of hydroxylbastnäsite-(Ce) is shown in Figure 2. In this spectrum, the peak observed at 726 cm^{-1} corresponds to the ν_4 in-plane bending region of the $(\text{CO}_3)^{2-}$ units. The high-intensity bands at 1079 and 1097 cm^{-1} were assigned to the ν_1 symmetric stretching mode of the $(\text{CO}_3)^{2-}$ units. Further, splitting was observed in the ν_1 symmetric stretching mode for hydroxylbastnäsite-(Ce). No bands corresponding to the ν_2 bending modes of the $(\text{CO}_3)^{2-}$ units (at around 879 cm^{-1}) were observed because of the Raman inactive vibration mode. The splitting bands at 1390 and 1425 cm^{-1} were assigned

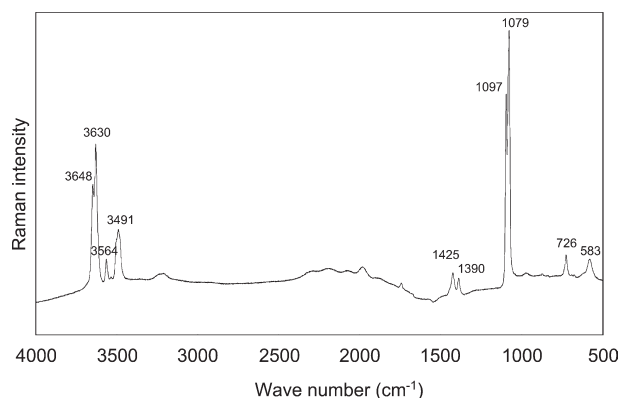


Figure 2. Raman spectrum of hydroxylbastnäsit-(Ce) from Kami-houri, Miyazaki Prefecture, Japan.

to the ν_3 asymmetric stretching vibrations of the $(\text{CO}_3)^{2-}$ units. Furthermore, some O-H stretching vibrations were observed in the range $3400\text{--}3700\text{ cm}^{-1}$.

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

Powder X-ray diffraction data were obtained using a 114.6 mm Gandolfi camera with a synchrotron radiation source at BL-37XU of SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), Hyogo, Japan. The synchrotron radiation was monochromatized using a monochromator of Si(111) double crystals ($\lambda = 2.0675\text{ \AA}$). Diffraction images of Debye rings were recorded on an imaging plate, processed with a Fuji BAS-2500 image analyzer, and quantified into a diffraction pattern using a computer program written by Nakamura (1999). The cell parameters of hydroxylbastnäsit-(Ce) were refined using a program, CellCalc (Miura, 2003), as: $a = 12.4258\text{ (9)}$ and $c = 9.9095\text{ (9)}$ Å. The powder diffraction pattern of hydroxylbastnäsit-(Ce) was congruent with those of synthetic hexagonal $\text{RE}(\text{CO}_3)\text{OH}$ (Michiba et al., 2011). The powder diffraction data and refined lattice parameters of hydroxylbastnäsit-(Ce) are listed in Table 2.

The X-ray diffraction data of a single crystal of hydroxylbastnäsit-(Ce) were collected on a Bruker AXS SMART diffractometer with a CCD area-detector having a crystal-to-detector distance of 62.06 mm, using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) generated at 55 kV and 30 mA. The spatial distributions of intensities in the CCD data showed that the unit cell of hydroxylbastnäsit-(Ce) is different from that of bastnäsit-(Ce), but is identical to those of synthetic $\text{RE}(\text{CO}_3)\text{OH}$ (Michiba et al., 2011). More than a hemisphere of three dimensional data was collected ($-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-13 \leq l \leq 11$) in the range $1.89 \leq \theta \leq 28.27^\circ$, utilizing the ω -scan mode with a scan width of 0.3° . The unit-

cell parameters were refined from 3382 reflections by using least-squares techniques. The frames were integrated using the Bruker SAINTPLUS (Bruker, 1997) software package utilizing a narrow-frame integration algorithm. Empirical collection for absorption based on symmetry equivalent reflections was performed with SADABS software (Sheldrick, 1997). Symmetry-equivalent reflections were averaged ($R_{\text{int}} = 0.0206$). The crystal structure of hydroxylbastnäsit-(Ce) was solved and refined using the SHELXTL (Sheldrick, 2008) program by a direct method and expanded using Fourier syntheses. Full-matrix least-square refinement was carried out. The scattering factor curve of Ce was adopted as the curve of lanthanides in the calculation; this is because the atomic number of Ce (58) is close to the weighted average of the atomic numbers of lanthanides (58.4), calculated from the chemical composition of present sample. The trace elements substituting the rare earths, such as Ca, Sr, and Th, were ignored in the calculation. Site-occupancy factors were fixed on the basis of the chemical composition: $0.97\text{Ce} + 0.03\text{Y}$ for the Ce site, and $0.85(\text{OH}) + 0.15\text{F}$ for the O13–O17 sites. The Ce sites were refined anisotropically in the final cycles of refinement.

The crystallographic data for hydroxylbastnäsit-(Ce) are listed in Table 3. The final atomic coordinates and isotropic displacement parameters for all atoms are listed in Table 4. Table 5 shows the anisotropic displacement parameters for the Ce sites. The values in parentheses show standard deviations in the last digit. Selected bond lengths calculated from the atomic parameters are listed in Table 6. Bond-valence sums were calculated using the parameters of Brese and O'Keeffe (1991) (Table 4).

The position of the hydrogen atoms could not be determined in this study. Refinements with anisotropic displacement parameters for all atoms converged with lower R factors, but resulted in the “non-positive definite” for principal mean square atomic displacements (U) for some C and O sites.

DESCRIPTION OF AND DISCUSSION ON CRYSTAL STRUCTURE

The unit cell of hydroxylbastnäsit-(Ce) contains 18 $\text{Ce}(\text{CO}_3)\text{OH}$ formula units. The crystal structure of hydroxylbastnäsit-(Ce) is isomorphous with the series of synthesized hexagonal $\text{RE}(\text{CO}_3)\text{OH}$ (Michiba, et al., 2011). The CeO_9 tricapped trigonal prisms are the building units in the crystal structure (Fig.3). The $(\text{OH})^-$ ions are located at the center of triangles formed by three Ce cations to connect these Ce cations (Fig. 3, lower). The crystal structure of hydroxylbastnäsit-(Ce) can be de-

Table 2. Powder X-ray diffraction data for hydroxylbastnäsite-(Ce)

This work*						**			Kirillov (1964)		Farkas et al. (1985)		Podporina and Burkov (1986)		Minakawa et al. (1992)	
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs.}	<i>I</i> / <i>I</i> ₀	<i>d</i> _{obs.}	<i>I</i> / <i>I</i> ₀	<i>d</i> _{obs.}	<i>I</i> / <i>I</i> ₀	<i>d</i> _{obs.}	<i>I</i> / <i>I</i> ₀
0	0	2	4.961	4.955	35	0	0	2	4.97	20	4.955	88	7.18 4.77	40 40b	4.983	30
2	1	0	4.071	4.067	2											
1	1	2	3.876	3.874	1											
3	0	0	3.586	3.587	86	1	1	0	3.59	90	3.596	79	3.52	80b	3.604	100
2	2	1	2.966	2.964	1											
3	0	2	2.906	2.906	100	1	1	2	2.92	100	2.911	100	2.83	100	2.917	70
2	2	2	2.632	2.632	3	2	0	2			2.633	3				
1	2	3	2.563	2.564	1											
0	0	4	2.477	2.477	11	0	0	4	2.49	10b	2.481	16	2.41	10b	2.488	5
1	4	1	2.285	2.285	5	2	1	1			2.292	3				
2	2	3	2.263	2.263	1											
3	1	3	2.214	2.215	1											
1	4	2	2.121	2.122	2	2	1	2			2.126	2				
3	3	0	2.070	2.071	41	3	0	0	2.09	90	2.077	29	2.02	50b	2.079	50
3	0	4	2.038	2.038	53	3	0	1					1.99	60b	2.047	40
						1	1	4	2.05	80	2.042	51				
3	3	2	1.910	1.911	36	3	0	2	1.923	90	1.914	30	1.86	30b	1.918	35
6	0	0	1.793	1.794	12	2	2	0	1.805	40	1.798	10			1.800	20
									1.761	10						
6	0	2	1.686	1.686	19	2	2	2	1.698	70	1.690	16	1.64	5b	1.692	25
0	0	6	1.651	1.652	3	0	0	6			1.655	3				
5	0	4	1.626	1.625	1											
3	3	4	1.588	1.589	14	3	0	4	1.600	40	1.591	12	1.54	5b	1.595	15
3	0	6	1.500	1.500	11	1	1	6	1.466	30	1.502	9			1.464	5b
6	0	4	1.452	1.453	10	2	2	4	1.460	50	1.455	9			1.457	5b
1	7	2	1.370	1.370	1	4	1	0	1.369	40	1.359	5			1.360	5
6	3	0	1.356	1.356	7											
1	2	7	1.337	1.337	1											
						4	0	4	1.319	70	1.311	10			1.313	15
6	3	2	1.307	1.308	15	4	1	1					1.32	5b		
3	3	6	1.291	1.291	6	3	0	6	1.298	20	1.294	5				
0	0	8	1.239	1.239	2						1.217	4				
6	0	6	1.215	1.215	5	2	2	6								
9	0	0	1.196	1.196	3	3	3	0	1.198	40						
6	3	4	1.189	1.189	10	4	1	4			1.192	7				
3	0	8	1.171	1.171	5	4	2	1	1.172	40						
9	0	2	1.162	1.162	6	3	3	2			1.165	4				
2	8	2	1.142	1.142	1											
						5	1	3	1.086	10						
9	0	4	1.077	1.077	4											
3	3	8	1.063	1.063	5											
3	6	6	1.048	1.048	5											
						5	0	5	1.023	10						

* *d* values were calculated by assuming *a* = 12.4258 (9) and *c* = 9.9095 (9) Å.Only reflections with *I*/*I*₀ ≥ 1 are listed.** The indices are based on the bastnäsite-(Ce)-type unit cell with *a* ≈ 7, *c* ≈ 10 Å, *Z* = 6.

scribed as stackings of ${}^2_{\infty}[(\text{OH})\text{Ce}_{3/3}]^{2+}$ layers extending parallel to the *ab* plane. The layers are linked by $(\text{CO}_3)^{2-}$ groups as bidentate and monodentate ligands, and stack in the [001] direction (Fig. 3, upper).

Although all the Ce sites in bastnäsite-(Ce) are crystallographically equivalent, the crystal structure of hydroxylbastnäsite-(Ce) consists of three independent Ce sites at general positions that are correlated by a pseudo $\bar{6}$ axis (Fig. 4). The coordination of Ce is formed with three

$(\text{OH})^-$ ions and five $(\text{CO}_3)^{2-}$ ions, of which four are monodentate ligands and one is a bidentate ligand (Fig. 4, lower). On the contrary, the crystallographically equivalent 9-fold Ce cations in bastnäsite-(Ce) are coordinated by three F^- and six monodentate $(\text{CO}_3)^{2-}$ ions (Fig. 4, upper).

Two-thirds of O atoms in individual $(\text{CO}_3)^{2-}$ ions (O2, O4, O6, O8, O10, and O12) are superimposed on each other in the direction of the *c*-axis. The other one-third of O atoms (O1, O3, O5, O7, O9, and O11) and C

Table 3. Crystallographic data for hydroxylbastnäsité-(Ce)

Crystal system	Hexagonal	Total Ref.	8268
Space group	$P\bar{6}$	Unique Ref.	2203
$a(\text{\AA})$	12.4730(9)	R_{int}	0.0206
$c(\text{\AA})$	9.9607(14)	$R1[I > 2\sigma(I)]$	0.0364
$V(\text{\AA}^3)$	1342.0(2)	$wR2[I > 2\sigma(I)]$	0.0871
D_{calc}	4.789	$R1(\text{all data})$	0.0381
Z	18	$wR2(\text{all data})$	0.0886
$\mu(\text{cm}^{-1})$	15.210	S	1.248
Crystal size(mm)	$0.30 \times 0.20 \times 0.20$	Largest diff. peak($\text{e.\AA}^{-3}$)	1.771
Radiation	Mo $K\alpha$	Largest diff. hole($\text{e.\AA}^{-3}$)	-1.741

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}.$$

$$S = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}; \text{ for } n \text{ observations and } p \text{ parameters.}$$

$$w = 1/[\sigma^2(F_o^2) + (0.0182P)^2 + (16.7632P)], \text{ where } P = (2F_o^2 + F_c^2)/3.$$

Table 4. Atomic coordinates, Wyckoff position, equivalent isotropic displacement parameters, and bond valence sum (BVS, valence units) for atoms in hydroxylbastnäsité-(Ce)

Atom	Position	x	y	z	U_{iso}	BVS
Ce1	6l	0.10783(9)	0.22796(6)	0.23530(5)	0.00901(19)*	3.11
Ce2	6l	0.77882(15)	0.56268(6)	0.2542(2)	0.01374(19)*	3.09
Ce3	6l	0.43856(6)	0.54375(7)	0.25769(18)	0.0107(2)*	3.09
C1	3j	0.8655(15)	0.5103(15)	0	0.030(4)	4.14
C2	3j	-0.0902(11)	0.1104(10)	0	0.007(2)	4.08
C3	3j	0.3037(14)	0.4637(14)	0	0.025(3)	3.86
C4	3k	0.5531(14)	0.4206(15)	0.5	0.026(3)	3.78
C5	3k	0.5356(13)	0.7746(12)	0.5	0.017(3)	3.56
C6	3k	-0.0247(12)	0.1777(12)	0.5	0.016(3)	3.95
O1	3j	0.7601(11)	0.5088(11)	0	0.034(3)	1.84
O2	6l	0.9117(6)	0.5098(6)	0.1118(7)	0.0178(14)	2.11
O3	3j	0.0286(9)	0.1691(9)	0	0.0168(19)	2.09
O4	6l	0.2316(6)	0.1469(6)	0.1119(6)	0.0139(13)	2.06
O5	3j	0.4114(12)	0.5726(12)	0	0.040(3)	1.65
O6	6l	0.2516(7)	0.4173(7)	0.1117(8)	0.0256(17)	2.16
O7	3k	0.8033(11)	0.5032(11)	0.5	0.030(3)	1.83
O8	6l	0.5796(6)	0.4838(6)	0.3884(7)	0.0186(14)	1.90
O9	3k	0.3638(11)	0.5249(11)	0.5	0.033(3)	1.78
O10	6l	0.5671(6)	0.7415(6)	0.3879(7)	0.0218(15)	1.79
O11	3k	0.0822(7)	0.1794(7)	0.5	0.0043(15)	1.66
O12	6l	-0.0721(6)	0.1799(6)	0.3875(6)	0.0142(13)	2.14
O13	2g	0	0	0.2723(10)	0.0091(18)	1.13
O14	2h	0.6667	0.3333	0.2377(14)	0.027(3)	1.15
O15	2i	0.3333	0.6667	0.2356(13)	0.023(3)	1.17
O16	6l	0.9998(6)	0.6804(6)	0.3218(7)	0.0168(14)	1.17
O17	6l	0.6532(6)	0.6543(6)	0.1778(7)	0.0204(15)	1.17

Notes: Numbers in parentheses denote 1 esd of last unit cited.

Bond valence sum is weighted assuming 0.97Ce + 0.03Y for the Ce site and 0.85O + 0.15F for the O13–O17 sites.

* U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor (see Table 5).

Table 5. Anisotropic displacement parameters ($\text{\AA}^2$) for hydroxylbastnäsité-(Ce)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce1	0.0111(3)	0.0104(3)	0.0044(2)	0.0016(2)	-0.0010(2)	0.0046(3)
Ce2	0.0137(3)	0.0080(3)	0.0185(3)	0.0011(2)	0.0102(2)	0.0047(2)
Ce3	0.0076(3)	0.0081(3)	0.0160(4)	-0.0031(3)	-0.0038(3)	0.0036(3)

The anisotropic displacement factor takes the following form:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

Table 6. Selected interatomic distances (Å) for hydroxylbastnäsité-(Ce)

Ce1-O3	2.507(3)	Ce2-O1	2.600(3)	Ce3-O2	2.607(7)
Ce1-O4	2.545(6)	Ce2-O2	2.508(7)	Ce3-O5	2.637(3)
Ce1-O6	2.464(7)	Ce2-O4	2.669(6)	Ce3-O6	2.522(7)
Ce1-O10	2.722(7)	Ce2-O7	2.620(4)	Ce3-O8	2.581(7)
Ce1-O11	2.6883(17)	Ce2-O8	2.547(7)	Ce3-O9	2.556(4)
Ce1-O12	2.520(6)	Ce2-O12	2.486(6)	Ce3-O10	2.526(7)
Ce1-O13	2.4911(17)	Ce2-O14	2.4830(12)	Ce3-O15	2.4767(13)
Ce1-O16	2.451(6)	Ce2-O16	2.481(6)	Ce3-O16	2.508(6)
Ce1-O17	2.504(7)	Ce2-O17	2.477(6)	Ce3-O17	2.451(7)
Mean	2.544	Mean	2.541	Mean	2.541
C1-O1	1.306(19)	C3-O5	1.35(2)	C5-O9	1.348(18)
C1-O2 × 2	1.255(10)	C3-O6 × 2	1.273(10)	C5-O10 × 2	1.317(10)
Mean	1.272	Mean	1.299	Mean	1.327
C2-O3	1.284(15)	C4-O7	1.302(19)	C6-O11	1.322(15)
C2-O4 × 2	1.272(8)	C4-O8 × 2	1.306(11)	C6-O12 × 2	1.273(9)
Mean	1.276	Mean	1.305	Mean	1.289

atoms (C1, C2, C3, C4, C5, and C6) are located on mirror planes perpendicular to the *c*-axis. The C–O bond lengths on the mirror planes are shorter than the others of a (CO₃)²⁻, suggesting a distortion of triangle. The Ce–O interatomic distances are comparable to those reported previously for rare-earth carbonate minerals, e.g., 2.58(3)–2.62(2) Å for bastnäsité-(Ce) (Terada et al., 1993) and 2.38(1)–2.785(8) Å for kozoite-(Nd) (Miyawaki et al., 2000).

The bond-valence sums of cations (Table 4) are in good agreement with the ideal values, except for some C atoms, i.e., C4 and C5. The deviations in valency from the ideal values result from the deviations in interatomic distances from the typical C–O bond distances in the carbonate groups. The bond-valence sums for O1–O12 anions are in the range 1.65–2.16 v.u., which approximate 2, the ideal value for divalent O²⁻. Those for O13–17 [(OH)_{0.85}F_{0.15}] are in the range 1.13–1.17 v.u., which is close to the ideal value for monovalent (OH)⁻ and F⁻.

In terms of its splitting feature, the Raman spectrum of hydroxylbastnäsité-(Ce) (Fig. 2) is very similar to those of the series of synthesized hexagonal RE(CO₃)OH (Michiba et al., 2011). The ν_1 symmetric stretching O–C–O mode shows splitting in the Raman spectrum of hydroxylbastnäsité-(Ce) (1079 and 1097 cm⁻¹ in Fig. 2), whereas that of bastnäsité-(Ce) shows a single sharp peak. This splitting feature suggests a slight lowering in the symmetry of the (CO₃)²⁻ triangle units among the three crystallographically independent sites in the crystal structure of hydroxylbastnäsité-(Ce). Further, the two intense bands of O–H stretching vibrations (3400–3700 cm⁻¹ in Fig. 2) show splitting and broadening, indicating several kinds of O–H bonds resulting from the lowered symmetry in the crystal structure of hydroxylbastnäsité-(Ce).

The characteristic feature of the powder diffraction

patterns of hydroxylbastnäsité-(Ce), as well as those of synthetic hexagonal RE(CO₃)OH is that significant diffraction intensities can be observed only for reflections of $h = 3n$, $k = 3n$, and $l = 2n$. This diffraction pattern can be attributed to the sequence of rare-earth elements, the heavier atoms having significant scattering power, in intervals of $a/3$ and $c/2$ in the crystal structure of hydroxylbastnäsité-(Ce). Some of the weak reflections cannot be indexed with the bastnäsité-type unit-cell ($a = 7.23$, $c = 9.98$ Å) but can be indexed with the unit-cell of synthetic hexagonal RE(CO₃)OH (e.g., $a = 12.47$, $c = 9.96$ Å). The intensities of these reflections are so weak that these were possibly overlooked in previous powder X-ray diffraction studies on hydroxylbastnäsité-(Ce) (Kirillov, 1964), hydroxylbastnäsité-(Nd) (Farkas, 1985; Podporina and Burkov, 1986), and hydroxylbastnäsité-(Ce) from Kamihouri (Minakawa et al., 1992), our primary X-ray diffraction study.

The present determination of the crystal structure of hydroxylbastnäsité-(Ce) from Kamihouri demonstrated that this mineral is the natural analogue of the synthetic hexagonal RE(CO₃)OH with space group $P\bar{6}$. Hydroxylbastnäsité-(Ce) differs from bastnäsité-(Ce) not only in the chemistry, but also in the crystallography. In the crystal structure of hydroxylbastnäsité-(Ce), the replacement of F by OH modifies the coordination of RE polyhedra, thereby lowering the symmetry and enlarging the unit cell.

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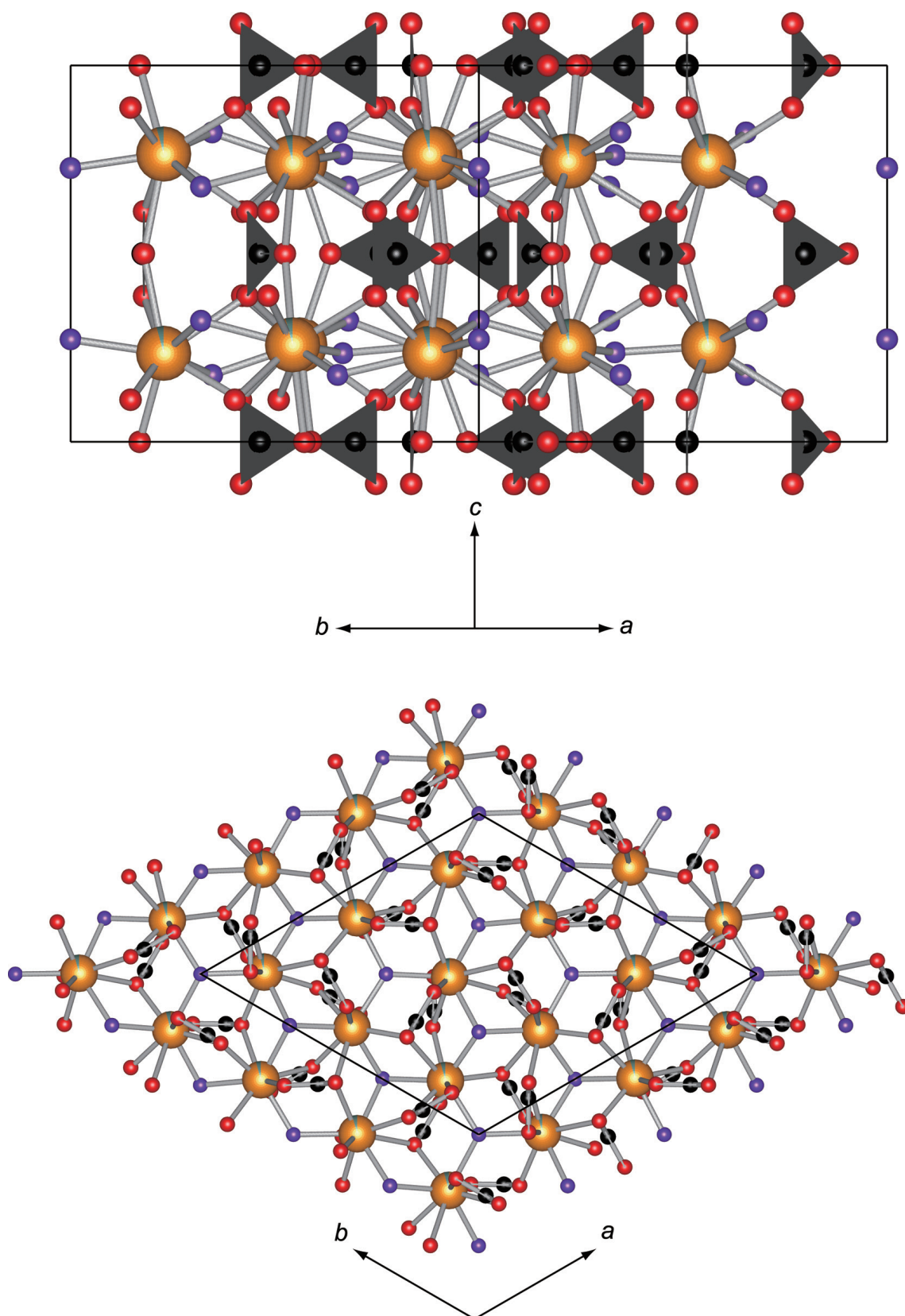


Figure 3. Projection of the crystal structure of hydroxylbastnäsite-(Ce) onto (001) (lower) and (110) (upper). Orange, dark grey, red, and purple spheres represent Ce, C, O of carbonate, and O of hydroxyl ion, respectively. The crystal structures were rendered by the structure-drawing program 'VESTA 3' (Momma and Izumi, 2011).

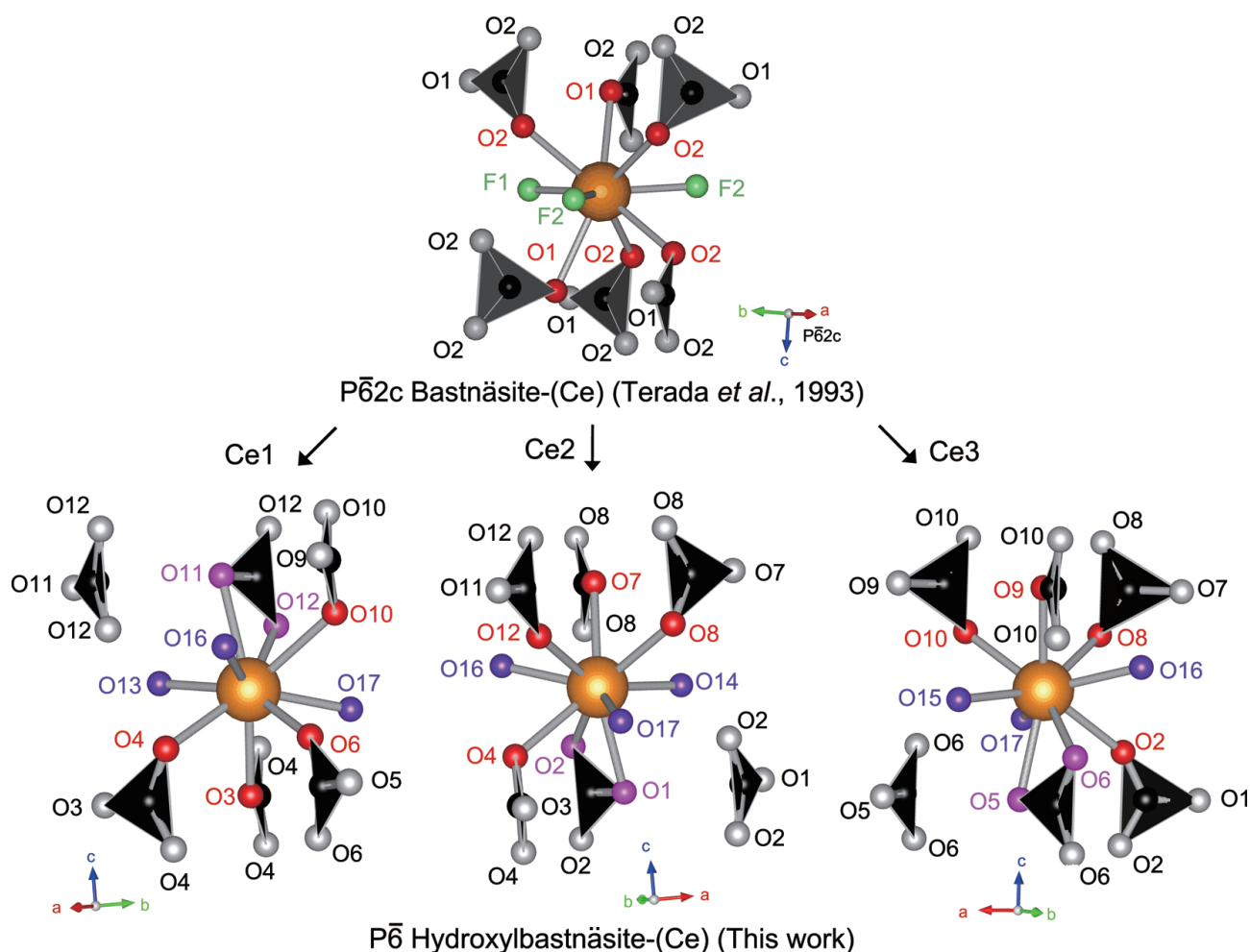


Figure 4. A comparison of the coordination environments of Ce sites in hydroxylbastnäsite-(Ce) and bastnäsite-(Ce). Orange, dark grey, and green spheres represent Ce, C, and F atoms, respectively. Red, purple, and blue spheres represent O atoms of monodentate carbonates, bidentate carbonate, and hydroxyl ions, respectively. Grey spheres represent other O atoms. The drawings were rendered by the structure-drawing program 'VESTA 3' (Momma and Izumi, 2011).

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