

LETTER

Crystal structure and Raman spectrum of hydroxyl-bästnasite-(Ce), $\text{CeCO}_3(\text{OH})$

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ABSTRACT

Hydroxyl-bästnasite-(Ce), ideally $\text{CeCO}_3(\text{OH})$, had been regarded isostructural with bästnasite-(Ce), CeCO_3F , the dominant member of the bästnasite family that produces ~70% of the world's supply of rare-earth elements. Using single-crystal X-ray diffraction and Raman spectroscopy, our structural analysis on hydroxyl-bästnasite-(Ce) shows that the previous assumption is incorrect. The crystal structure of hydroxyl-bästnasite-(Ce) possesses $P\bar{6}$ symmetry with unit-cell parameters $a = 12.4112(2)$, $c = 9.8511(3)$ Å, and $V = 1314.2(1)$ Å³, in contrast to the space group $P\bar{6}2c$ and $a \approx 7.10$, $c \approx 9.76$ Å, and $V \approx 430$ Å³ for bästnasite-(Ce). Moreover, there are 6, 3, and 5 symmetrically-distinct CO_3 groups, Ce cations, and (OH/F) ions, respectively, in hydroxyl-bästnasite-(Ce), but 1, 1, and 2 in bästnasite-(Ce). The two structures, nevertheless, are similarly characterized by the layers of CO_3 groups alternating with the Ce-(OH/F) layers along the c direction. The Raman spectrum of hydroxyl-bästnasite-(Ce) is dominated by three strong bands at 1080, 1087, and 1098 cm^{-1} in the CO_3 symmetrical stretching region, along with at least four bands in the OH stretching region. Our study further suggests that natural hydroxyl-bästnasite-(Nd) is most likely isotypic with hydroxyl-bästnasite-(Ce), rather than with bästnasite-(Ce), as previously proposed.

Keywords: Bästnasite, hydroxyl-bästnasite-(Ce), single-crystal X-ray diffraction, crystal structure, Raman spectra

INTRODUCTION

Recent developments in high-technology industries, such as laser materials, high-power magnetic materials, and ionic conductors, have generated a tremendous demand for rare earth elements (REE) (Bünzli et al. 2007 and references therein). Among all REE-bearing mineral resources in the world, bästnasite, $(\text{REE})\text{CO}_3\text{F}$, is the most abundant, and about 70% of REE products come from bästnasite production (Chi et al. 2004). The crystal structure of bästnasite-(Ce) was first proposed by Oftedal (1931) and confirmed by Donnay and Donnay (1953) on the basis of X-ray photographic data. More detailed structure analyses on this mineral, however, were not conducted until the 1990s (Ni et al. 1993; Terada et al. 1993; Mi et al. 1996). The structure of bästnasite-(Ce), hexagonal with space group $P\bar{6}2c$, consists of (001) layers of CO_3 groups sandwiched by Ce-F sheets. Notably, many REE-bearing fluorcarbonate minerals, such as parisite $\text{CaCe}_2(\text{CO}_3)_3\text{F}_2$, röntgenite-(Ce) $\text{Ca}_2\text{Ce}_3(\text{CO}_3)_3\text{F}_3$, and synchysite-(Ce) $\text{CaCe}(\text{CO}_3)_2\text{F}$, contain the bästnasite structure as a basic building module (Ni et al. 1993, 2000).

Hydroxyl-bästnasite-(Ce), ideally $\text{CeCO}_3(\text{OH})$, was first described as a new variety and the OH-analog of bästnasite-(Ce) by Kirillov (1964) and later by Minakawa et al. (1992). Maksimović and Pantó (1985) reported hydroxyl-bästnasite-(Nd). Based on the strong similarities in powder X-ray diffraction patterns and crystal chemistry, all previous studies assumed that hydroxyl-bästnasite and bästnasite were isotypic. In this paper, we report

the first structural investigation of hydroxyl-bästnasite-(Ce) using single-crystal X-ray diffraction and Raman spectroscopy and demonstrate that this mineral is not isomorphous with bästnasite-(Ce).

EXPERIMENTAL METHODS

The hydroxyl-bästnasite-(Ce) specimen used in this study is from Trimouns, Luzenac, France and is in the collection of the RRUFF project (deposition no. R060283; <http://rruff.info>), donated by Herb Obodda. The chemical composition was determined with a CAMECA SX50 electron microprobe (<http://rruff.info>). The OH content was estimated based on the charge balance and the CO_3 content was calculated from the difference off 100 wt%. The average composition (12 point analyses), normalized to $\text{CO}_3 = 1.0$, yielded a formula of $(\text{Ce}_{0.50}\text{Nd}_{0.24}\text{La}_{0.23}\text{Y}_{0.03})_{\Sigma=1}\text{CO}_3[(\text{OH})_{0.65}\text{F}_{0.35}]_{\Sigma=1}$.

Based on optical examination and X-ray diffraction peak profiles, a nearly equidimensional crystal was selected and mounted on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized $\text{MoK}\alpha$ radiation. X-ray diffraction data were collected with frame widths of 0.5° in ω and 30 s counting time per frame. All reflections were indexed on the basis of a hexagonal unit-cell (Table 1). The intensity data were corrected for X-ray absorption using the Bruker program SADABS. The lack of systematic absences of reflections is consistent with the space group $P6$, $P\bar{6}$, or $P6/m$. The crystal structure was solved and refined with space group $P6$ using the direct methods (SHELX97) (Sheldrick 1997), because only this space group gave the reasonable refinement statistics (bond lengths and angles, atomic displacement parameters, and R factors). In the structure refinement, the REE sites were assumed to be fully occupied by Ce, as the average atomic number of $(\text{Ce}_{0.50}\text{Nd}_{0.24}\text{La}_{0.23}\text{Y}_{0.03})$ is close to that of Ce. The chemical analysis showed the presence of F^- substituting for OH^- , but the final refinement assumed that all OH sites were occupied by O only. The positions of all atoms were refined with anisotropic displacement parameters, except for H atoms, which were not located by the difference Fourier syntheses. Final coordinates and displacement parameters of non-H atoms are listed in Table 2, and selected bond-distances in Table 3.

Raman spectra of the sample were collected from a randomly oriented crystal

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TABLE 1. Summary of crystal data and refinement results for hydroxyl-bästnasite-(Ce)

Structural formula	$(\text{Ce}_{0.50}\text{Nd}_{0.24}\text{La}_{0.23}\text{Y}_{0.03})_{\Sigma=1}\text{CO}_3[(\text{OH})_{0.65}\text{F}_{0.35}]_{\Sigma=1}$
Crystal size (mm)	$0.06 \times 0.06 \times 0.06$
Space group	$P\bar{6}$ (No. 174)
a (Å)	12.4112(2)
c (Å)	9.8511(3)
V (Å ³)	1314.2(1)
Z	18
ρ_{calc} (g/cm ³)	4.936
λ (Å)	0.71069
μ (mm ⁻¹)	15.84
θ range for data collection	2.07 to 34.02
No. of reflections collected	23310
No. of independent reflections	3742
No. of reflections with $I > 2\sigma(I)$	3262
No. of parameters refined	183
$R(\text{int})$	0.043
Final R factors [$I > 2\sigma(I)$]	$R_1 = 0.028, wR_2 = 0.067$
Final R factors (all data)	$R_1 = 0.035, wR_2 = 0.072$
Goodness-of-fit	1.069

TABLE 2. Atomic coordinates and isotropic displacement parameters for hydroxyl-bästnasite-(Ce)

Atom	x	y	z	U_{eq} (Å ²)
Ce1	0.1099(1)	0.2290(1)	0.2395(1)	0.0075(1)
Ce2	0.4385(1)	0.2171(1)	0.2555(1)	0.0087(1)
Ce3	0.1050(1)	0.5591(1)	0.2590(1)	0.0077(1)
C1	0.4896(7)	0.3571(7)	0	0.019(1)
C2	0.2012(6)	0.0893(6)	0	0.010(1)
C3	0.3015(7)	0.4669(8)	0	0.022(2)
C4	0.5518(6)	0.4178(7)	1/2	0.013(1)
C5	0.2397(6)	0.4656(6)	1/2	0.011(1)
C6	0.2028(6)	0.0255(6)	1/2	0.010(1)
O1	0.4887(6)	0.2479(6)	0	0.025(1)
O2	0.4924(4)	0.4052(3)	0.1139(3)	0.014(1)
O3	0.0288(4)	0.1690(5)	0	0.014(1)
O4	0.2341(3)	0.1490(3)	0.1136(3)	0.010(1)
O5	0.1619(6)	0.5875(6)	0	0.029(2)
O6	0.2515(3)	0.4195(3)	0.1130(3)	0.016(1)
O7	0.4997(5)	0.2993(5)	1/2	0.014(1)
O8	0.5185(4)	0.0962(3)	0.3865(4)	0.012(1)
O9	0.3596(5)	0.5242(5)	1/2	0.013(1)
O10	0.1787(3)	0.4333(3)	0.3863(3)	0.010(1)
O11	0.0819(5)	0.1799(5)	1/2	0.012(1)
O12	0.2511(3)	0.0738(3)	0.3868(3)	0.010(1)
OH1	0	0	0.2681(6)	0.019(1)
OH2	2/3	1/3	0.2375(7)	0.022(1)
OH3	1/3	2/3	0.2377(6)	0.018(1)
OH4	0.3226(3)	0.3212(3)	0.3217(3)	0.018(1)
OH5	0.3438(3)	0.0002(3)	0.1793(3)	0.018(1)

at 100% power on a Thermo Almega microRaman system, using a solid-state laser with a frequency of 532 nm and a thermoelectric cooled CCD detector. The laser is partially polarized with 4 cm⁻¹ resolution and a spot size of 1 μm. For comparison, the Raman spectrum for a bästnasite-(Ce) sample from our RRUFF project collection (R060359) was also reported here.

RESULTS AND DISCUSSION

Hydroxyl-bästnasite-(Ce) is found to be isostructural with the synthetic compounds NdCO₃(OH) (Christensen 1973) and Dy(CO₃)(OH) (Kutlu and Meyer 1999), rather than with bästnasite-(Ce) (Ni et al. 1993; Terada et al. 1993; Mi et al. 1996), which has space group $P\bar{6}2c$ and unit-cell parameters $a_{\text{bästnasite}} \approx a/\sqrt{3}$, $c_{\text{bästnasite}} \approx c$, and $V_{\text{bästnasite}} \approx V/3$, where a , c , and V are the unit-cell parameters for hydroxyl-bästnasite-(Ce). The crystal structure of hydroxyl-bästnasite-(Ce), nevertheless, exhibits many features similar to that of bästnasite-(Ce). For example, both structures are composed of layers of CO₃ groups alternating with the Ce-(OH/F) layers in the c direction (Fig. 1). In the CO₃ layers, two

TABLE 3. Selected interatomic distances (Å) in hydroxyl-bästnasite-(Ce)

	Distance		Distance
Ce1-O3	2.527(2)	C1-O1	1.350(9)
Ce1-O4	2.535(3)	C1-O2 (×2)	1.263(5)
Ce1-O6	2.466(3)	Average	1.292
Ce1-O10	2.662(3)		
Ce1-O11	2.620(1)		
Ce1-O12	2.501(3)		
Ce1-OH1	2.478(1)	C2-O3	1.270(8)
Ce1-OH4	2.431(3)	C2-O4 (×2)	1.291(5)
Ce1-OH5	2.488(3)	Average	1.284
Average	2.523		
Ce2-O1	2.575(2)	C3-O5	1.357(9)
Ce2-O2	2.506(3)	C3-O6 (×2)	1.267(5)
Ce2-O4	2.638(3)	Average	1.297
Ce2-O7	2.577(2)		
Ce2-O8	2.529(3)		
Ce2-O12	2.472(3)		
Ce2-OH2	2.459(1)	C4-O7	1.277(9)
Ce2-OH4	2.455(3)	C4-O8 (×2)	1.313(5)
Ce2-OH5	2.456(3)	Average	1.301
Average	2.519		
Ce3-O2	2.566(3)	C5-O9	1.289(9)
Ce3-O5	2.614(2)	C5-O10 (×2)	1.298(5)
Ce3-O6	2.518(4)	Average	1.295
Ce3-O8	2.546(3)		
Ce3-O9	2.551(2)		
Ce3-O10	2.510(3)		
Ce3-OH3	2.464(1)	C6-O11	1.317(8)
Ce3-OH4	2.497(3)	C6-O12 (×2)	1.266(4)
Ce3-OH5	2.442(3)	Average	1.283
Average	2.523		

of three O atoms within a CO₃ group are superimposed upon each other in the c direction, whereas the third O atom and the C atom are situated on the mirror planes perpendicular to the c axis. Moreover, all Ce cations in both structures are bonded by nine ions: three (OH/F) ions in the same layer and six O ions from the CO₃ layers. The principal difference between the two structures are that there are 6, 3, and 5 symmetrically-independent CO₃ groups, Ce cations, and (OH/F) ions, respectively, in hydroxyl-bästnasite-(Ce), but 1, 1, and 2 in bästnasite-(Ce). The average C-O distances of 1.28–1.30 Å in hydroxyl-bästnasite-(Ce) match those observed in bästnasite-(Ce) (Ni et al. 1993; Terada et al. 1993; Mi et al. 1996), synthetic NdCO₃(OH) (Christensen 1973), and DyCO₃(OH) (Kutlu and Meyer 1999). However, the average Ce-(OH/F) and Ce-O bond lengths in hydroxyl-bästnasite-(Ce), which are ~2.460(3) and 2.551(3) Å, respectively, are significantly different from the corresponding ones in bästnasite-(Ce) [2.407(2) and 2.571(5) Å, respectively].

The structural differences between hydroxyl-bästnasite-(Ce) and bästnasite-(Ce) are also manifest in their Raman spectra (Fig. 2). Specifically, the Raman spectrum of bästnasite-(Ce) is dominated by a strong, narrow band at 1096 cm⁻¹ that can be assigned to the CO₃ symmetrical stretching vibrations and there are no significant bands in the region between 3200 and 3700 cm⁻¹. In contrast, the Raman spectrum of hydroxyl-bästnasite-(Ce) displays three strong bands at 1080, 1087, and 1098 cm⁻¹ in the CO₃ symmetrical stretching region, along with at least four bands in the OH stretching region. The observation of three discrete CO₃ symmetrical stretching bands, instead of one, indicates that there may be at least three structurally-nonequivalent CO₃ groups in the hydroxyl-bästnasite-(Ce) structure, consistent with

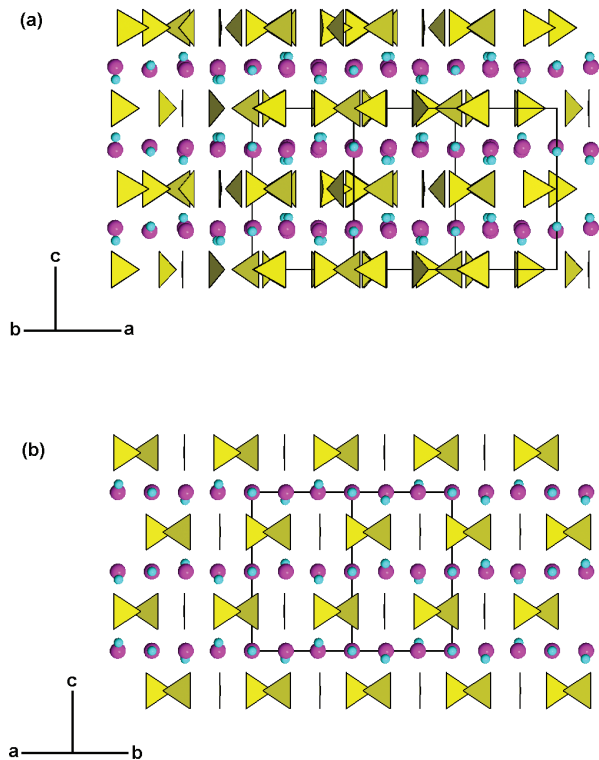


FIGURE 1. Comparison of crystal structures of (a) hydroxyl-bastnasite-(Ce) viewed along [120] and (b) bastnasite-(Ce) viewed along [110]. Yellow triangles, large purple, and small light-blue spheres represent CO_3 groups, F, and Ce atoms, respectively.

our structure refinement data.

Although our structure refinement did not locate the positions of H atoms in hydroxyl-bastnasite-(Ce) owing to the presence of the heavy REE, the four bands in the OH stretching region point to the possible existence of at least four distinct O-H bonding environments in the structure. According to Nakamoto et al. (1955), Novak (1974), and Libowitzky (1999), the Raman bands we observed at 3235, 3493, 3568, and 3638 cm^{-1} would correspond to the O-H \cdots O distances of ~ 2.72 , ~ 2.85 , 2.95–3.00, and 3.2–3.3 Å, respectively. These values can all be found around the five OH sites in the hydroxyl-bastnasite-(Ce) structure. In fact, 30 O atoms in total are at distances between 2.719 and 3.239 Å from the five OH ions, which makes it difficult for us to resolve which individual O \cdots O pairs are probably H-bonded.

Between the two symmetrically distinct F atoms in bastnasite-(Ce), the F1 atom, which is situated at the $2a$ position (site symmetry 32), shows longer separations to the three bonded Ce atoms and six nearest neighboring O atoms than the F2 atom at the $4f$ position (site symmetry 3) (Ni et al. 1993; Terada et al. 1993; Mi et al. 1996). Thus, the F1 atom is less closely-packed and would be energetically more favorable for OH substitution than the F2 site. Similarly, the OH sites with higher site symmetry in hydroxyl-bastnasite-(Ce), namely OH1, OH2, and OH3, are also less closely-packed than those (OH4 and OH5) with lower site symmetry. By the same token, we may expect some enrichment of F in the OH4 and OH5 sites in our sample, as it contains a considerable amount of F. The bond-valence sums (Brown 1996) for the five OH sites, calculated by assuming that they are all solely occupied by O atoms, however, did not yield much useful information about the possible F-OH ordering in our sample, as they all fall between 1.24 and 1.30 v.u. Note that a consideration of the substitution of some F for OH will reduce these values close to one, lending support to our chemical analysis results.

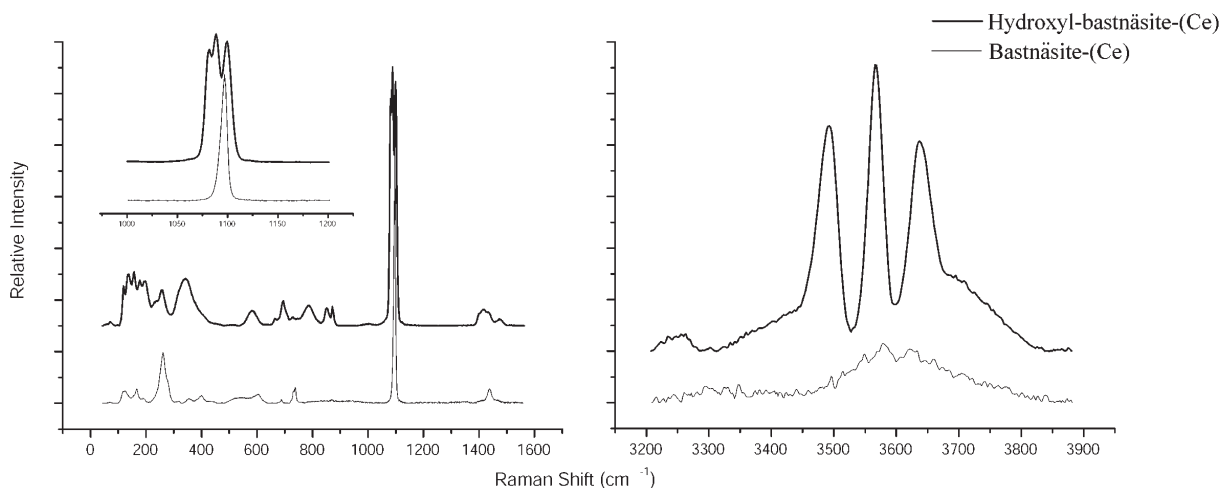


FIGURE 2. Raman spectra of hydroxyl-bastnasite-(Ce) and bastnasite-(Ce). The band assignments are as follows: between 1000–1200 cm^{-1} = ν_1 CO_3 symmetric stretching modes; between 1300–1500 cm^{-1} = ν_3 CO_3 anti-symmetrical stretching modes; between 530–930 cm^{-1} = ν_2 and ν_4 CO_3 in-plane and out-of-plane bending modes; below 500 cm^{-1} = hydroxyl deformation modes, Ce-(OH/F) stretching vibrations, and lattice modes; between 3200–3800 cm^{-1} = OH stretching vibrations.

There have been considerable discussions about the effects of the F-OH substitution on crystal structures and properties of minerals (Groat et al. 1990; Cooper and Hawthorne 1995; Yang et al. 2007a, 2007b). For some minerals, the OH- and F-members form a continuous solid solution, such as for the amblygonite [LiAl(PO₄F)]-montebrasite [LiAl(PO₄)(OH)] and fluorapatite [Ca₅(PO₄)₃F]-hydroxylapatite [Ca₅(PO₄)₃(OH)] series. However, there are also many examples in which the F-OH substitution results in structural transformations or symmetry changes, such as the cases between *C2/c* tilasite [CaMg(AsO₄)F] and *P2₁2₁2₁* adelite [CaMg(AsO₄)(OH)], and between *C2/c* triplite [Mn₂(PO₄F)] and *P2₁/c* triploidite [Mn₂(PO₄)(OH)]. Our data on hydroxyl-bästnasite-(Ce) provide another example for an incomplete solid solution arising from the OH-F substitution. Although it appears that the *P6₂c* bästnasite-type structure is capable of accommodating a certain amount of OH, as the Raman spectra of most bästnasite-(Ce) and bästnasite-(La) samples in our RRUFF project collection (<http://rruff.info>) show some weak bands in the OH-stretching region, it is unclear to what extent OH can substitute for F without causing the *P6₂c* to *P6₃* structural transformation,

Akhmanova and Orlova (1966) measured infrared spectra on both bästnasite-(Ce) and hydroxyl-bästnasite-(Ce) and noted that, in addition to the three bands between 3470 and 3620 cm⁻¹, the number of bands in the region of CO₃ symmetrical vibrations for hydroxyl-bästnasite-(Ce) is much greater than that predicted by the selection rules based on the structural symmetry for bästnasite-(Ce). Their interpretation was that the incorporation of OH into the bästnasite structure resulted in a change in the local symmetry of the CO₃ ions, with one group having local symmetry *C3* and the other *C1*, giving rise to the splitting of the absorption bands for the CO₃ symmetrical vibrations in hydroxyl-bästnasite-(Ce). Apparently, the structure model we report here for hydroxyl-bästnasite-(Ce) offers a better explanation for the observations made by Akhmanova and Orlova (1966) on their hydroxyl-bästnasite-(Ce). Interestingly, although natural hydroxyl-bästnasite-(Nd) with the composition (Nd_{0.41}La_{0.36}Pr_{0.11}Sm_{0.06}Gd_{0.02}Eu_{0.02}Ca_{0.01})_{Σ0.99}(CO₃)_{1.03}[(OH)_{0.55}F_{0.38}]_{Σ0.93} was described to be isomorphous with bästnasite-(Ce) from the X-ray powder diffraction data, its infrared spectrum was more compatible with that reported by Akhmanova and Orlova (1966) for their hydroxyl-bästnasite-(Ce) (Maksimović and Pantó 1985). This observation, together with the *P6₃* structure of synthetic NdCO₃(OH) (Christensen 1973), leads us to conclude that natural hydroxyl-bästnasite-(Nd) is actually isostructural with hydroxyl-bästnasite-(Ce), rather than with bästnasite-(Ce). A re-indexing of X-ray powder diffraction data for hydroxyl-bästnasite-(Nd) (Maksimović and Pantó 1985) based on the hydroxyl-bästnasite-(Ce) structure yielded $a = 12.455(2)$ (i.e., $\sqrt{3} \times 7.191$), $c = 9.921(2)$ Å, and $V = 1332.9$ Å³ (i.e., 3×444.3).

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