Crystal structure and Raman spectrum of hydroxyl-bästnasite-(Ce), CeCO₃(OH)

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ABSTRACT

Hydroxyl-bästnasite-(Ce), ideally CeCO₃(OH), had been regarded isostructural with bästnasite-(Ce), CeCO₃F, 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 P63 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 P62c and a = 7.10, c = 9.76 Å, and V = 430 Å³ for bästnasite-(Ce). Moreover, there are 6, 3, and 5 symmetrically-distinct CO₃ groups, Ce sites, 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 CO₃ 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 CO₃ 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, (REE)CO₃F, is the most abundant, and about 70% of REE products come from bästnasite production (Chi et al. 2004). The crystal structure of bästnasite-(Ce), hexagonal with space group P62c, consists of (001) layers of CO₃ groups sandwiched by Ce-F sheets. Notably, many REE-bearing fluorocarbonate minerals, such as parsite CaCe₂(CO₃)₃F₂, röntgenite-(Ce) Ca₂Ce₆(CO₃)₉F₃, and synchysite-(Ce) CaCe(CO₃)₂F, contain the bästnasite structure as a basic building module (Ni et al. 1993, 2000).

Hydroxyl-bästnasite-(Ce), ideally CeCO₃(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 Timrouns, 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 CO₃ content was calculated from the difference off 100 wt%. The average composition (12 point analyses), normalized to CO₃ = 1, yielded a formula of [Ce₀.8Nd₀.2La₀.2Y₀.03OH₀.05]CO₃([OH]₀.06F₀.35)₁.₄.₁.

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 MoKα radiation. X-ray diffraction data were collected with frame widths of 0.5° in θ 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 P6₃, P6₃, or P6₃m. The crystal structure was solved and refined with space group P6₃ 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 (Ce₀.8Nd₀.2La₀.2Y₀.03) 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...
HYDROXYL-BÄSTNASITE-(Ce)

The hydroxyl-bästnasite-(Ce) structure is 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 $P6_3$ and unit-cell parameters $a_{\text{bästnasite}} = \sqrt{3}a$, $c_{\text{bästnasite}} = c$, and $V_{\text{bästnasite}} = V/3$, 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 of three O atoms within a CO³⁻ group are superimposed upon each other in the $c$ direction, whereas the third O atom and the Ce 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 is 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-O distances in hydroxyl-bästnasite-(Ce) 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].

## 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 $P6_3$ and unit-cell parameters $a_{\text{bästnasite}} = \sqrt{3}a$, $c_{\text{bästnasite}} = c$, and $V_{\text{bästnasite}} = V/3$, 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 of three O atoms within a CO³⁻ group are superimposed upon each other in the $c$ direction, whereas the third O atom and the Ce 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 is 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-O distances in hydroxyl-bästnasite-(Ce) 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...
our structure refinement data.

Although our structure refinement did not locate the positions of H atoms in hydroxyl-bästnasite-(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···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-bästnasite-(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···O pairs are probably H-bonded.

Between the two symmetrically distinct F atoms in bästnasite-(Ce), the F1 atom, which is situated at the 2\(a\) 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 4\(f\) 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-bästnasite-(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 1.** Comparison of crystal structures of (a) hydroxyl-bästnasite-(Ce) viewed along [120] and (b) bästnasite-(Ce) viewed along [110]. Yellow triangles, large purple, and small light-blue spheres represent CO\(_3\) groups, F, and Ce atoms, respectively.

**FIGURE 2.** Raman spectra of hydroxyl-bästnasite-(Ce) and bästnasite-(Ce). The band assignments are as follows: between 1000–1200 cm\(^{-1}\) = \(\nu_1\) CO\(_3\) symmetric al stretching modes; between 1300–1500 cm\(^{-1}\) = \(\nu_3\) CO\(_3\) anti-symmetrical stretching modes; between 530–930 cm\(^{-1}\) = \(\nu_2\) and \(\nu_4\) 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(PO₄)F]-montebrasite [LiAl(PO₄)(OH)] and fluorapatite [Ca₅(PO₄)F]-hydroxylapatite [Ca₅(PO₄)₂(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 P2₁₂₁₂ₐ adelite [CaMg(AsO₄)(OH)], and between C2/c triplite [Mn₄(PO₄)F] and P2₁/₃ tripleite [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 P₆₃mc bästnasite-type structure is capable of accommodating a certain amount of OH, as the Roman 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 P₆₃mc to P₆ 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 Nd₀.₄₁La₀.₃₀Pr₀.₁₁Sm₀.₀₈Nd₀.₀₂Eu₀.₀₂Ca₀.₀₀Co₀.₀₁(OH)₀.₀₁(PO₄)₀.₃₅(F₀.₁₈O₂)₀.₃₃ 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 Pantö 1985). This observation, together with the P₆ structure of synthetic NdCo₂(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 Pantö 1985) based on the hydroxyl-bästnasite-(Ce) structure yielded a = 12.455(2) (i.e., √3 × 7.191), c = 9.921(2) Å, and V = 1332.9 Å³ (i.e., 3 × 444.3).

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