The atomic arrangement of bastnäsite-(Ce), Ce(CO₃)F, and structural elements of synchysite-(Ce), röntgenite-(Ce), and parisite-(Ce)

YUNXIANG NI, JOHN M. HUGHES

Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.

ANTHONY N. MARIANO

48 Page Brook Road, Carlisle, Massachusetts 01741, U.S.A.

ABSTRACT

Bastnäsite-(Ce), which yields more than half of the world's supply of rare-earth elements, is the most abundant member of the rare-earth fluorcarbonate group of minerals. We have solved the crystal structure of bastnäsite-(Ce) in space group $P\bar{6}2c$ and refined the atomic arrangement to $R = 0.018$ using three-dimensional X-ray diffraction data obtained from a crystal of composition $(La_{2.22}Ce_{2.88}Pr_{0.22}Nd_{0.58}Sm_{0.04}Eu_{0.01}Gd_{0.02}Y_{0.03})(CO_3)_6F_6$.

The atomic arrangement of bastnäsite-(Ce) is composed of (0001) layers of Ce and F interspersed with carbonate layers in a 1:1 ratio. The Ce atom is coordinated in CeO_6F_3 polyhedra; the three Ce-F bonds are within the (CeF) layer, and that layer is linked to the (CO_3) layer by interlayer bonding of the Ce atom to six O atoms of the carbonate groups. The (CeF) layers are 2.64 Å thick, and the intervening (CO_3) layers are 2.24 Å thick, measured parallel to [0001].

The atomic arrangements of several rare-earth fluorcarbonates can be deduced as layer structures formed of the bastnäsite-(Ce) (CeF) and (CO_3) layers, and a postulated $[Ca(CO_3)]$ layer (calculated thickness = 4.25 Å). The minerals have ratios of (CeF):(CO_3):$[Ca(CO_3)]$ layers of 1:1:0 [bastnäsite-(Ce)], 2:2:1 [parisite-(Ce)], 3:3:2 [röntgenite-(Ce)], and 1:1:1 [synchysite-(Ce)]. Using this model and the measured layer thicknesses from the bastnäsite-(Ce) structure, the unit-cell parameters of these rare-earth fluorcarbonates can be reproduced within 0.2%. The layer structure also gives a physical basis for the (0001) syntaxy in the rare-earth fluorcarbonates, as the (CeF) and (CO_3) layers common to all the structures provide an identical growth surface in every RE fluorcarbonate, a surface amenable to growth of any of the phases as the composition of the ore fluid changes.

INTRODUCTION

Bastnäsite-(Ce), Ce(CO₃)F, is a member of the rare-earth (RE) fluorcarbonate group of minerals that has generated considerable interest in earlier studies. Because of its abundance at such deposits as Mountain Pass, California (31 million tons of bastnäsite ore), and Bayan Obo, China (37 million tons), bastnäsite is the most abundant RE ore mineral, supplying more than half the world's rare-earth elements. Despite this abundance and principal economic importance among RE minerals, the crystal structure of this mineral with its parsimonious chemical content has not been solved, although attempts have been made. In addition, because the atomic arrangements of several RE fluorcarbonates have resisted crystal structure determination, the structure of bastnäsite (the RE fluorcarbonate with the smallest unit cell) may provide a model for components of more complex RE fluorcarbonate structures such as parisite-(Ce), $CaCe_2(CO_3)_3F_2$, which has a translation of $c = 84$ Å (Ni and Hughes, in preparation).

In a study of several RE fluorcarbonate minerals (bastnäsite, parisite, röntgenite, and synchysite), Donnay and Donnay (1953) predicted the atomic positions in bast-

näsite, in accord with the earlier deduction of Oftedal (1931a, 1931b). Experimental determination of the atomic arrangement was precluded, however, by the ubiquitous syntaxial intergrowths observed between all pairs of minerals from among bastnäsite, parisite, röntgenite, and synchysite, except bastnäsite-synchysite (Donnay and Donnay, 1953). The atomic arrangements of the RE fluorcarbonate minerals, the most abundant RE ore minerals, thus remained unconfirmed.

Contradicting the assertion that syntaxial intergrowths among mineral pairs of the bastnäsite group are the rule, however, Mariano (1989) suggested that syntaxy among the minerals is not pervasive. Analysis of optical-quality bastnäsite and parisite from Mountain Pass and several other localities yielded chemical analyses with the ideal bastnäsite and parisite formulas, and backscattered electron images show the pure phases devoid of syntaxy (Mariano, 1989). The following structure study undertaken on bastnäsite-(Ce) confirms the presence of the pure phase and provides a high-precision structure determination that may help unravel the atomic arrangements of other RE fluorcarbonates.

TABLE 1. Crystal data and results of structure refinements for bastnäsite

Dimension (mm)	0.15 × 0.13 × 0.12
Unit cell	
Least squares	
a (Å)	7.118(1)
b	7.117(1)
c	9.762(1)
α (°)	89.99(1)
β	90.01(1)
γ	119.97(1)
Constrained (space group: $P\bar{6}2c$)	
a	7.1175
c	9.7619
μ_i (MoKα, cm^{-1})	157.3
Composition (La$_{2.22}$Ce$_{2.88}$Pr$_{0.22}$Nd$_{0.58}$Sm$_{0.04}$Eu$_{0.01}$Gd$_{0.02}$Y$_{0.03}$)$_6$- (CO$_3$)$_6$F$_6$	
θ limit	0.10–32.00°
Scan type	$\theta/2\theta$
Scan time (s)	≤120
Standards	
Intensity	3 per 4 h
Orientation	3 per 300 reflections
Data collected	3120
Unique data	588
Data >3σ_I	339
R_{merge} (%)	1.5
R (%)	1.8
R_w (%)	2.3
Goodness of fit	2.47
Largest peaks on difference map (e/Å^3)	
(+)	0.700
(−)	0.691

Note: Numbers in parentheses denote 1 esd of least unit cited.

EXPERIMENTAL

A transparent, optical-quality sample of bastnäsite-(Ce) from the Gallinas Mountains, New Mexico, was chosen for the study. A complete precession study confirmed space group $P\bar{6}2c$ (no. 190), as suggested by Donnay and Donnay (1953; note those authors used the then-standard $C\bar{6}2c$ setting of space group no. 190).

Unit-cell parameters (Table 1) were refined from the setting angles of 25 automatically centered reflections measured on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated MoKα radiation. Intensity data were obtained on the same instrument for the hemisphere of reciprocal space encompassing $l \geq 0$.

Intensity data were reduced to structure factors and corrected for Lorentz and polarization effects. All structure calculations were undertaken using the SDP set of computer programs (Frenz, 1985). Absorption was corrected using 360° ψ-scan data for six reflections and, subsequent to solution, an absorption surface method as implemented in program Difabs (Walker and Stuart, 1983). Symmetry-equivalent reflections were averaged; unit weights, $I > 3\sigma_I$ data, and neutral-atoms scattering factors with terms for anomalous dispersion were used throughout the structure calculations. The phases were determined using direct methods (Multan-80; Main et al., 1980) and difference Fourier maps. Bond valence sums (Brown, 1981) calculated for all atoms after refinement yielded Ce = 3.06 vu, C = 3.98 vu, O1 = 2.02 vu, O2 = 1.96 vu, F1 = 1.08 vu, and F2 = 1.11 vu.

TABLE 2. Atomic coordinates and equivalent isotropic B for atoms in bastnäsite

Atom	Site	x	y	z	B (Å^2)
Ce	6g	0.33941(6)	0	0	0.360(7)
		⅓	0	0	
C	6h	0.322(2)	0.290(2)	¼	0.6(2)
		⅓	0.245	¼	
O1	6h	0.316(1)	0.109(1)	¼	0.9(2)
		⅓	0.067	¼	
O2	12i	0.3245(9)	0.3828(9)	0.1354(6)	1.0(1)
		⅓	⅓	0.138	
F1	2a	0	0	0	0.8(1)
		0	0	0	
F2	4f	⅔	⅓	0.051(1)	0.7(1)
		⅔	⅓	0	

Note: The second row of coordinates for each atom contains the positions deduced by Donnay and Donnay (1953). Numbers in parentheses denote 1 esd of least unit cited.

Details of data measurement and the structure refinement are contained in Table 1, and Table 2 contains positional parameters and equivalent isotropic temperature factors for all atoms in bastnäsite; anisotropic thermal parameters are contained in Table 3[1]. Table 4 presents selected bond distances, and Table 5[1] contains observed and calculated structure factors.

Chemical analysis of the RE content of an aliquot of the Gallinas Mountains material was obtained by wet chemical methods. The formula derived from this analysis, assuming the formula (RE)FCO$_3$, is given in Table 1. Because Ce is the dominant rare-earth element, the subsequent discussion will cite the occupant of the RE site as Ce, although there is extensive substitution, particularly among the light RE elements.

DISCUSSION OF THE STRUCTURE

A pronounced subcell with $c' = c/2$ is evident in precession photographs of bastnäsite-(Ce), and thus any description of the atomic arrangement must emphasize the pseudoperiodicity along [0001]. The structure of bastnäsite-(Ce) is composed of two layers, a (CeF) layer at $z = 0$, ½($\pm$0.06), and intervening (CO$_3$) layers, with the C atoms at $z = $ ¼, ¾. The (CeF) layers are related by mirrors at $z = $ ¼ and ¾, and the $c/2$ subcell thus differs from the real cell only by the orientation of the carbonate groups at $z = $ ¼, ¾. Because of the small scattering power of these layers relative to the (CeF) layer, the pronounced subcell results.

Figure 1 depicts the atomic arrangement of bastnäsite-(Ce) and illustrates the (0001) layer nature of the structure. The (CeF) layers are composed of the Ce atom in the 6g position, coordinated by one F1 (2a position) and two F2 atoms (4f position) in that layer; both F atoms, and only the F atoms, lie on $\bar{6}$ axes. The Ce atom is also

---

[1] Copies of Tables 3 and 5 may be ordered as document AM-93-521 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 4. Selected atomic distances in bastnäsite (Å)

	This study	Donnay and Donnay (1953)
Ce–O1 × 2	2.591(4)	2.49
O2 × 2	2.542(7)	2.74
O2 × 2	2.579(5)	2.74
F1	2.4157(4)	2.39
F2 × 2	2.403(2)	2.39
C–O1	1.27(2)	1.27
O2 × 2	1.293(9)	1.27
O1–O2 × 2 (intraionic)	2.22(1)	2.19
O2 × 2 (interionic)	2.913(9)	
O2–O2 (intraionic)	2.237(8)	2.19
O2 (interionic)	2.740(8)	2.70
F1	2.866(5)	2.74
F2–O1 × 3	2.926(9)	
O2 × 3	2.756(8)	2.74
O2 × 3	2.695(8)	2.74

Note: Numbers in parentheses denote 1 esd of least unit cited.
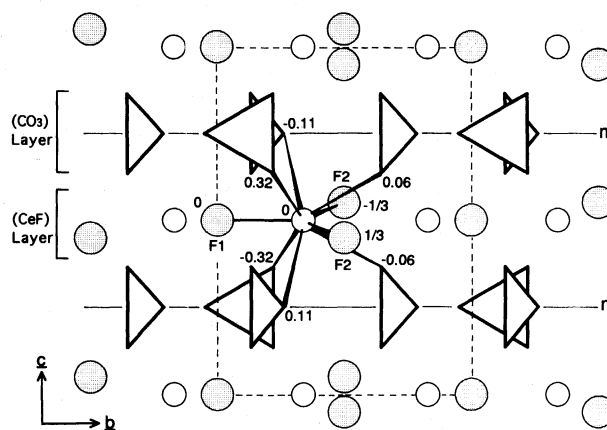

Fig. 1. Atomic arrangement of bastnäsite projected on (100). Triangles represent (CO₃) groups, and O atoms in bastnäsite lie at the apices of the triangles; F atoms are stippled, and Ce atoms are depicted as open circles. (CeF) and (CO₃) layers are denoted, and *x* coordinates of atoms are given. Dashed line outlines unit cell.

bonded to six O atoms (O1 × 2, O2 × 4) in the intervening (0001) carbonate layers. Ce is linked to the carbonate layers by sharing vertices of the (CO₃) group, yielding CeO₆F₃ coordination.

The solution of the bastnäsite-(Ce) structure with modern diffractometer techniques serves to underscore the remarkable deductive powers of earlier workers (Oftedal, 1931a, 1931b; Donnay and Donnay, 1953), who predicted the atomic arrangement solely on the basis of crystal chemical arguments. After solution of the structure, we found that the atomic positions could be successfully refined using the coordinates proffered by Donnay and Donnay. Although some predicted atomic positions differed from the refined positions by up to 0.5 Å, the fundamental crystal chemical principles derived forty years ago are correct.

STRUCTURAL RELATIONSHIP TO OTHER RE FLUORCARBONATES

Solution of the bastnäsite-(Ce) structure allows speculation on structural elements that several RE fluorcarbonates may have in common and that may provide insight into the solution of these more complex atomic arrangements, as well as the cause of the syntaxy noted among the minerals.

The RE fluorcarbonates studied by Donnay and Donnay (1953) have a common *a* axis length near 7.12 Å ($a_{parisite}$ = 7.12 Å, $a_{röntgenite}$ = 7.13 Å, $a_{synchysite}$ = 7.10 Å). In bastnäsite-(Ce) the *a* = 7.118 Å distance corresponds to the repeat distance in the CeF layers, suggesting that this layer is common to these RE fluorcarbonates. Indeed, the Ce/F ratio in all these phases is 1:1, further supporting the presence of this common structural element. The minerals differ, however, in their interlayer (carbonate layer) contents and thus also in their *c* axial length.

Throughout their work Donnay and Donnay (1953) emphasized the layered nature of the structures of bast-

näsite, synchysite, röntgenite, and parisite. The formulas of the minerals can be written to emphasize the content of their carbonate layers, e.g., bastnäsite = (CeF)·(CO₃), synchysite = (CeF)·[Ca(CO₃)₂], parisite = 2(CeF)·[Ca(CO₃)₃], and röntgenite = 3(CeF)·[Ca₂(CO₃)₅]. The layers can be further subdivided to yield three types of layers in the various fluorcarbonates, the (CeF) and (CO₃) layers as in bastnäsite-(Ce), and a Ca(CO₃) layer of unknown geometry that is present in synchysite, parisite, and röntgenite; the existence of these layer types was confirmed by multiple-beam direct lattice imaging (van Landuyt and Amelinckx, 1975). The structural formulas can thus be cast as bastnäsite = (CeF)·(CO₃), synchysite = (CeF)·(CO₃)·[Ca(CO₃)], parisite = 2(CeF)·2(CO₃)·[Ca(CO₃)], and röntgenite = 3(CeF)·3(CO₃)·2[Ca(CO₃)].

The layer thickness of the (0001) (CeF) and (CO₃) layers can be obtained from the bastnäsite-(Ce) structure. The (CeF) layer is 2.64 Å thick and the (CO₃) layer is 2.24 Å thick, the latter distance being the length of the [0001] edge of the (CO₃) triangle. From knowledge of the formulas and *c* axial dimension of the other RE fluorcarbonates, a layer thickness can be calculated for the [Ca(CO₃)] layer. By assigning a length of 4.25 Å to this layer, the *c* axial lengths and the lengths of the numerous pseudoperiodicities present in several RE fluorcarbonates can be reproduced (Table 6). Thus the atomic arrangements of parisite-(Ce), röntgenite-(Ce), and synchysite-(Ce) are postulated as layer structures composed of (CeF) layers (2.64 Å thick), (CO₃) layers (2.24 Å thick), and [Ca(CO₃)] layers (4.25 Å thick). Structure studies of these fluorcarbonates are underway to confirm the structure hypothesis and to identify the geometry of the [Ca(CO₃)] layer and the stacking sequences present in the various minerals.

A pervasive feature of many RE fluorcarbonates is the

TABLE 6. Observed and calculated *c* axis lengths for RE fluor-carbonates

Mineral	(CeF):(CO₃): [Ca(CO₃)]	Composite thickness (Å)	c_{calc} (Å)	c_{obs} (Å)
Bastnäsite	1:1:0 (×2)	4.88 (×2)	9.76	9.78
Parisite	2:2:1 (×6)	14.01 (×6)	84.06	84.1
Röntgenite	3:3:2 (×3)	23.14 (×3)	69.42	69.4
Synchysite	1:1:1 (×6)	9.13 (×6)	54.78	54.7

Note: Observed data are from Donnay and Donnay (1953); calculated lengths are obtained as noted in the text.

presence of (0001) syntaxial intergrowths of the different members of the mineral group. Because of the common structural elements, however, the reason for the syntaxy is now apparent. All the structures have both (CeF) and (CO₃) layers in common, and the deductions above suggest that the layers are identical in all structures. Thus the layers provide an identical growth surface in every RE fluorcarbonate, a surface amenable to growth of any of the phases. This common growth surface allows the growing phase to accommodate changes in the ore fluid merely by changing the RE fluorcarbonate that precipitates on the (0001) growth surface. Thus the solid phase in equilibrium with the fluid changes, causing the (0001) syntaxial growth. An interesting outgrowth of this is the observation that the pattern of syntaxial growth in the phases then serves as a record of *PTX* changes in the fluid from which the phases crystallized.

REFERENCES CITED

Brown, I.D. (1981) The bond-valance method: An empirical approach to chemical structure and bonding. In M. O'Keeffe and A. Navrotsky, Eds., Structure and bonding in crystals II, p. 1–30. Academic, New York.
Donnay, G., and Donnay, J.D.H. (1953) The crystallography of bastnäsite, parisite, röntgenite and synchisite. American Mineralogist, 38, 932–963.
Frenz, B.A. (1985) Enraf-Nonius structure determination package. In SDP user's guide, version 4. Enraf-Nonius, Delft, The Netherlands.
Main, P., Fiske, S.J., Hull, S.E., Lessinger, L., Germaine, G., Declercq, J.-P., and Woolfson, M.M. (1980) Multan-80. A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data. Universities of York, England, and Louvain, Belgium.
Mariano, A.N. (1989) Economic geology of rare earth minerals. In Mineralogical Society of America Reviews in Mineralogy, 21, 308–338.
Oftedal, I. (1931a) Zur Kristallstruktur von Bastnäsit. Zeitschrift für Kristallographie, 78, 462–469.
———(1931b) Über Parisit, Synchisit und Kordylit. Zeitschrift für Kristallographie, 79, 437–464.
van Landuyt, J., and Amelinckx, S. (1975) Multiple beam direct lattice imaging of new mixed-layer compounds of the bastnaesite-synchesite series. American Mineralogist, 60, 351–358.
Walker, N., and Stuart, D. (1983) An empirical method for correcting diffractometer data for absorption effects. Acta Crystallographica, A39, 158–166.