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THE ATOMIC ARRANGEMENT OF SYNCHYSITE-(Ce), $CeCaF(CO_3)_2$

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ABSTRACT

The arrangement of atoms in synchysite-(Ce) has been solved and refined to $R = 0.036$ using three-dimensional X-ray-diffraction data. In contrast to the putative hexagonal cell, weak X-ray-diffraction maxima on precession films demonstrate that synchysite-(Ce) is monoclinic, *C2/c*, *a* 12.329(2), *b* 7.110(1), *c* 18.741(2) Å, β 102.68(1)°. It possesses a (001) layer structure, with layers of (Ca) and (CeF) separated by layers of carbonate groups. The layers stack in a manner analogous to *C2/c* muscovite, where (Ca) layers in synchysite are equivalent to (K) layers in muscovite, (CO_3) layers in synchysite, to layers of tetrahedra in muscovite, and (CeF) layers in synchysite, to layers of octahedra in muscovite. As in muscovite, the monoclinic symmetry results from the oblique stacking of the individual layers. Also as in micas, offsets of adjacent (CO_3) layers are similar to those in $2M_2$ polytypes; polytypism similar to the micas may also exist in synchysite.

Keywords: synchysite-(Ce), crystal structure, Mont Saint-Hilaire, Quebec.

SOMMAIRE

Nous avons déterminé l'agencement structural des atomes dans la synchysite-(Ce) au moyen d'un affinement de données de diffraction X tri-dimensionnelles, jusqu'à un résidu *R* de 0.036. Au lieu de la maille hexagonale proposée antérieurement, des maxima de diffraction de faible intensité sur des clichés de précession montrent que la synchysite-(Ce) est monoclinique, *C2/c*, *a* 12.329(2), *b* 7.110(1), *c* 18.741(2) Å, β 102.68(1)°. Elle possède une structure en feuillets (001), avec des couches de (Ca) et (CeF) séparées par des groupes de carbonate. Les couches sont empilées d'une façon complètement analogue au cas de la muscovite *C2/c*; les couches de (Ca) dans la synchysite équivaudraient aux niveaux de (K) dans la muscovite, les couches de (CO_3) seraient analogues des niveaux de tétraèdres dans la muscovite, et les couches de (CeF) seraient analogues des couches d'octaèdres dans la muscovite. Comme dans cette dernière, la symétrie monoclinique résulte de l'empilement oblique des couches individuelles, et les décalages de couches (CO_3) adjacentes ressemblent à celles qui caractérisent les polytypes $2M_2$. On peut donc s'attendre à un polytypisme dans la synchysite, tout comme dans les micas.

(Traduit par la Rédaction)

Mots-clés: synchysite-(Ce), structure cristalline, mont Saint-Hilaire, Québec.

INTRODUCTION

Synchysite-(Ce), $CeCaF(CO_3)_2$, is a member of the rare-earth (*RE*) fluorcarbonate chemical class of minerals, the principal ore minerals of the *RE* elements. The *RE* fluorcarbonates have generated considerable interest because of their economic importance, the pervasive syntactic intergrowths among the phases, and the fact that the atomic arrangements of several *RE* fluorcarbonates have resisted solution despite their importance among *RE* minerals.

Recently, Ni *et al.* (1993) profferred a high-precision analysis of the structure of bastnäsite-(Ce) and confirmed the earlier predictions of several authors (Donnay & Donnay 1953, Oftedal 1931a, b). Ni *et al.* showed that, as suggested by these investigators, bastnäsite-(Ce) possesses a structure composed of (CeF) layers and (CO_3) layers. They demonstrated that the unit-cell parameters of other *RE* fluorcarbonates could be replicated by adding the bastnäsite-(Ce) (CeF) and (CO_3) layers and a 4.25 Å thick $[Ca(CO_3)]$ layer of unknown geometry in accord with the mineral formulas. The structure of synchysite-(Ce) described herein elucidates the nature of the layer stacking in the *RE* fluorcarbonates and illustrates the layer geometry in one of the more common *RE* fluorcarbonates.

EXPERIMENTAL

A crystal of synchysite-(Ce) from Mont Saint-Hilaire, Quebec (Harvard Mineralogical Museum #127254) was ground to a sphere. Precession photographs showed sharp diffraction-maxima, and no evidence of the pervasive syntactic intergrowths was observed. Detailed examination of a complete precession suite indicated that the true symmetry of synchysite-(Ce) is monoclinic, despite the strong hexagonal pseudosymmetry, which earlier studies emphasized; the true monoclinic cell is related to the hexagonal pseudocell (*a* 7.11, *c* 18.285 Å) by the matrix $\bar{1},1,0/\bar{1},\bar{1},0/0.333,\overline{0.333},1$. Examination of the photographs taken about the a_1, a_2, and a_3 "hexagonal" axes shows several weak reflections that are not equivalent among the axes, and reveals that only one of the "hexagonal" *a* axes is a diad perpendicular to a *c*-glide plane; thus, the diffraction symbol is 2/m C*c*, yielding space groups *C*2/*c* or *Cc* and the cell parameters contained in Table 1. The atomic arrangement successfully refined in space group *C*2/*c*.

X-ray intensity data for synchysite-(Ce) were collected on an Enraf–Nonius CAD4 diffractometer utilizing graphite-monochromated Mo$K\alpha$ radiation. Unit-cell parameters were refined (no symmetry constraints) using diffraction angles from 25 automatically centered reflections. Crystal data are given in Table 1, which records details of data collection and

TABLE 1. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENTS FOR SYNCHYSITE-(Ce)

Occurrence	Mont Saint-Hilaire, Quebec		
Dimension	Sphere, *r* = 0.065 mm		
Unit cell			
Least squares			
a(Å)	12.329(2)	α(°)	90.00(1)
b	7.110(1)	β	102.68(1)
c	18.741(2)	γ	89.99(1)
Constrained (space group: *C*2/*c*)			
a(Å)	12.3287	*c*	18.7414
b	7.1099	β(°)	102.6761
Composition			
$(Ce_{0.617}La_{0.321}Th_{0.010}Eu_{0.008})_{0.956}(Ca_{0.939}Y_{0.017})_{0.956}F_{0.643}C_{1.962}O_6$			
Z	12	μ_l (Mo$K\alpha$, cm^{-1})	99.13
θ limit	0 - 30°	Scan type	$\theta/2\theta$
Standards		Scan time(s)	$\leq$60
Intensity	3 per 4 hrs	R_{merge}	0.016
Orientation	3 per 300 reflections	*R*	0.036
Data collected	4982	R_w	0.038
Unique data	2319	Goodness-of-fit	2.448
Data > $3\sigma_l$	703	Variables	95
Largest peaks on difference map (e/Å^3)			
(+)	1.558		
(-)	1.536		

Notes: Numbers in parentheses denote 1 esd of last unit cited.
Chemical formula is from electron-microprobe analysis of a fragment of the crystal used for structure analysis; sum=100.99 wt.%.

structure refinement.

The SDP package of computer programs (Frenz 1985) was used throughout the refinement and solution. Intensity data were reduced to structure factors and corrected for Lorentz and polarization effects. Absorption effects were corrected using a spherical absorption correction; the spherical nature of the crystal was confirmed by the small range of transmission values noted in 360° ψ-scans. Subsequent to solution, we employed the absorption surface method, as implemented in the program DIFABS (Walker & Stuart 1983).

The atomic arrangement of synchysite-(Y) was originally solved by the senior author using intensity data collected on a different instrument than described here, but has not been reported; that atomic arrangement served as a model for the synchysite-(Ce) structure described here, which was under study by Ni, Hughes, and Drexler. The synchysite-(Y) structure was solved using Patterson maps and direct methods, which revealed the location of *RE*, Ca, and F atoms. Successive difference-Fourier syntheses and least-squares refinement subsequently revealed the positions of the carbon and oxygen atoms.

During early stages of refinement of the synchysite-(Ce) data set reported here, the thermal parameters of the Ca atoms refined to anomalously low values, suggesting that the electron occupancy described by the Ca scattering factors was not sufficient to describe the scattering contributed by the Ca sites. Refinement was altered to allow substituent Ce at the Ca sites. Occupancy at Ca1 refined to $\mathrm{Ca}_{0.71}\mathrm{Ce}_{0.29}$, and $\mathrm{Ca}_{0.75}\mathrm{Ce}_{0.25}$ at Ca2. It is not known if this substitution is real or an artifact of the data, although such Ce-for-Ca substitution is not unknown. The charge-balancing mechanism for such a substitution, if real, is not known.

Table 2 contains positional parameters and equivalent isotropic thermal parameters for all atoms, and Table 3 contains selected bond-lengths for atoms in synchysite-(Ce). Table 4 presents observed and calculated structure-factors; this table has been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 2. ATOMIC COORDINATES AND ISOTROPIC B VALUE FOR ATOMS IN SYNCHYSITE-(Ce)

Atom	site	*x*	*y*	*z*	*B*(Å²)
Ce1	4e	0.500	0.2529(3)	0.250	1.04(2) *
Ce2	8f	0.6688(1)	0.2531(2)	0.7499(1)	1.12(1) *
Ca1	4c	0.250	0.250	0.500	2.01(6) *
Ca2	8f	0.9128(3)	0.2499(6)	0.5002(2)	1.48(3) *
C1	8f	0.973(1)	0.099(3)	0.116(1)	1.2(3)
C2	8f	0.397(2)	0.100(3)	0.386(1)	1.3(3)
C3	8f	0.289(2)	0.043(3)	0.119(1)	1.3(3)
O1	8f	0.435(1)	0.303(2)	0.8794(7)	1.5(2)
O2	8f	0.922(1)	0.071(2)	0.0490(8)	2.2(3)
O3	8f	0.948(1)	0.055(2)	0.1742(7)	1.4(2)
O4	8f	0.489(1)	0.186(2)	0.3802(8)	1.8(3)
O5	8f	0.607(1)	0.076(2)	0.0470(8)	1.6(2)
O6	8f	0.670(1)	0.052(2)	0.1723(7)	1.3(2)
O7	8f	0.311(1)	0.135(2)	0.1786(7)	0.9(2)
O8	8f	0.705(1)	0.134(2)	0.8783(8)	2.0(3)
O9	8f	0.269(1)	0.111(2)	0.0534(8)	1.6(2)
F1	4e	0.500	0.087(2)	0.750	1.3(3) *
F2	8f	0.8402(9)	0.087(1)	0.7733(5)	1.1(2) *

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

* Equivalent isotropic *B* value calculated from refined anisotropic parameters.

TABLE 3. SELECTED INTERATOMIC DISTANCES IN SYNCHYSITE-(Ce) (Å)

Ce1 -	F1	2.42(2)	C1 -	O1	1.32(2)
	F2 x2	2.40(2)		O2	1.30(2)
	mean	**2.407**		O3	1.24(3)
	O3 x2	2.58(1)		**mean**	**1.287**
	O4 x2	2.52(1)		O1-O2	2.16(2)
	O7 x2	2.57(1)		O1-O3	2.18(3)
	mean	**2.557**		O2-O3	2.30(3)
Ce2 -	F1	2.393(9)	C2 -	O4	1.31(3)
	F2	2.38(2)		O5	1.29(3)
	F2	2.41(2)		O6	1.27(2)
	mean	**2.394**		**mean**	**1.29**
	O1	2.50(1)		O4-O5	2.14(2)
	O3	2.62(1)		O4-O6	2.20(2)
	O6	2.60(1)		O5-O6	2.31(2)
	O6	2.62(1)	C3 -	O7	1.27(2)
	O7	2.56(1)		O8	1.26(3)
	O8	2.50(1)		O9	1.29(2)
	mean	**2.567**		**mean**	**1.273**
Ca1 -	O2 x2	2.47(1)		O7-O8	2.18(3)
	O5 x2	2.47(2)		O7-O9	2.29(2)
	O8 x2	2.37(1)		O8-O9	2.15(2)
	O9 x2	2.75(2)			
	mean	**2.515**			
Ca2 -	O1	2.37(1)			
	O2	2.45(2)			
	O4	2.35(1)			
	O5	2.47(2)			
	O5	2.66(1)			
	O9	2.45(1)			
	O9	2.43(2)			
	mean	**2.454**			

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

DESCRIPTION OF THE STRUCTURE

Synchysite-(Ce) displays a pronounced pseudohexagonal cell, with a putative hexagonal cell having an *a′* of 7.11 and a *c′* of 18.285 Å [note that there is disagreement regarding the *c* period of the pseudohexagonal cell, as Oftedal (1931b) determined the 18 Å length noted above, and Donnay & Donnay (1953) suggested that weak superstructure reflections yield a 54 Å *c* period; our cell confirms the 54 Å cell of Donnay & Donnay and indexes all the weak reflections they noted]. The pseudocell has been predicted from the bastnäsite-(Ce) unit cell, with the addition of two 4.25 Å thick (001) $CaCO_3$ layers (Ni *et al.* 1993).

Donnay & Donnay (1953) suggested the *RE* fluorcarbonates to be layer structures, and Ni *et al.* (1993) confirmed the layer nature of the atomic arrangement of bastnäsite-(Ce) and provided dimensions for the layers in the *RE* fluorcarbonates. In their prediction of aspects of the synchysite structure, Donnay & Donnay suggested that the Ca and Ce atoms must exist in vertical columns perpendicular to (001), in alternating Ca- and Ce-bearing layers. As noted above, weak reflections in the precession photographs reveal a monoclinic structure; the lower symmetry results from the carbonate groups that stack in a manner non-orthogonal to (001). Figures 1 and 2 depict the atomic arrangement of synchysite-(Ce) projected on (010) and (001), respectively.

Figure 1 illustrates the (001) layer nature of the synchysite-(Ce) atomic arrangement and depicts the (CeF), (CO_3), and (Ca) layers [note that in their description of the bastnäsite-(Ce) atomic arrangement, Ni *et al.* (1993) combined the predicted Ca and (CO_3) layers and wrote of a [Ca(CO_3)] layer; their analysis was indeed correct, but here we separate those layers to (Ca) and (CO_3) in the description of synchysite-(Ce) for reasons that are now obvious]. The unit cell of synchysite-(Ce) includes two (CeF) layers and two (Ca) layers with four intervening (CO_3) layers. The (Ca) layers are located at z = 0, ½, and the (CeF) layers, at ¼, ¾; the intervening (CO_3) layers are located slightly closer to the (Ca) layer than to the (CeF) layer.

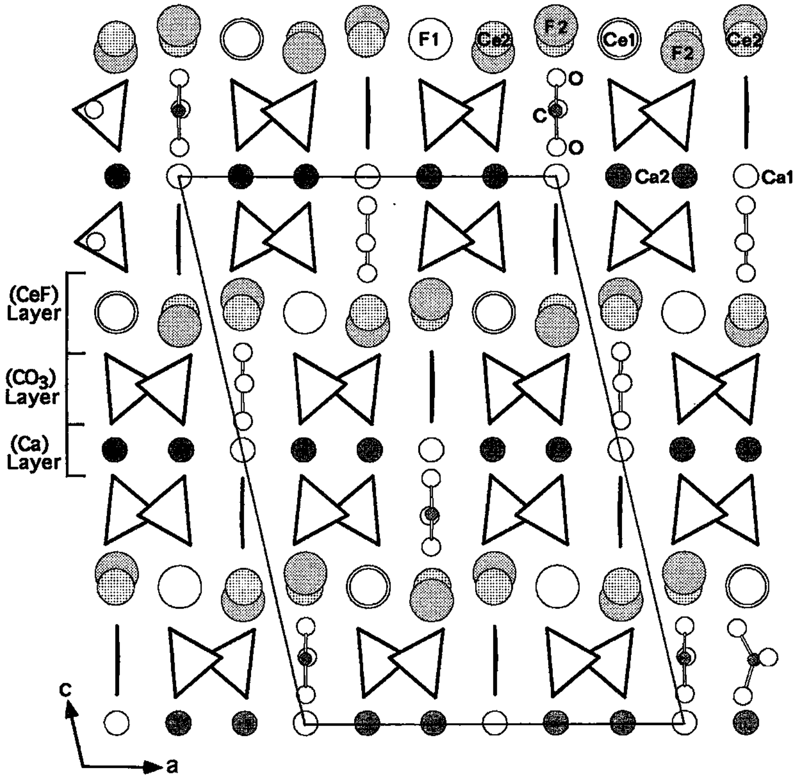

FIG. 1. Arrangement of atoms in synchysite-(Ce), projected on (010). Triangles represent (CO_3) groups, and O atoms lie at the apices of the triangles. Circles from the largest to smallest represent F, Ce, Ca, O, and C atoms, respectively. The unit cell is outlined.

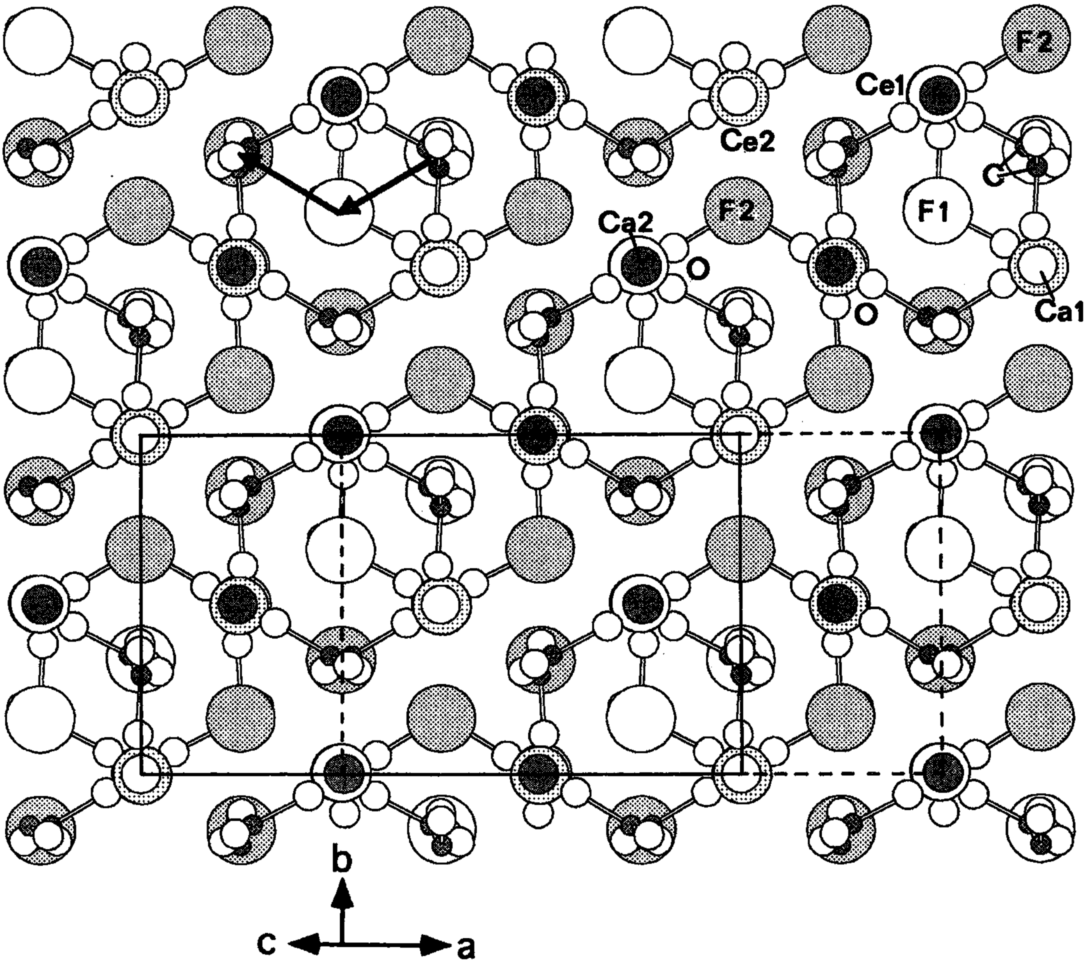

FIG. 2. Arrangement of atoms in synchysite-(Ce), projected on (001). C–O bonds are depicted, and atomic symbols are the same as in Fig. 1. Arrows indicate the shift direction of the layer structure. Dashed line outlines the bottom of the unit cell, and fine line outlines the top of the unit cell.

In their presentation of the atomic arrangement of bastnäsite-(Ce), Ni *et al.* (1993) elucidated the layer-nature of that phase and demonstrated that the unit-cell parameters of synchysite were predictable by addition of the thickness of the component layers. That structure is here confirmed; the geometries of the (CO_3) layer and the (CeF) layer are essentially identical to those in bastnäsite-(Ce). The fundamental difference, however, is the presence of the Ca layer in synchysite that is absent in bastnäsite. It is the presence of the Ca layer that allows shifts of the other layers; the neighboring carbonate layers can link to the Ca layer in several ways, all of which are related by translations similar to those in the mica polytypes.

Figures 1 and 2 show that in each (CO_3) layer, the carbonate triangles are almost "vertical", with the perpendicular to the carbonate plane lying in (001). Unlike the carbonate layers in bastnäsite-(Ce), one edge of a triangle is not exactly perpendicular to (001), but is skewed by about 5° from c^*.

Although the (CeF) and (CO_3) layers are similar to the analogous layers in bastnäsite-(Ce), the geometry of the (Ca) layer has not yet been described from any structure. All Ca in any layer is coplanar parallel to (001), with Ca1 in a special position and Ca2 in a general position; the plane contains an inversion center at Ca1 and midway between Ca2 atoms. The geometry of the layer is similar to that of the (Ca) layer in vaterite (Meyer 1969).

In synchysite-(Ce), both Ce1 and Ce2 coordinate to F1 and 2 × F2 in the (CeF) layer, and six oxygen atoms, three from each neighboring (CO_3) layer (see

Table 3, Figs. 1, 2). Ca1 coordinates with eight oxygen atoms, four from each neighboring (CO_3) layer; Ca2 coordinates to seven oxygen atoms, three from one adjoining carbonate layer and four from the other adjacent carbonate layer. The bond-valence sums of all cations and anions are in good agreement with the expected formal valence.

DISCUSSION OF THE STRUCTURE

The atomic arrangement of synchysite has long resisted determination. We can speculate that the structure was so recalcitrant because of the strong pseudohexagonal symmetry; our attempts at solution in hexagonal space-groups invariably terminated with successful location of only the heavy atoms. The light atoms could not be precisely located, a problem symptomatic of incorrect assignment of space group.

As noted previously, careful examination of precession photographs revealed the true monoclinic symmetry. This lower symmetry results from the orientation and stacking of carbonate groups; because of their weak scattering power relative to the heavy atoms in synchysite-(Ce), the X-ray evidence for monoclinic character is subtle. Neglecting the carbonate groups, a pronounced pseudohexagonal cell with $c' = 18.28$ Å is derivable. A more complicated stacking sequence of the *heavy* atoms along c^* can be described as ...Ce1–Ca2–Ce2–Ca1–Ce2–Ca2–Ce1... (Fig. 1), which suggests the existence of a pseudohexagonal cell with $c'' = 18.28 \times 3 = 54.84$ Å, the c value suggested by Donnay & Donnay (1953). The orthorhombic unit-cell suggested by Smith *et al.* (1960) and Levinson & Borup (1962) for synchysite-(Y) may be described as the orthorhombic expression of a pseudohexagonal cell (*i.e.*, $a' = a$, $b' = b \cos 30°$, $c' = c$) rather than an independent cell.

Although the individual layers in synchysite-(Ce) possess hexagonal symmetry, the stacking of the (CO_3) layers yields monoclinic symmetry. In bastnäsite-(Ce), there is one column of F1 atoms on the $\bar{6}$ axis and two columns of F2 atoms on the [0001] triad, and the F1–F1 distance is $c/2$, or 4.88 Å (Ni *et al.* 1993). In synchysite-(Ce), there is no corresponding F atom in the adjacent layer because of the addition of the intervening Ca layer; a large void would thus be created in the atomic arrangement without structural adjustments, as F1–F1 distances in the F1 column are as long as $c/2 = 9.14$ Å. To fill these potential voids in the structure, the atoms above $z = ½$ shift in the (001) plane by approximately 2.37 Å along $[\bar{1}\bar{1}0]$ (Fig. 2). The atoms above $z = 1$ also shift the same amount, along $[\bar{1}10]$, such that the oxygen atoms of the near-vertical edges of two overlying CO_3 triangles will occupy the voids (Fig. 2). As a result of these shifts in the layers, the columns of F atoms in bastnäsite-(Ce) do not exist in synchysite-(Ce), but are replaced by a column of ...F1, (CO_3 edge), (CO_3 edge), F2, (CO_3 edge), (CO_3 edge), F2, (CO_3 edge), (CO_3 edge), F1... in the stacking sequence along c^*. Thus, the hexad and triads are lost in synchysite-(Ce), and no symmetry exists along c^*, but the diad in the (001) layer remains, and monoclinic symmetry results. The shift of the carbonate groups along a in each unit cell can be calculated as $2 \times (b/3) \cos 30° = 4.11$ Å. From this layer offset, a β angle of $90° + \arctan(4.11 \text{ Å}/c' \text{ Å}) = 102.67°$ can be calculated, in perfect agreement with the observed value of β.

The stacking sequence of synchysite-(Ce) is analogous to that in a 2:1 mica with an interlayer cation; the layer-nature of the synchysite-(Ce) atomic arrangement invites comparison to phyllosilicate structures such as muscovite, which also crystallizes in space group *C*2/*c*. The layer sequence in synchysite-(Ce) is identical to that in muscovite if the (CO_3) layer of synchysite is likened to the layer of tetrahedra in muscovite, the (CeF) layer in synchysite, to the [$AlO_5(OH)$] layer in muscovite, and the Ca layer in synchysite, to the K^+ layer in muscovite. As in synchysite, muscovite displays a diad in the layer of octahedra and an inversion center in the K layer; each layer also has hexagonal or trigonal symmetry, but the symmetry after stacking is monoclinic.

Mica polytypes result from translation of [$(Si,Al)O_4$] sheets relative to each other, and the polytype concept can be extended to the atomic arrangement of synchysite. The synchysite-(Ce) studied herein exhibits shifts of adjacent (CO_3) layers by the vectors noted in Figure 2, similar to the offsets in the layer of tetrahedra in $2M_2$ lepidolite. We could also presume the existence of $2M_1$ synchysite, with layer-offsets similar to those in $2M_1$ muscovite.

The atomic arrangement in synchysite-(Ce) may provide useful information for understanding the atomic arrangement of parisite-(Ce) and other *RE* fluorcarbonate minerals. It is reasonable to predict that the parisite-(Ce) structure is based on stacking of layers similar to those in synchysite-(Ce). Our attempts at solving the atomic arrangement in hexagonal space-groups have failed, however; the stacking of carbonate groups may also result in lower symmetry in parisite-(Ce). We are currently investigating that possibility.

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