Transmission electron microscopic study of new, regular, mixed-layer structures in calcium-rare-earth fluorocarbonate minerals

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ABSTRACT

Structures of calcium-rare-earth (Ca-*RE*) fluorocarbonate minerals from southwest China have been investigated using selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). They are described as combinations of layers of bastnäsite-(Ce), CeFCO₃ (*B* layers), and synchysite-(Ce), CeFCO₃·CaCO₃ (*S* layers) (Donnay and Donnay, 1953). We report here the discovery of six new, regular, mixed-layer structures in parisite-(Ce) observed using SAED and HRTEM. The symmetry, cell parameters, chemical formulae and stacking of the structural unit layers, etc., were determined for each. The regular, mixed-layer structures are formed by stacking unit layers of bastnäsite-(Ce) and synchysite-(Ce) in varying proportions along the c axis. HRTEM shows that there are different distribution modes for the Ce-F ion layers, the CO₃ ion groups between the Ce-F ion layers. The minerals may be regarded as polymorphs with the same chemical composition and the same spacing of the unit layers, but different arrangements of ion layers in the structural unit layers and different stacking sequences of the structural unit layers.

Keywords: Ca-RE fluorocarbonate mineral, mixed-layer structure, high-resolution transmission electron microscopy.

Introduction

DONNAY and Donnay (1953) and Van Landuyt and Amelinckx (1975) showed that calcium rare-earth fluorocarbonate minerals can be described in terms of four different types of layer parallel to the hexagonal (0001) plane. The layers have the general chemical formula $Ca_xCe_y(CO_3)_{x+y}F_y$ where x < y, and are described as combinations of layers of bastnäsite-(Ce), CeFCO₃ (*B* layers), and synchysite-(Ce) CeFCO₃·CaCO₃ (*S* layers). Other minerals of the group may be described as different combinations of *B* and *S* layers, for example parisite (2CeFCO₃·CaCO₃) as *BS*, and röntgenite-(Ce) (3CeFCO₃·2CaCO₃) as BS_2 . Van Landuyt and Amelincks (1975) discovered three other mixed-layer compounds (B_3S_2 , B_3S_4 and BS_4) by transmission electron microscopy (TEM). Previous further investigations of mixed-layer structure of minerals in this series have concentrated on bastnäsite-(Ce) (e.g. Ni *et al.*, 1993). We have discovered six new, regular, mixed-layer structures in parisite-(Ce), which may be described by the formulae B_7S_4 , B_8S_6 and $B_{10}S_6$, with two different stacking sequences in each case. We describe the structures in decreasing order of CaCO₃ content (Table 1) as B_8S_6 -I, B_8S_6 -II, $B_{10}S_6$ -I, $B_{10}S_6$ -II, B_7S_4 -I and B_7S_4 -II.

Name	Symmetry	Cell a	(nm) c	Chemical formula	CaCO ₃ (%)	Structural layer stacking mode	Layer size (nm)
bastnäsite-(Ce)	* H	0.710	0.978	CeCO ₃ F	0	de/	0.489
synchysite-(Ce))* R	0.710	5.472	CaCe(CO ₃) ₂ F	50.00	dgfg/	0.912
röntgenite-(Ce)	* R	0.713	7.056	$Ca_2Ce_3(CO_3)_5F_3$	40.00	dedgfgdgfg/	2.355
parisite-(Ce)*	R	0.712	8.412	CaCe ₂ (CO ₃) ₃ F ₂	33.00	dedgfg/	1.402
B ₈ S ₆ -1	Н	0.707	9.420	$Ca_6Ce_{14}(CO_3)_{20}F_{14}$	30.00	dedededgfgdedgfgdedgfgde dgfgdedgfgdedgfg/	9.420
<i>B</i> ₈ <i>S</i> ₆ -II	Н	0.713	9.420	$Ca_6Ce_{14}(CO_3)_{20}F_{14}$	30.00	dededgfgdedgfgdedgfgded gfgdededgfgdedgfg/	9.420
<i>B</i> ₁₀ <i>S</i> ₆ -I	R	0.710	31.086	$Ca_6Ce_{16}(CO_3)_{22}F_{16}$	27.27	dededgfgdededgfgdededgfg dededgfgdedgfgdedgfg/	10.362
$B_{10}S_6$ -II	Н	0.703	10.362	$Ca_6Ce_{16}(CO_3)_{22}F_{16}$	27.27	dededgfgdededgfgdededgfg dedafgdededgfgdedgfg/	10.362
<i>B</i> ₇ <i>S</i> ₄ -I	R	0.703	21.195	$Ca_4Ce_{11}(CO_3)_{15}F_{11}$	26.67	dededededgfgdedgfgdedgfg dedgfg/	7.065
<i>B</i> ₇ <i>S</i> ₄ -II	R	0.710	21.195	$Ca_4Ce_{11}(CO_3)_{15}F_{11}$	26.67	dededgfgdededgfgdededgfg dedgfg/	7.065

TABLE 1. Crystal structure analyses of Ca-RE fluorocarbonate minerals

* Donnay, G. (1953); R = rhombohedral; H = hexagonal

Experimental

Results

Structures B₈S₆-I and B₈S₆-II

Particles of a polycrystal of parisite-(Ce) (about 0.08-0.2 mm in diameter) that had been collected from a rare-earth mineral deposit within an aegirine alkali granite massif of Sichuan Province, Southwest China, were chosen carefully using the binocular microscope. These particles were crushed into fine fragments in an agate mortar and suspended in absolute alcohol, and an ultrasonic vibrator was used to disperse them uniformly. A drop of the suspension was put on a copper grid coated with a perforated carbon film, in turn coated with gold, for determining λL , the camera constant. It was then examined at 200 kV in a JEOL-2000EX II electron microscope equipped with a top-entry goniometer stage (\pm 10° tilt) and an ultra-highresolution pole piece (Cs = 0.7 mm) with an interpretable point resolution of 0.21 nm. Electron diffraction patterns were observed at 120 kV with a Philips-CM12 transmission electron microscope which has a side-entry, doubletilting sample holder (\pm 45° tilt). Crystals with <0001> parallel to the support film were chosen so that the images would always contain the caxis, making it easy to identify the superstructure along this axis. The crystals studied were well away from the gold on the grid.

Selected-area electron diffraction (SAED) patterns were obtained by tilting the sample about c^* . Fig. 1(a-d) shows the patterns from $B_{8}S_{6}$ -I with the electron beam parallel respectively to [1210], [4510], [1100] and [2110]. The angles between successive zones are 19.08°, 10.79° and 29.97°. Because there are 19 weak reflections between the strongest diffraction spots (indicated positions in Fig. 1) and the transmitted spot (see Fig. 7), the first strong diffraction spot was indexed as 00020. Fig. le is the [0001], twodimensional reciprocal lattice plane deduced from the four SAED patterns la-ld and their mutual angular relationships. Four straight lines are the directions perpendicular to c* in each of the sections in la-ld. Fig. 1f is the high-resolution lattice image of B_8S_6 -I taken in the [1210] orientation and displays a structural unit layer with a 9.42 nm repeat. The structural unit layer of B_8S_6 -I is composed of eight Ce-Ce unit layers of bastnäsite-(Ce) and six Ca-Ce unit layers of synchysite-(Ce). In terms of the criteria adopted by Van Landuyt and Amelinckx (1975), i.e. (d) LnF ionic layers, (e) layers of CO₃ groups between two LnF layers, (f) layers of Ca ions, (g) layers of CO_3 groups between a calcium-and a

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FIG. 1(*a-d*) SAED patterns of B_8S_6 -I obtained by tilting the crystal about [0001]. (e) A diagram of the reciprocal lattice plane determined from the SAED patterns a-d, the relative size of the circles is a rough measure of the relative intensities. (f) HRTEM image of B_8S_6 -I corresponding to crystal zone [$\overline{1}2\overline{1}0$].

LnF layer, the stacking order is dedededgfg-dedgfgdedgfgdedgfgdedgfgdedgfgdedgfg...... (see Fig. 8). The crystal structure parameters and the structural symmetry determined from Fig. <math>la and d are listed in Tables 1 and 2.

Figure 2 (a) to (d) show SAED patterns obtained from B_8S_6 -II by tilting the crystal about [0001], (a) is [01 $\overline{10}$], (b) [$\overline{12}\overline{10}$], (c) [$\overline{45}\overline{10}$], (d) [$\overline{1100}$]. Figure 2e is a schematic diagram of the $(\mathbf{a}^*, \mathbf{b}^*)$ section in reciprocal space, 2f is a lattice image taken in the $[\bar{1}2\bar{1}0]$ orientation. Figure 2f displays the structure unit layers (9.42 nm) of B_8S_6 -II with the stacking order dededgfgdedgfgdedgfgdedgfgdeddgfgdedgfg/.... The type and the repeat periods of a regularly mixed-layer structure are determined by the compositions of the structural unit layer and the

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FIG. 2(*a*-*d*) SAED patterns of B_8S_6 -II obtained by tilting the crystal about [0001]. (e) A diagram of the reciprocal lattice plane determined from the SAED patterns *a*-*d*, the relative size of the circles as in Fig. 1. (f) HRTEM image of B_8S_6 -II corresponding to crystal zone [$\bar{1}2\bar{1}0$].

arrangement sequences of ion layers. From the analysis of electron diffraction patterns and lattice fringe images, it was determined that B_8S_6 -I and B_8S_6 -II have the same structural chemical formula: $Ca_6Ce_{14}(CO_3)_{20}F_{14}$ and that both structures have hexagonal symmetry. B_8S_6 -I and B_8S_6 -II both show regular, mixed-layer structures with a long period and ordered stacking.

The electron diffraction patterns and lattice images of $B_{10}S_6\text{--}I$ and $B_{10}S_6\text{--}II$

Figure 3 shows the SAED patterns from $B_{10}S_6$ -I with the electron beam respectively parallel to [1120] (*a*), [0110] (*b*) and [1210] (*c*) directions, the [0001] reciprocal lattice plane (*d*) and a high-resolution lattice image (*f*) taken in the [1210]

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FIG. 3(a-c) SAED patterns of $B_{10}S_6$ -I obtained by tilting the crystal about [0001]. (d) A diagram of the reciprocal lattice plane determined from the SAED patterns a-c, the circles and triangles represent the spots projected onto the reciprocal lattice plane (0001)* from $1/3d_{(0003)}$ and $2/3d_{(0003)}$ above respectively. (e) SAED pattern of $B_{10}S_6$ -I corresponding to zone [$\overline{1}2\overline{1}0$]. (f) HRTEM image of $B_{10}S_6$ -I corresponding to zone [$\overline{1}2\overline{1}0$].

orientation. The diffraction spots are consistent with rhombohedral symmetry: they are in accordance with the reflection conditions: hkil, -h+k+l = 3n ($n = 0, \pm 1, \pm 2, ...$); $h\overline{h}0l$, h+l = 3n; 000l, l = 3n. There are two groups of fringe spacings in the lattice image, where the smaller one (spacing 1.413 nm) is the height of unit layers in parisite-(Ce) (*dedgfg*), which is equal to the height of one Ce-Ce unit layer plus the height of one Ca-Ce unit layer, while the larger one (spacing 1.884 nm) is *dededgfg*, equal to the height of two Ce-Ce unit layers plus the height of one Ca-Ce unit layer. In lattice images taken from different crystal fragments, these fringes are



FIG. 4(a) SAED pattern of $B_{10}S_6$ -II corresponding to zone [$\overline{1}100$]. (b) HRTEM image of $B_{10}S_6$ -II corresponding to zone [$\overline{1}100$].

regularly ordered. The repeat period of the structural unit layer in $B_{10}S_6$ -I along the **c** direction (spacing 10.362 nm) is composed of four unit layers of *dededgfg* plus two unit layers of *dedgfg*. The height of the triple hexagonal cell is c = 10.362 nm $\times 3 = 31.086$ nm, and the chemical composition is Ca₆Ce₁₆(CO₃)₂₂F₁₆.

In the [$\overline{1}100$] SAED pattern taken from $B_{10}S_6$ -II (Fig. 4), there are twenty-one weak diffraction spots between 0000 and 000<u>22</u> ($B_{10}S_6$ -I, 0000 and 000<u>66</u> in Fig. 3c) along the **c*** axis. From the HREM image the stacking along the **c** axis is dededgfgdededgfgdededgfgdedgfgdededgfgdedgfg/.... The structure of $B_{10}S_6$ -II belongs to the hexagonal system with c = 10.362 nm (see Table 1, Table 2, Fig. 7 and Fig. 8).

New, regular, mixed-layer structures B₇S₄-I and B₇S₄-II

In Fig. 5d and Fig. 6d the [0001] reciprocal lattice planes from B_7S_4 -I and B_7S_4 -II have been

constructed from the diffraction patterns in Figs 5a-c and 6a-c respectively. These crystals both have rhombohedral symmetry, but there are some essential differences between the two structures. In the lattice images taken in the $[\bar{1}2\bar{1}0]$ orientation (Figs 5f and 6f), it is clear that a structure unit layer of B_7S_4 -I is composed of a group *dededededgfg* and three groups *dedgfg*, but in B_7S_4 -II three groups *dededgfg* and a group *dedgfg* (of spacing 7.065 nm) can be seen. The lattice parameters and the symmetry of B_7S_4 -I and B_7S_4 -II determined by SAED and HREM images are listed in Tables 1 and 2.

Discussion

Donnay and Donnay (1953) observed ubiquitous syntaxial intergrowths among all pairs of the calcium-rare-earth fluorocarbonate minerals bastnäsite-(Ce), parisite-(Ce), röntgenite-(Ce) and synchysite-(Ce), except for bastnäsite-(Ce)-synch-

Name	Symmetry	Laue	Reflection conditions				Possible
		group	hkil	hh2ħ1	$h\bar{h}0l$	0001	space groups
B_8S_6 -I	н	6/m			_	_	P6/m, P6, P6
B_8S_6 -II	Н	6/m	_	_	_	_	$P6/m, P6, P\overline{6}$
$B_{10}S_{6}$ -I	R	Зm	-h+k+1 = 3n	l = 3n	h+l=3n	l = 3n	$R3m, R32, R\overline{3}m$
$B_{10}S_6$ -II	Н	6/m	—	_	_	_	$P6/m, P6, P\bar{6}$
B_7S_4 -I	R	3	h-k+l=3n	l = 3n	2h+l = 3n	l = 3n	$R3, R\overline{3}$
B_7S_4 -II	R	3m	-h+k+l=3n	l = 3n	h+l=3n	l = 3n	R3m, R32, R3m

TABLE 2. Crystal structure symmetry of new, regular, mixed-layer structures

* R = rhombohedral; H = hexagonal

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FIG. 5(a-c) SAED patterns of B₇S₄-I obtained by tilting the crystal about [0001]. (d) A diagram of the reciprocal lattice plane determined from the SAED patterns a-c. The circles and triangles are as in Fig. 3. (e) SAED pattern of B₇S₄-I corresponding to zone [1210]. (f) HRTEM image of B₇S₄-I corresponding to zone [1210].

ysite-(Ce). In this paper, six new, regular, mixedlayer structures with different stacking sequences $(B_8S_6\text{-I}, B_8S_6\text{-II}, B_{10}S_6\text{-II}, B_7S_4\text{-I}, \text{ and} B_7S_4\text{-II})$ have been found associated with parisite by means of SAED and HREM. These structures are composed of unit layers of bastnäsite-(Ce) and synchysite-(Ce) with ordered stacking along the **c** direction. The maximum dimension of the new phases is about 0.5 μ m, and they contain at least ten identical repeat sequences. Moreover, the same regular, mixed-layer structure occurs in at least four different crystal fragments. So far it has not been reported that two more regular, mixed-layer structures occur for the same B_mS_n composition. In this paper, the new mixed-layer structures with long period order stacking were described respecWU XIULING ETAL.



FIG. 6(a-c) SAED patterns of B_7S_4 -II obtained by tilting the crystal about [0001]. (d) A diagram of the reciprocal lattice plane determined from the SAED patterns a-c, the circles and triangles as in Fig. 3. (e) SAED pattern of B_7S_4 -II corresponding to zone [$\overline{1}2\overline{1}0$]. (f) HRTEM image of B_7S_4 -II corresponding to zone [$\overline{1}2\overline{1}0$].

tively as B_8S_6 -I, B_8S_6 -II, $B_{10}S_6$ -I, $B_{10}S_6$ -II, B_7S_4 -I, and B_7S_4 -II.

 B_7S_4 -I, and B_7S_4 -II (or B_8S_6 -I, and B_8S_6 -II, or $B_{10}S_6$ -I, and $B_{10}S_6$ -II) are similar in some respects. For example, they have the same chemical composition $Ca_4Ce_{11}(CO_3)_{15}F_{11}$ and

the same spacing of the unit layers, 7.065 nm, but there are some essential differences between them: the arrangement of the ion layer in the structural unit layer and the stacking sequences of the structural unit layer are different. The crystallite dimension of the two B_7S_4 phases (or



FIG. 7 Schematic representations of SAED patterns of new, regular, mixed-layer structures in calcium rare-earth fluorocarbonate minerals.

the two B_8S_6 phases, or the two $B_{10}S_6$ phases) are within 500 nm, and they coexist in the form of derived microcrystals together with other minerals in the complex polycrystal. Therefore, the pairs B_8S_6 -I, and B_8S_6 -II, $B_{10}S_6$ -I, and $B_{10}S_6$ -II, B_7S_4 -I and B_7S_4 -II can be regarded as polymorphs.

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FIG. 8 Schematic representation of the crystallostructural stacking mode of new, regular, mixed-layer structures.

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