

# 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),  $\text{CeFCO}_3$  (*B* layers), and synchysite-(Ce),  $\text{CeFCO}_3 \cdot \text{CaCO}_3$  (*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  $\text{CO}_3$  ion groups between the Ce-F ion layers and the  $\text{CO}_3$  ion groups between the Ce-F and Ca 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  $\text{Ca}_x\text{Ce}_y(\text{CO}_3)_{x+y}\text{F}_y$ , where  $x < y$ , and are described as combinations of layers of bastnäsite-(Ce),  $\text{CeFCO}_3$  (*B* layers), and synchysite-(Ce)  $\text{CeFCO}_3 \cdot \text{CaCO}_3$  (*S* layers). Other minerals of the group may be described as different combinations of *B* and *S* layers, for example parisite ( $2\text{CeFCO}_3 \cdot \text{CaCO}_3$ ) as *BS*, and

röntgenite-(Ce) ( $3\text{CeFCO}_3 \cdot 2\text{CaCO}_3$ ) as  $BS_2$ . Van Landuyt and Amelinckx (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  $\text{CaCO}_3$  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.

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

Name	Symmetry	Cell (nm)		Chemical formula	CaCO <sub>3</sub> (%)	Structural layer stacking mode	Layer size (nm)
		<i>a</i>	<i>c</i>				
bastnäsite-(Ce)*	H	0.710	0.978	CeCO <sub>3</sub> F	0	<i>de/.....</i>	0.489
synchysite-(Ce)*	R	0.710	5.472	CaCe(CO <sub>3</sub> ) <sub>2</sub> F	50.00	<i>dgfg/.....</i>	0.912
röntgenite-(Ce)*	R	0.713	7.056	Ca <sub>2</sub> Ce <sub>3</sub> (CO <sub>3</sub> ) <sub>5</sub> F <sub>3</sub>	40.00	<i>dedgfgdgfg/.....</i>	2.355
parisite-(Ce)*	R	0.712	8.412	CaCe <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> F <sub>2</sub>	33.00	<i>dedgfg/.....</i>	1.402
<i>B</i> <sub>8</sub> <i>S</i> <sub>6</sub> -I	H	0.707	9.420	Ca <sub>6</sub> Ce <sub>14</sub> (CO <sub>3</sub> ) <sub>20</sub> F <sub>14</sub>	30.00	<i>dedededgfgdedgfgdedgfgde</i> <i>dgfgdedgfgdedgfg/.....</i>	9.420
<i>B</i> <sub>8</sub> <i>S</i> <sub>6</sub> -II	H	0.713	9.420	Ca <sub>6</sub> Ce <sub>14</sub> (CO <sub>3</sub> ) <sub>20</sub> F <sub>14</sub>	30.00	<i>dededgfgdedgfgdedgfgded</i> <i>gfgdededgfgdedgfg/.....</i>	9.420
<i>B</i> <sub>10</sub> <i>S</i> <sub>6</sub> -I	R	0.710	31.086	Ca <sub>6</sub> Ce <sub>16</sub> (CO <sub>3</sub> ) <sub>22</sub> F <sub>16</sub>	27.27	<i>dededgfgdededgfgdededgfg</i> <i>dededgfgdedgfgdedgfg/.....</i>	10.362
<i>B</i> <sub>10</sub> <i>S</i> <sub>6</sub> -II	H	0.703	10.362	Ca <sub>6</sub> Ce <sub>16</sub> (CO <sub>3</sub> ) <sub>22</sub> F <sub>16</sub>	27.27	<i>dededgfgdededgfgdededgfg</i> <i>dedgfgdededgfgdedgfg/.....</i>	10.362
<i>B</i> <sub>7</sub> <i>S</i> <sub>4</sub> -I	R	0.703	21.195	Ca <sub>4</sub> Ce <sub>11</sub> (CO <sub>3</sub> ) <sub>15</sub> F <sub>11</sub>	26.67	<i>dedededgfgdedgfgdedgfg</i> <i>dedgfg/.....</i>	7.065
<i>B</i> <sub>7</sub> <i>S</i> <sub>4</sub> -II	R	0.710	21.195	Ca <sub>4</sub> Ce <sub>11</sub> (CO <sub>3</sub> ) <sub>15</sub> F <sub>11</sub>	26.67	<i>dededgfgdededgfgdededgfg</i> <i>dedgfg/.....</i>	7.065

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

## Experimental

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  $\lambda L$ , the camera constant. It was then examined at 200 kV in a JEOL-2000EX II electron microscope equipped with a top-entry goniometer stage ( $\pm 10^\circ$  tilt) and an ultra-high-resolution pole piece ( $C_s = 0.7$  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, double-tilting sample holder ( $\pm 45^\circ$  tilt). Crystals with  $\langle 0001 \rangle$  parallel to the support film were chosen so that the images would always contain the *c* axis, making it easy to identify the superstructure along this axis. The crystals studied were well away from the gold on the grid.

## Results

### Structures *B*<sub>8</sub>*S*<sub>6</sub>-I and *B*<sub>8</sub>*S*<sub>6</sub>-II

Selected-area electron diffraction (SAED) patterns were obtained by tilting the sample about *c*\*. Fig. 1(a–d) shows the patterns from *B*<sub>8</sub>*S*<sub>6</sub>-I with the electron beam parallel respectively to  $[\bar{1}2\bar{1}0]$ ,  $[\bar{4}5\bar{1}0]$ ,  $[\bar{1}100]$  and  $[2\bar{1}\bar{1}0]$ . The angles between successive zones are  $19.08^\circ$ ,  $10.79^\circ$  and  $29.97^\circ$ . 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. 1e is the [0001], two-dimensional reciprocal lattice plane deduced from the four SAED patterns *1a–1d* and their mutual angular relationships. Four straight lines are the directions perpendicular to *c*\* in each of the sections in *1a–1d*. Fig. 1f is the high-resolution lattice image of *B*<sub>8</sub>*S*<sub>6</sub>-I taken in the  $[\bar{1}2\bar{1}0]$  orientation and displays a structural unit layer with a 9.42 nm repeat. The structural unit layer of *B*<sub>8</sub>*S*<sub>6</sub>-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 CO<sub>3</sub> groups between two LnF layers, (f) layers of Ca ions, (g) layers of CO<sub>3</sub> groups between a calcium- and a



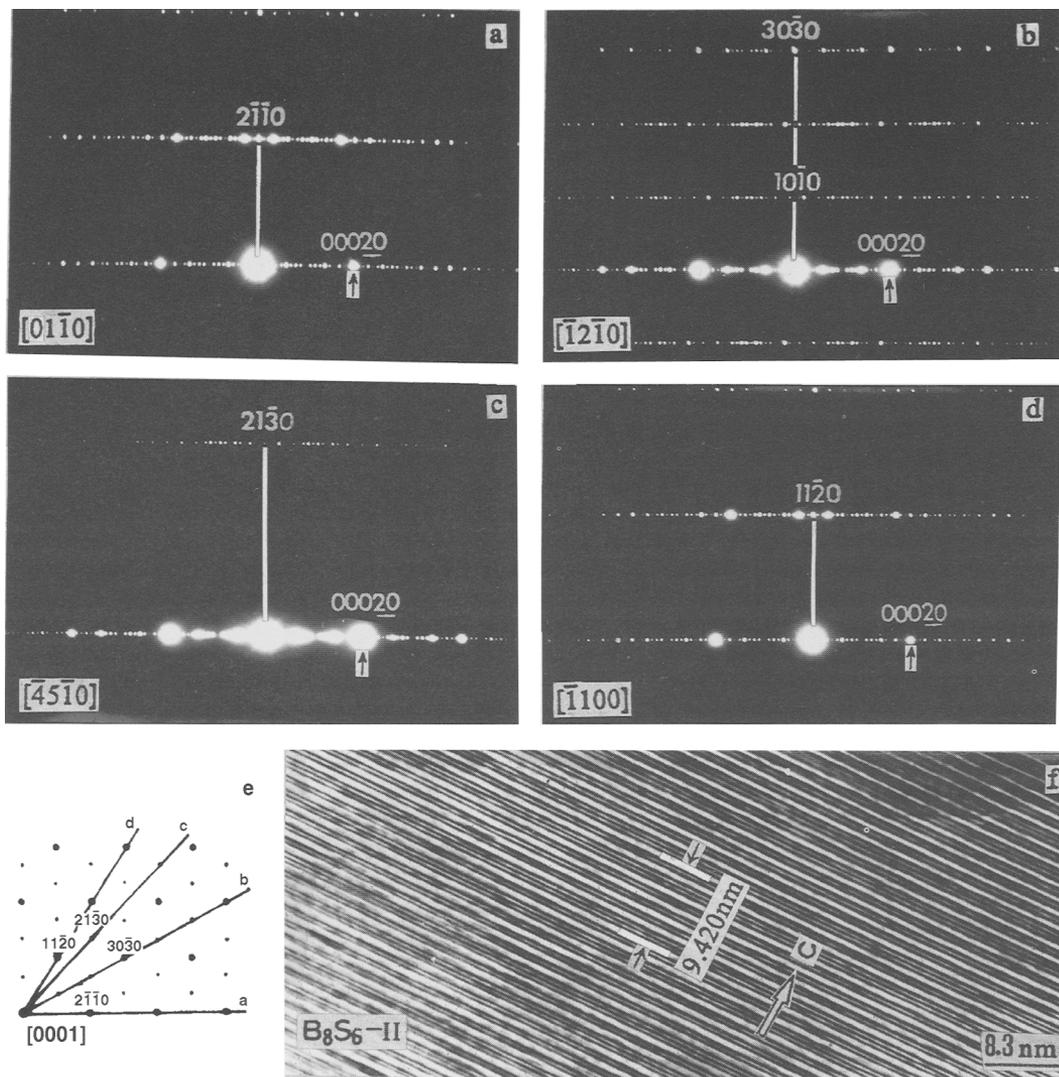


FIG. 2(a–d) SAED patterns of  $B_8S_6$ -II obtained by tilting the crystal about  $[0001]$ . (e) A diagram of the reciprocal lattice plane determined from the SAED patterns a–d, the relative size of the circles as in Fig. 1. (f) HRTEM image of  $B_8S_6$ -II corresponding to crystal zone  $[\bar{1}2\bar{1}0]$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

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 $B_{10}S_6$ -I and $B_{10}S_6$ -II

Figure 3 shows the SAED patterns from  $B_{10}S_6$ -I with the electron beam respectively parallel to  $[11\bar{2}0]$  (a),  $[01\bar{1}0]$  (b) and  $[\bar{1}2\bar{1}0]$  (c) directions, the  $[0001]$  reciprocal lattice plane (d) and a high-resolution lattice image (f) taken in the  $[\bar{1}2\bar{1}0]$

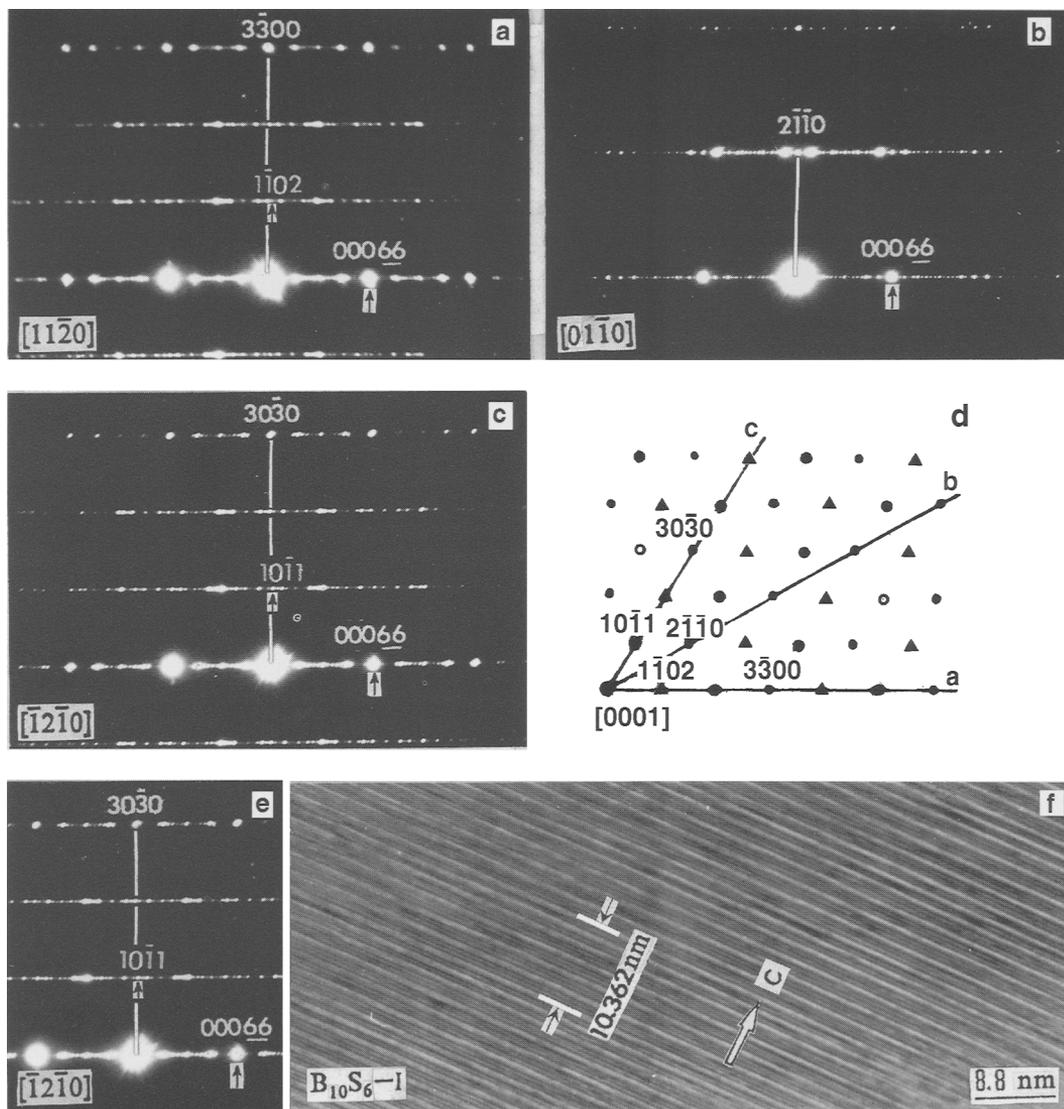


FIG. 3(a-c) SAED patterns of  $B_{10}S_6$ -I obtained by tilting the crystal about  $[0001]$ . (d) A diagram of the reciprocal lattice plane determined from the SAED patterns a-c, the circles and triangles represent the spots projected onto the reciprocal lattice plane  $(0001)^*$  from  $1/3d_{(0003)}$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

orientation. The diffraction spots are consistent with rhombohedral symmetry: they are in accordance with the reflection conditions:  $hkl$ ,  $-h+k+l = 3n$  ( $n = 0, \pm 1, \pm 2, \dots$ );  $hh0l$ ,  $h+l = 3n$ ;  $000l$ ,  $l = 3n$ . 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 parsite-(Ce) ( $dcdgfg$ ), 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  $dcdedgfg$ , 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



MIXED-LAYER STRUCTURES

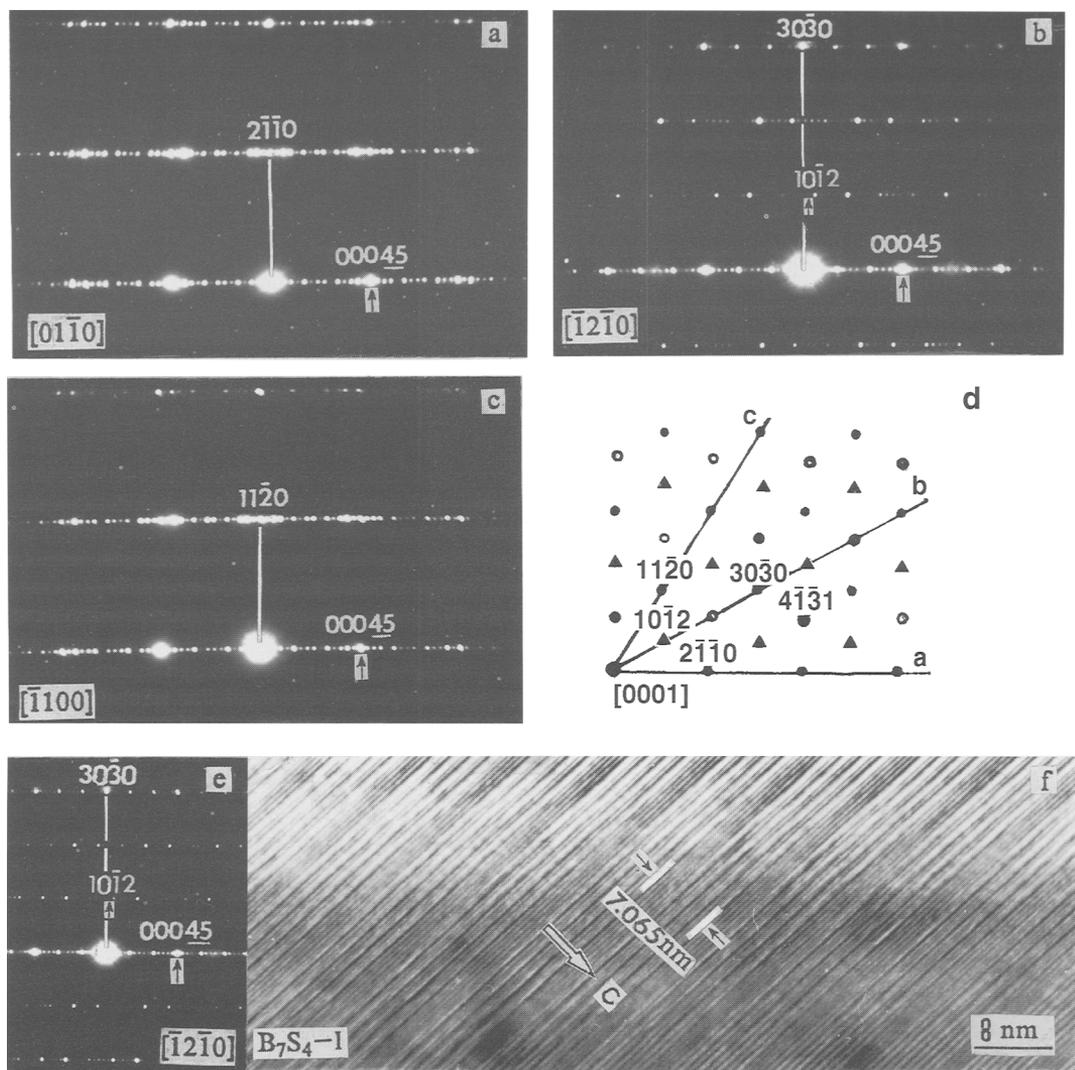


FIG. 5(a-c) SAED patterns of  $B_7S_4$ -I obtained by tilting the crystal about  $[0001]$ . (d) A diagram of the reciprocal lattice plane determined from the SAED patterns a-c. The circles and triangles are as in Fig. 3. (e) SAED pattern of  $B_7S_4$ -I corresponding to zone  $[\bar{1}2\bar{1}0]$ . (f) HRTEM image of  $B_7S_4$ -I corresponding to zone  $[\bar{1}2\bar{1}0]$ .

ysite-(Ce). In this paper, six new, regular, mixed-layer structures with different stacking sequences ( $B_8S_6$ -I,  $B_8S_6$ -II,  $B_{10}S_6$ -I,  $B_{10}S_6$ -II,  $B_7S_4$ -I, and  $B_7S_4$ -II) have been found associated with parisyte by means of SAED and HREM. These structures are composed of unit layers of bastnäsité-(Ce) and synchysité-(Ce) with ordered stacking along the c direction. The maximum dimension of the new

phases is about 0.5  $\mu\text{m}$ , 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 respec-

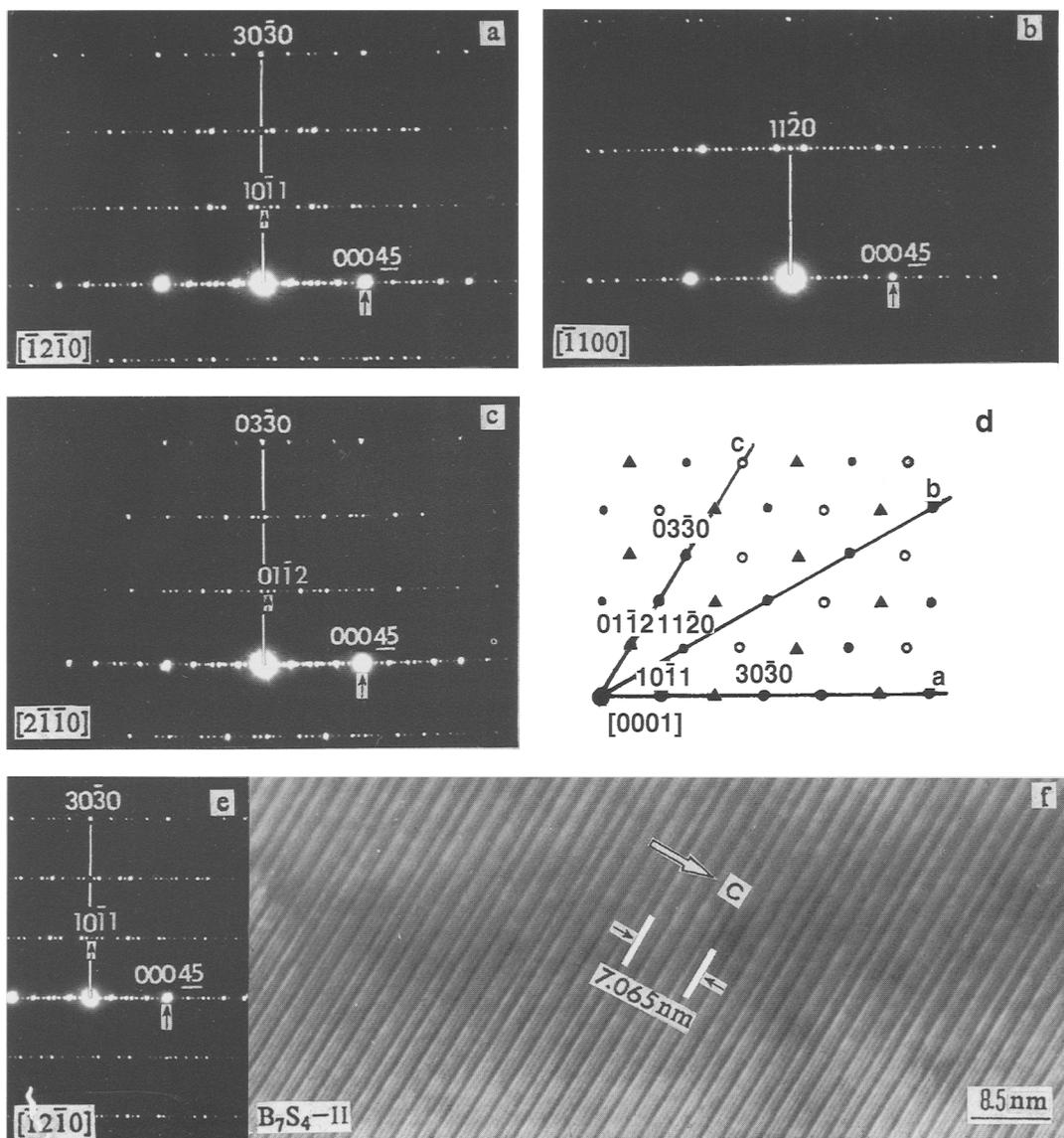


FIG. 6(a-c) SAED patterns of  $B_7S_4$ -II obtained by tilting the crystal about  $[0001]$ . (d) A diagram of the reciprocal lattice plane determined from the SAED patterns a-c, the circles and triangles as in Fig. 3. (e) SAED pattern of  $B_7S_4$ -II corresponding to zone  $[\bar{1}2\bar{1}0]$ . (f)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

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

MIXED-LAYER STRUCTURES

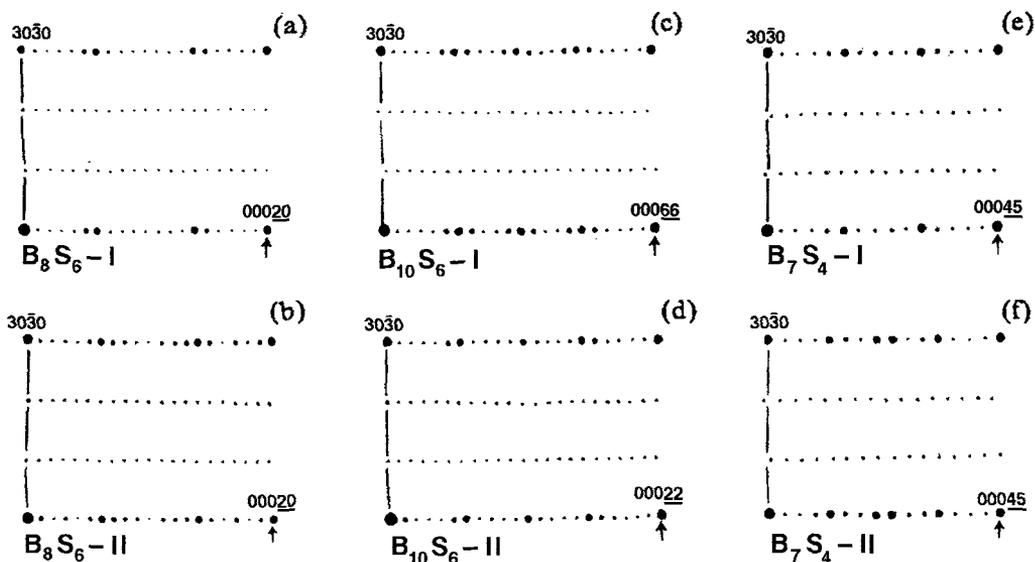


FIG. 7 Schematic representations of SAED patterns of new, regular, mixed-layer structures in calcium rare-earth fluorocarbonate minerals.

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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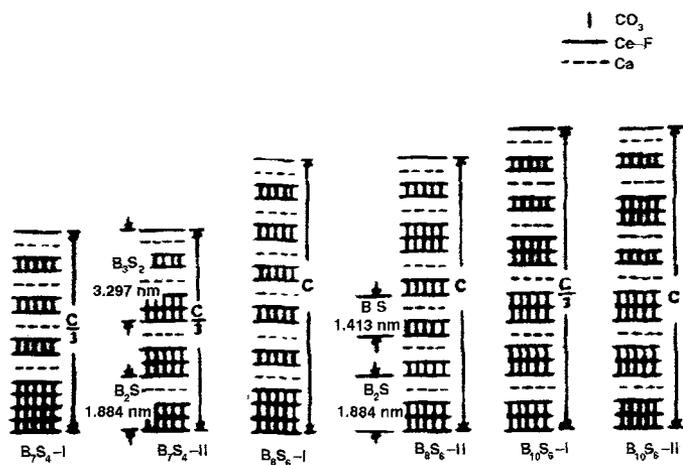


FIG. 8 Schematic representation of the crystallostructural stacking mode of new, regular, mixed-layer structures.

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