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THE CRYSTAL STRUCTURE OF SEIDITE-(Ce), $Na_4(Ce,Sr)_2\{Ti(OH)_2(Si_8O_{18})\}(O,OH,F)_4{\bullet}5H_2O$, A MODULAR MICROPOROUS TITANOSILICATE OF THE RHODESITE GROUP

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Abstract

Seidite-(Ce), $Na_4(Ce,Sr)_2\{Ti(OH)_2(Si_8O_{18})\}(O,OH,F)_4{\bullet}5H_2O$, is a titanosilicate recently discovered in the Yubileynaya pegmatite at Mount Karnasurt, Lovozero alkaline massif, Kola Peninsula, Russia. Grains consist of disordered [010] fibers; no single crystals suitable for X-ray diffraction have found. On the basis of chemical composition, electron and X-ray powder-diffraction data, and by comparison with the structure of miserite, $KCa_5(Si_2O_7)(Si_6O_{15})(OH)F$, a structure model for seidite-(Ce) has been developed in space group $C2/c$ [a 24.61(5), b 7.23(1), c 14.53(3) Å, β 94.6(3)°, $Z = 4$]. In the crystal structure of seidite-(Ce), the isolated eight-membered silicate channels of miserite are condensed into (100) layers that are connected by isolated TiO_6 octahedra to form a framework. In the chemical formula, the composition of the framework is shown within braces. There are two types of channels involving TiO_6 octahedra and SiO_4 tetrahedra: one is eight-membered and is parallel to the silicate channel along [010]; the other is ten-membered and extends along [001]. Cations other than Si and Ti occur within the channels, together with H_2O groups and OH,F anions. The Na cations are easily exchanged for Tl, K, Rb, Cs and Ba, indicating the microporous behavior of the seidite-(Ce) structure. We describe the mero-plesiotype modular aspects of seidite-(Ce) and related compounds belonging to the rhodesite group.

Keywords: seidite-(Ce), miserite, titanosilicate, structure model, microporous compounds, modular structure, mero-plesiotype series, Lovozero massif, Russia.

Sommaire

La seidite-(Ce), $Na_4(Ce,Sr)_2\{Ti(OH)_2(Si_8O_{18})\}(O,OH,F)_4{\bullet}5H_2O$, est un titanosilicate découvert récemment dans la pegmatite de Yubileynaya, au mont Karnasurt, complexe alcalin de Lovozero, péninsule de Kola, en Russie. Les grains sont des fibres [010] désordonnées; aucun monocristal apte à une étude par diffraction X n'a été trouvé. A la lumière de données sur la composition chimique, la diffraction d'électrons et la diffraction X (méthode des poudres), et par comparaison avec la structure de la misérite, $KCa_5(Si_2O_7)(Si_6O_{15})(OH)F$, nous avons développé un modèle structural pour la seidite-(Ce) dans le groupe spatial $C2/c$ [a 24.61(5), b 7.23(1), c 14.53(3) Å, β 94.6(3)°, $Z = 4$]. Dans cette structure, les canaux isolés à huit membres dans la trame silicatée de la misérite sont condensés en couches (100) connectées par des octaèdres TiO_6 isolés pour former une trame. Dans la formule chimique, la composition de la trame paraît entre crochets. La structure contient deux sortes de canaux impliquant des octaèdres TiO_6 et des tétraèdres SiO_4: un de ceux-ci possède huit membres, et il est parallèle au canal dans la trame silicatée, le long de [010]; l'autre en possède dix, et il est disposé le long de [001]. Les cations autres que Si et Ti sont situés dans les canaux, ainsi que les groupes H_2O et les anions OH,F. Les cations Na sont facilement échangeables pour Tl, K, Rb, Cs et Ba, indication d'un

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comportement microporeux par la structure de la seidite-(Ce). Nous décrivons les aspects modulaires de type méro-plésiotype de la seidite-(Ce) et des composés semblables faisant partie du groupe de la rhodesite.

(Traduit par la Rédaction)

Mots-clés: seidite-(Ce), misérite, titanosilicate, modèle structural, composés microporeux, structure modulaire, série méro-plésiotype, complexe alcalin de Lovozero, Russie.

INTRODUCTION

The geochemistry of the pegmatites that intrude hyperagpaitic alkaline rocks, like those of the Kola Peninsula (Khomyakov 1995), favors crystal structures that host rare elements (*e.g.,* Ti, Zr, Nb, REE) and alkali cations. Several structures consist of silicate frameworks or layers crossed by channels, and are similar to microporous zeolites. The concomitant presence of channels, Ti, and OH groups and the possibility of incorporating heteroatoms into the framework have attracted the attention of material scientists, and several compounds of technological interest have been synthesised having mineral structures as models (*cf.* Rocha & Anderson 2000).

As in the case for other titanosilicates occurring in the Kola Peninsula (Khomyakov 1995, Pekov 2000), crystals of seidite-(Ce) are not suitable for X-ray single-crystal diffractometry because of the disordered fibrous character. Here, we report on the structure of seidite-(Ce) to complete the previous data published by Khomyakov *et al.* (1998) and summarized in the following lines.

Seidite-(Ce) occurs in the hyperagpaitic pegmatite Yubileynaya at Mt. Karnasurt, in the Lovozero alkaline massif, Kola Peninsula, Russia and was described as a new species by Khomyakov *et al.* (1998). The mineral occurs as spherical aggregates 0.5 mm to 1 cm in diameter consisting of single fibers elongate on [010] that are about 0.01 mm in width. It is light yellow and shows perfect {100} and good {001} cleavage; it is biaxial (–), α 1.542(2), β 1.569(2), γ 1.571(2). On the basis of electron-microprobe and classical (H_2O and F) analyses and 8 Si atoms per formula unit (*apfu*), an empirical formula $(Na_{3.19}K_{0.27})$ $(Sr_{0.53}Ca_{0.19}Ba_{0.11})$ $(Ce_{0.42}La_{0.30}Nd_{0.10}Pr_{0.04}Sm_{0.02}Th_{0.12})$ $(Ti_{0.86}Nb_{0.06}Mn_{0.05}Fe_{0.02})$ $Si_8O_{28.03}F_{0.84}H_{12.81}$ was published by Khomyakov *et al.* (1998); it was idealized as $Na_4SrCeTiSi_8O_{22}F{\bullet}5H_2O$. In the same paper, variability of composition, mainly in Na, which was found to be higher in some samples, and the zeolite-like exchange properties of seidite-(Ce), were reported.

EXPERIMENTAL

Data were obtained by scanning electron microscopy (SEM; Cambridge Instruments Stereoscan 360; energy-dispersion spectrometry; EDS Link Analytical QX 2000; University of Torino) and transmission electron microscopy (TEM; Philips CM12, LaB_6 filament, operated at 120 kV; University of Torino). SEM observations (Fig. 1a) show lamellar single fibers of seidite-(Ce) that are a few μm in width and with a prominent fracture across the direction of elongation. Oriented patterns of selected-area electron diffraction (SAED) (Fig. 1) show that the lamellae are flattened on {100}, elongate along [010], and with cleavage parallel to {100} and {001}. The most frequent SAED patterns correspond to orientations with the electron beam perpendicular to a cleavage plane, *i.e.*, either (100) or (001); diffraction patterns corresponding to the (010) plane were rarely obtained. SAED with the following characteristics were observed: 1) ($h0l$): oblique pattern with twofold symmetry; $h, l = 2n$ (Fig. 1b), 2) ($hk0$): *mm* symmetry; $h + k = 2n$ (Fig. 1c), and 3) ($0kl$): *mm* symmetry; no systematic absences are observed, but the rows with k odd, whose overall intensity is decreasing with increasing k, are actually due to $\pm 1kl$ reflections that are registered because of the small value of $a^* = 0.04078$ Å^{-1} (Fig. 1d).

On the basis of the SAED patterns, the space group $C2/c$ was adopted to constrain the symmetry of the structure model, as discussed below.

The X-ray powder-diffraction pattern of Khomyakov *et al.* (1998) was averaged with new data obtained with a Guinier–de Wolff camera (Cu$K\alpha$ radiation). The full set of merged data was indexed from the cell parameters obtained by the SAED patterns, taking into account the diffraction intensities calculated from the structural model (Table 1). A least-squares refinement of the powder-diffraction data gave the following values: a 24.61(5), b 7.23(1), c 14.53(3) Å, β 94.6(3)°, V 2577 Å^3. For the chemical composition given above ($Z = 4$), the D_{calc}, 2.73 g/cm^3, compares well with D_{obs}, 2.76 g/cm^3.

THE STRUCTURE MODEL

Similarity of the unit-cell parameters and the chemical formula of miserite [$KCa_5(Si_2O_7)(Si_6O_{15})(OH)F$, a 10.100, b 16.014, c 7.377 Å, α 96.41, β 111.15, γ 76.57°, $P\bar{1}$; Scott 1976] and seidite-(Ce) suggested a way to model the crystal structure of our mineral. In particular, $a_s \cong 2a_m$, $c_s \cong b_m$, $b_s \cong c_m$ [s and m stand for seidite-(Ce) and miserite, respectively]; furthermore, the oblique (010) lattice plane of miserite has a centered rectangular cell with parameters very close to those of the centered (001) plane of seidite-(Ce) (Fig. 2). With

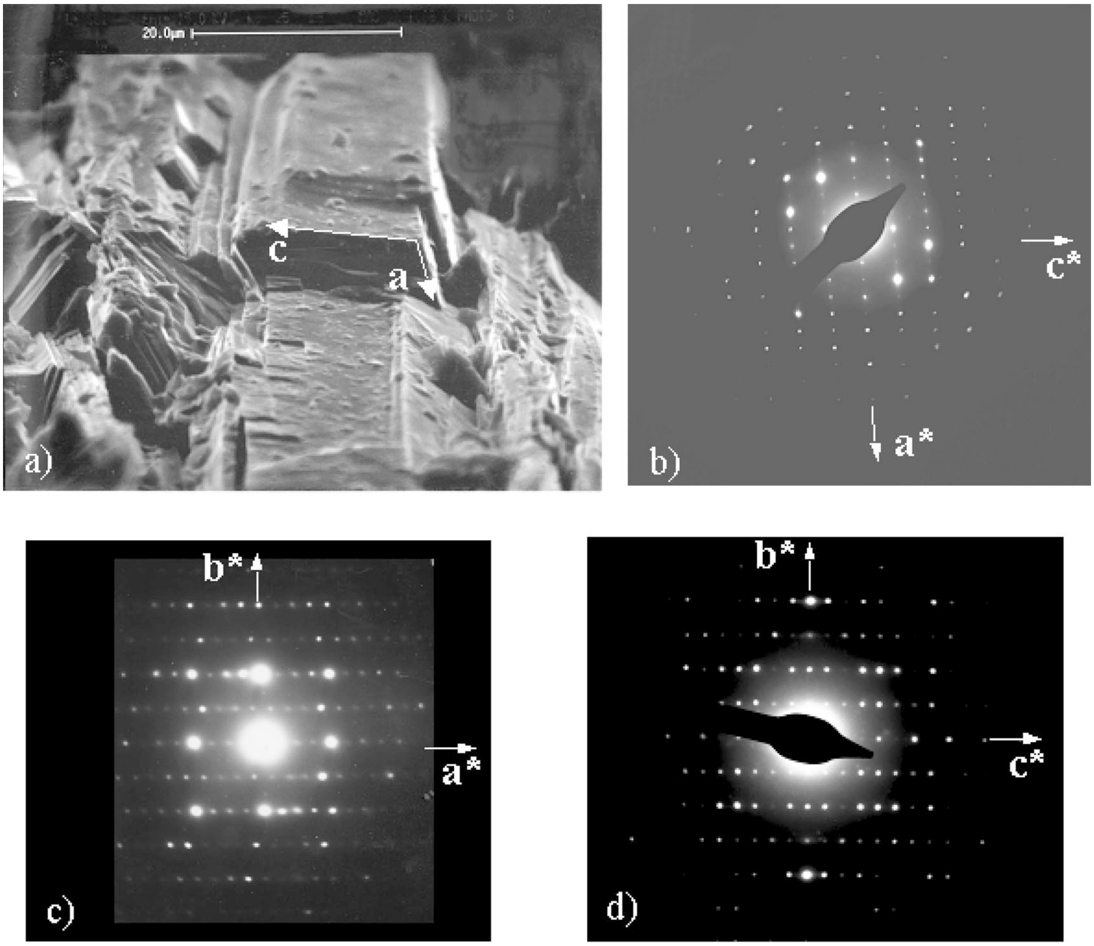

FIG. 1. SEM image (a) and SAED patterns (b, c, d) of seidite-(Ce).

respect to the chemical composition, we note that if the chemical formula of seidite-(Ce) is simplified as $Na_4SrCeTiSi_8O_{22}F\bullet5H_2O$, apparently it shares with miserite the silicate anion $(Si_8O_{22})^{12-}$ (but see below). On the other hand, the number of non-silicate cations is six in miserite and seven in seidite-(Ce), the chemically most important difference being the presence of the high-charge Ti^{4+} in the latter mineral.

Along [001], eight-membered channels (*i.e.*, channels delimited by rings consisting of eight corner-sharing tetrahedra) cross the structure of miserite (Fig. 3a). These channels are arranged in (010) layers and are formed by pairs of [001] wollastonite-type chains (*cf.* the value of $c_m = 7.377$ Å); locally, they show *mm* symmetry. A pair of such chains link to form a ribbon of alternating four- and six-membered rings in the (010) plane (Fig. 2a) and ten-membered rings in the (100) plane (not shown). Parallel layers of isolated Si_2O_7 groups alternate with layers of channels. Two observations gave the key to transforming the structure of miserite into a model fitting the experimental data of seidite-(Ce): (*i*) the Si_2O_7 groups can be rotated to join two adjacent channels along [010], thus obtaining (100) layers of connected channels; (*ii*) Ti can be positioned in octahedral coordination between two adjacent (100) layers, producing a three-dimensional framework based on SiO_4 tetrahedra and TiO_6 octahedra (Fig. 3b). In this order, the two operations shorten the periodicity along [010] and lengthen that along [100], modifying in an appropriate way the two periodicities which, in miserite, substantially differ from the corresponding periodicities in seidite-(Ce). The correspondence between directions is: $[010]_m = [001]_s$ and $[100]_m = [100]_s$. To complete the structure model, (REE, Sr) and Na atoms were placed in the channels together with H_2O molecules. In seidite-(Ce) (Fig. 2b), one member of a pair of wollastonite chains is offset by *b*/2 compared to the configuration in miserite (Fig. 2a).

The atom coordinates (Table 2) of the structure model were refined by the distance-least-square (DLS) method (Baerlocher *et al.* 1978) to $R = 0.047$. By assigning the highest weights to the expected distances within the (Si, Ti) framework, suitable sites for the extra-framework atoms were obtained. Selected bond-lengths are reported in Table 3.

Crystal chemistry and validation of the structure model

The poor quality of the X-ray powder data does not allow structure refinement by the Rietveld method. The best agreement between calculated and observed intensities of diffraction maxima (Table 1) was achieved by trial-and-error shift of coordinates and assignment of site contents in accord with results of the chemical analysis. The scattering curve for Na proved to be suitable for both Na sites. For the (REE, Sr) site, a scattering curve corresponding to atomic number 43 gave the best results. A deficiency in extra-framework cations is apparent from the empirical chemical formula given above, but could not be accounted for in the refinement. That fact and, in general, a lack of a reliable knowledge of the cation content in sites where isomorphous substitution occurs, do not allow a bond-valence calculation. However, inspection of the bond length (Table 2) and of the cation–anion bond connections (Table 4) allows us to draw the following conclusions on the crystal chemistry of seidite-(Ce).

- The extra-framework cations occupy two sites labeled Na1 and Na2 and a (REE, Sr) site. The latter has a distorted octahedral coordination with an average cation–anion distance of 2.40 Å; the Na1 and Na2 sites have a coordination of seven (average cation–anion distance of 2.83 and 2.52 Å, respectively).

TABLE 1. OBSERVED AND CALCULATED DATA FOR THE POWDER-DIFFRACTION PATTERN OF SEIDITE-(Ce)

I_{obs}	I_{calc}	d_{obs}	d_{calc}	*hkl*
100	100	12.32	12.26	200
20B	15	7.22	7.24	002
30B	25	6.93	6.94	110
3	1	6.46	6.47	$20\bar{2}$
20B	48	6.20	6.31 6.19	$11\bar{1}$* 111
3	1	5.42	5.42	310
10	13	5.11	5.16	$31\bar{1}$
2B	9	5.05	4.99 4.95	311 112
5B	1	4.47	4.45	$31\bar{2}$
15	23	4.12	4.09	600
10B	6	3.80	3.84 3.70	511 $31\bar{3}$*
6B	11	3.58	3.62	004
15	20	3.45	3.47 3.45	220 512
5	2	3.37	3.39 3.36	$22\bar{1}$ 221
20B	15	3.23	3.23 3.21	$40\bar{4}$ $51\bar{3}$
9	8	3.19	3.16 3.15	$22\bar{2}$ 710
24	10	3.11	3.13 3.11	$71\bar{1}$ 420
16	7	3.08	3.09 3.07	$31\bar{4}$ 800
12B	7	3.06	3.04 3.01	711 513
3	1	2.937	2.939	314
4B	6	2.900	2.904 2.894	$42\bar{2}$ $02\bar{3}$
2B	2	2.816	2.819 2.818	422 712
1	1	2.736	2.745	802
10	5	2.711	2.708 2.695	620 $\bar{1}15$
6B	13	2.656	2.616 2.613 2.609	514 $31\bar{5}$ 604*
10B	11	2.540	2.533	$22\bar{4}$
1	7	2.489	2.500 2.494	315 622
10	6	2.463	2.480	911
15	9	2.420	2.436	$51\bar{5}$
5	3	2.386	2.369	$13\bar{1}$
10	5	2.375	2.363	131
4B	10	2.337	2.338	820
1	2	2.299	2.310	$40\bar{6}$
10B	6	2.247	2.253 2.226	804 $62\bar{4}$
1B	4	2.110	2.115 2.111	624 $10.0.\bar{4}$
2	2	2.053	2.060 2.053	715 532
10	5	1.815	1.829 1.827 1.808	534 $33\bar{5}$ 733
10	4	1.797	1.807 1.796	040 517
3	4	1.780	1.783 1.780	$11.1.\bar{5}$ 931

Averaged values from DRON–3.0 diffractometer (Khomyakov *et al.* 1998) and Guinier–de Wolff camera data (Cu*K*α radiation in both cases). B: broad
* Not used in the cell refinement. Relative intensities *I*; *d* values in Å.

TABLE 2. ATOM COORDINATES IN THE STRUCTURE MODEL FOR SEIDITE-(Ce)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Si1	0.136	0.008	0.083	O5	0.161	0.807	0.116
Si2	0.126	0.068	0.870	O6	0.251	0.225	0.273
Si3	0.185	0.254	0.260	O7	0.159	0.134	0.171
Si4	0.183	0.699	0.212	O8	0.180	0.475	0.231
*Ti	0	0	0	O9	0.149	0.885	0.819
(REE, Sr)	0.195	0.750	0.960	O10	0.987	0.264	0.036
Na1	0.061	0.759	0.215	*O11	0	0.473	1/4
Na2	0.159	0.370	0.045	*O12	0	0.091	1/4
O1	0.071	0.966	0.072	O13	0.062	0.512	0.043
O2	0.150	0.048	0.977	O14	0.265	0.944	0.932
O3	0.157	0.204	0.800	*O15	1/4	1/4	0
O4	0.068	0.102	0.915	O16	0.127	0.514	0.909

* These atoms are in special position and have site multiplicity 4 instead of 8, that of the non-starred atoms, which are in general position.

TABLE 3. INTERATOMIC DISTANCES IN THE STRUCTURE MODEL FOR SEIDITE-(Ce)

Si1 -O1	1.62 Å	Si2 -O2	1.62 Å	Si3 -O6	1.63 Å
-O2	1.63	-O3	1.65	-O7	1.64
-O5	1.64	-O4	1.64	-O8	1.65
-O7	1.63	-O9	1.64	-O9	1.63
Average	1.63	Average	1.64	Average	1.64
Si4 -O3	1.63 Å	Ti -O1 × 2	1.98 Å		
-O5	1.65	-O4 × 2	2.28		
-O6	1.63	-O10 × 2	2.01		
-O8	1.65	Average	2.09		
Average	1.64				
(REE, Sr) -O2	2.44 Å	Na1 -O1	2.59 Å	Na2 -O2	2.53 Å
-O5	2.51	-O3	2.59	-O7	2.50
-O9	2.46	-O4	3.07	-O8	2.81
-O14	2.27	-O5	2.97	-O13	2.60
-O14	2.28	-O11	2.63	-O14	2.31
-O16	2.46	-O12	2.90	-O15	2.54
Average	2.40	-O13	3.07	-O16	2.32
		Average	2.83	Average	2.52

- O10, linked to Ti only, is an OH group.
- O11, O12, O13 and O15, bonded to Na only, account for five H_2O molecules per formula unit (see site multiplicity in Table 2).
- O14, bonded twice to (REE, Sr) and once to Na2, is O^{2-}.
- O16, bonded to both (REE, Sr) and Na2, corresponds to (F, OH).
- O1 to O9, bonded to Si, account for the 18 O atoms per formula unit belonging to the silicate anion. O1 and O4 belong also to the bridging TiO_6 octahedron.
- The silicate anion corresponds to $(Si_8O_{18})^{4-}$; in it, the SiO_4 tetrahedra show two types of connections: whereas Si1 and Si2 tetrahedra share three corners, the others (Si3 and Si4) share all four corners.

According to the structure model and the role assigned to the O atoms, the empirical formula of seidite-(Ce) given above can be written in the following way (REE = $Ce_{0.42}La_{0.30}Nd_{0.10}Pr_{0.04}Sm_{0.02}$): $[Na_{3.19}K_{0.27}Ba_{0.11}\square_{0.43}]_{\Sigma 4}[REE_{0.87}Sr_{0.53}Ca_{0.19}Th_{0.12}\square_{0.29}]_{\Sigma 2}\{(Ti_{0.86}Nb_{0.06}Mn_{0.05}Fe_{0.02})_{\Sigma 0.99}(OH)_2(Si_8O_{18})\}$ $[O_{2.22}(OH)_{0.81}F_{0.84}]_{\Sigma 3.87}{\bullet}5H_2O$. According to this formula, the average atomic numbers at the Na and (REE, Sr) sites are 11.6 and 42.6, respectively, in agreement with the scattering curves used for calculating the diffraction intensities. Barium and K are assigned to the Na sites, because exchange experiments (Khomyakov *et al.* 1998) clearly show that Na can almost fully be replaced by Ba and K. In the crystal-chemical formula, the mixed (Si, Ti) three-dimensional anion is shown between braces; the extra-brace cations, anions and H_2O groups occur in the channels and are not shown in the figures.

An ideal crystal-chemical formula of seidite-(Ce) can be written as $Na_4(Ce,Sr)_2\{Ti(OH)_2(Si_8O_{18})\}(O,OH,F)_4{\bullet}5H_2O$. End-members with maximum content of Ce and Sr have the formulae $Na_4Ce_2\{Ti(OH)_2(Si_8O_{18})\}O_4{\bullet}5H_2O$ and $Na_4Sr_2\{Ti(OH)_2(Si_8O_{18})\}O_2(OH,F)_2{\bullet}5H_2O$, which differ somewhat from the formula reported by Khomyakov *et al.* (1998).

Crystal-structure description

A continuous (100) layer of [010] eight-membered silicate channels with composition $(Si_8O_{18})^{4-}$ is connected along [100] by isolated TiO_6 octahedra. This feature (Fig. 3b) is the main difference between seidite-(Ce) and miserite, in which the eight-membered channels are not connected, and TiO_6 octahedra are absent. The (100) layer of eight-membered channels corresponds to the double silicate layer that occurs in the microporous mineral rhodesite (Hesse *et al.* 1992) and related compounds. The (010) front "windows" of this double layer are delimited by a xonotlite-like (Hejny & Armbruster 2001) chain, *i.e.*, a double wollastonite-like chain. Both upper and lower (100) walls of the silicate double layer consist of an apophyllite-type net formed by eight- and four-membered rings (not shown in the figures). The upper (100) wall is staggered by *b*/2 relative to the lower wall, the window rings are no longer aligned, and the [100] direction does not show pores. A second type of [010] eight-membered channels crosses the structure; in these channels, two polyhedra of the window ring are TiO_6 octahedra. A second set of channels of two different types extends along [001] (Fig. 2b). One type corresponds to ten-membered channels with two TiO_6 octahedra as ring members; the second type corresponds to five-membered channels consisting of tetrahedra only. Each type forms alternating (100) layers. The front windows of the pentagonal channels correspond to the (001) wall of the [010] eight-membered silicate channels. The wollastonite chains along both [010] and [001] directions determine the periodicity of both sets of channels. These two sets form two intersecting nets; whereas one net is generated by the ten- and eight-membered channels containing TiO_6 polyhedra, the second net consists of tetrahedra only.

Figure 2 shows the lateral walls of the octagonal silicate channels in miserite and seidite-(Ce). As mentioned above, along the direction of the channels, the relative position of the wollastonite chains is offset by a half period in the two minerals. Thus in seidite-(Ce), these walls contain five-membered rings only, whereas in miserite, they consist of alternating four- and six-membered rings.

The presence of (100) layers of [010] eight-membered silicate channels that are connected along [100] by isolated TiO_6 octahedra accounts for both the [010] elongation and the {100}-lamellar morphology of the fibers, as well as the perfect {100} cleavage of seidite-(Ce). Presumably, the observed {001} "cleavage" (Fig. 1a), which cuts Si–O bonds (Fig. 3b), is actually a separation surface between different fibers. The strength of the eight-membered silicate channels delimited by wollastonite chains confers valuable technological properties to miserite, which are used to prepare glass-ceramics with high-abrasion flexural strength (Pinckney *et al.*

TABLE 4. ANION–CATION BOND CONNECTIONS IN THE STRUCTURE MODEL FOR SEIDITE-(Ce)

	Si1	Si2	Si3	Si4	Ti	REE, Sr	Na1	Na2
O1	X				X		X	
O2	X	X				X		X
O3		X		X			X	
O4		X			X		X	
O5	X			X		X	X	
O6			X	X				
O7	X		X					X
O8			X	X				X
O9		X	X			X		
O10					X			
O11							XX	
O12							XX	
O13							X	X
O14						XX		X
O15								XX
O16						X		X

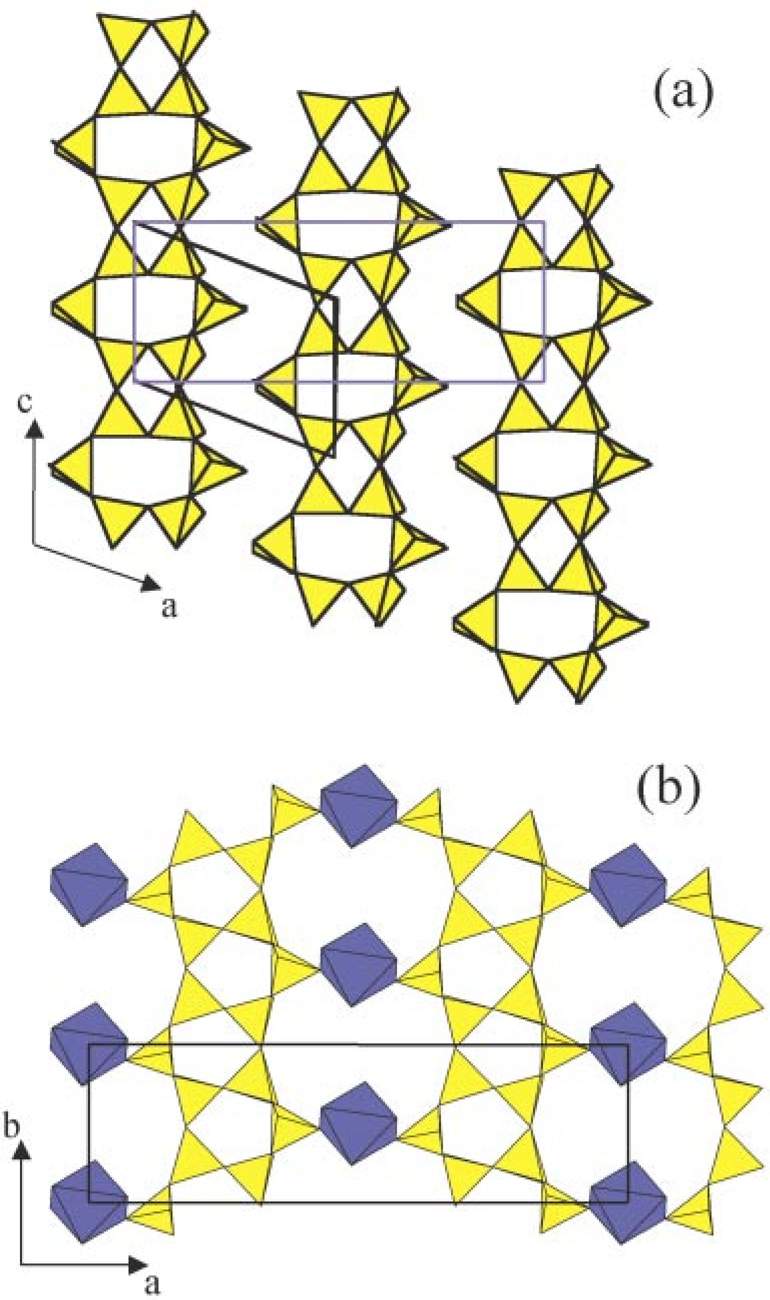

FIG. 2. Lateral view along [010] of the isolated silicate channels in miserite (a). In (b), the Si,Ti framework of seidite-(Ce) is shown along the [001] direction. In the (010) plane of miserite, besides the primitive cell (black), a centered rectangular cell (blue) is drawn. TiO_6 octahedra are blue. Cations other than Ti and Si are not shown.

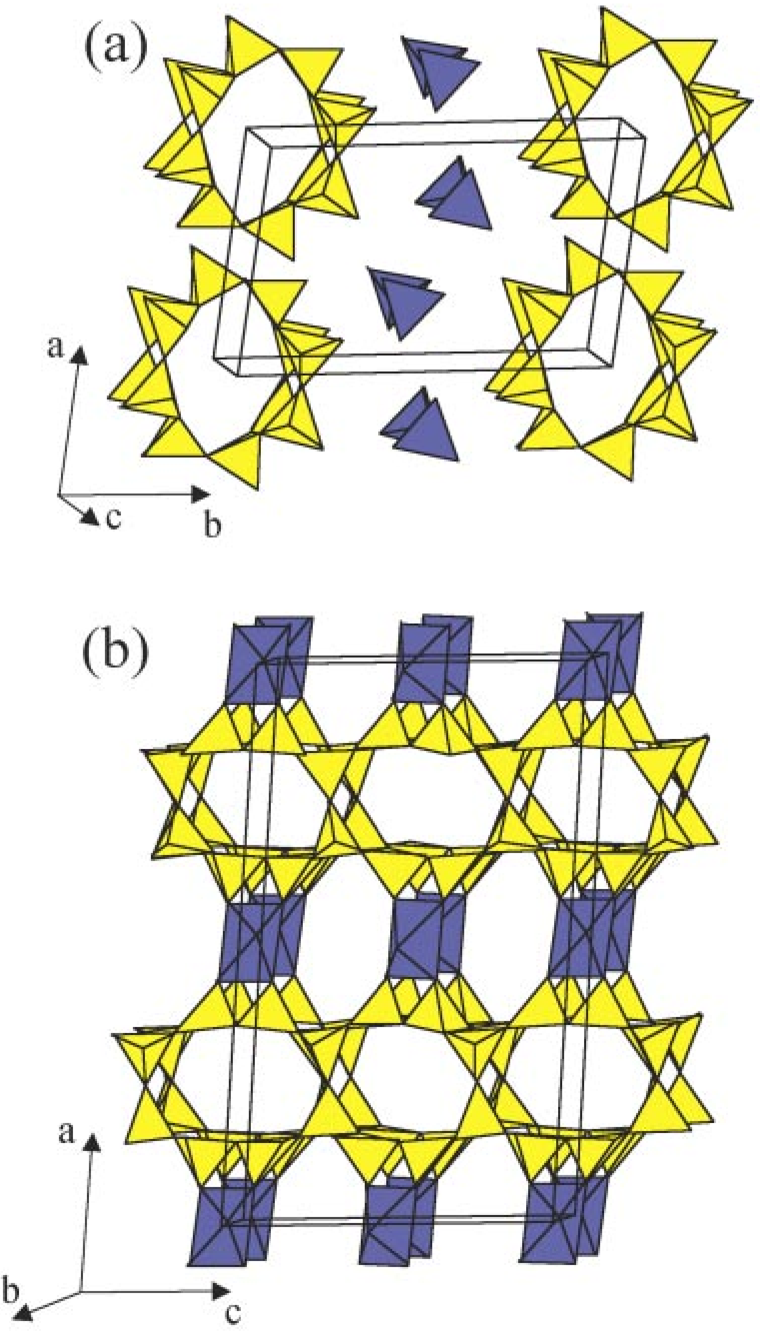

FIG. 3. View of the crystal structure of miserite about along [001] (a) and seidite-(Ce) approximately along [010] (b). The blue polyhedra represent Si_2O_7 groups in miserite and TiO_6 octahedra in seidite-(Ce). Cations other than Ti and Si are not shown.

1999). The occurrence of similar channels in seidite-(Ce), together with wollastonite chains along two orthogonal directions, makes the structure of this new titanosilicate a good candidate for technological applications similar to those of miserite.

Because of the presence of wollastonite chains, seidite-(Ce) can be included in the broad family of the pyroxenoids. Silicate chains consisting of five-membered rings are quite rare. Similar chains occur in nekoite, $Ca_5(Si_6O_{15})\bullet 7H_2O$ (Alberti & Galli 1980), okenite, $Ca_{10}(Si_6O_{16})(Si_6O_{15})_2\bullet 18H_2O$ (Merlino 1983), and $H_2NaNd(Si_6O_{15})\bullet nH_2O$ (Karpov *et al.* 1977). Pairs of five-membered rings occur in $Li_4Ca_4(Si_{10}O_{26})$ (Castrejòn *et al.* 1983). Alternating four- and five-membered rings occur in semenovite, $H_xNa_{0-2}(Ca,Na)_8(Fe,Mn,Zn,Ti)REE_2\,[(Si,Be)_{10}(O,F)_{24}]_2$ (Mazzi *et al.* 1979), and tuscanite, $(K,Sr,H_2O)_2(Ca,Na,\ Mg,Fe)_6[(Al_{3.66}Si_{6.34})O_{22}](SO_4)_{1.4}(CO_3)_{0.5}(O_4H_4)_{0.1}$ (Mellini *et al.* 1977).

Modular Aspects

The (100) layer of eight-membered channels occurring in seidite-(Ce) is well known as a double layer of corner-sharing SiO_4 tetrahedra, and occurs in rhodesite, $K_2Ca_4[Si_8O_{18}(OH)]_2\bullet 12H_2O$, macdonaldite, $BaCa_4[Si_8O_{18}(OH)]_2\bullet 10H_2O$, delhayelite, $K_7Na_3Ca_5[Si_7AlO_{19}]_2F_4Cl_2$, hydrodelayelite, $K_2Ca_4[Si_7AlO_{17}(OH)_2]_2\bullet 6H_2O$, and monteregianite, $K_2Na_4Y_2[Si_8O_{19}]_2\bullet 10H_2O$ (Hesse *et al.* 1992). Because of their microporous properties, $K_2Na_4Ce_2[Si_8O_{19}]_2\bullet 10H_2O$ (Rocha *et al.* 2000) [and its Eu and Tb equivalents (Ananias *et al.* 2001)] and the synthetic analogues of montregianite and rhodesite (Rocha & Anderson 2000), have been recently prepared. In all these compounds, the silicate double layer alternates with a layer of cations: chains of edge-sharing CaO_6 octahedra in rhodesite and macdonaldite, mixed $(Y,Na)O_6$ octahedra in monteregianite (similar layers occur in the two compounds studied by Ananias *et al.* 2001), a continuous layer of octahedra in delhayelite, and isolated TiO_6 octahedra in seidite-(Ce).

Ti^{4+} is the highest-charge cation occurring in the bridging layers of octahedra in the rhodesite group. The type of bridging cation influences the configuration and exact composition of the double silicate layer. Most of the mentioned compounds have a T:O ratio of 1:19 (T = Si, Al), corresponding to a ratio of 3:1 between the tetrahedra that share three and four corners, respectively. However, in seidite-(Ce), the ratio between the two types of tetrahedra is 1:1, and consequently T:O equals 1:18; the different connectivity of the tetrahedra is related to the shifts between the two layers forming the double silicate layer. Depending on this shift, the lateral view of the double layer shows either five- (Fig. 2b) or eight-membered rings [Fig. 1 for rhodesite in Hesse *et al.* (1992)]; in both cases, the view is along [001]. For comparison, in miserite, which contains ribbons and not a double layer, the lateral view of the channels (Fig. 2a) shows an alternation of four- and six-membered rings. In all compounds here discussed, the surface of the double layer corresponds to an apophyllite-like net consisting of four- and eight-membered rings (not shown in figures).

According to the categorization of "polysomatic" series given by Mackovicky (1997) (*cf.* Ferraris *et al.* 2004), the rhodesite group represents a mero-plesiotype series because, apart from slight modifications (plesiotype aspect), the same double silicate layer occurs in all members, alternating with a variable layer module (merotype aspect). Presumably, the unknown mineral UK61 reported from Mont Saint-Hilaire by Chao *et al.* (1990) is closer to seidite-(Ce) rather than to zorite.

Microporosity Property

The first experimental evidence of microporous features in seidite-(Ce) was the high value of the measured density, 3.21 g/cm^3 as determined by Clerici liquid, an aqueous solution of $CH_2(COO)_2Tl_2\bullet HCOOTl$, *versus* the calculated value of 2.75 g/cm^3. This high measured density was due to absorption of Tl, as indicated by electron-microprobe analysis of grains of the mineral kept in aqueous solutions of Tl^+, K^+, Rb^+, Cs^+ and Ba^{2+} at room temperature for periods of 6 to 8 weeks; Na was replaced by the indicated cations (Khomyakov *et al.* 1998).

The presence of channels (pores) in the structure and weak bonding of Na to the framework, particularly Na1 (Table 3), clearly explains the exchange properties of seidite-(Ce). Presumably, all the extra-framework ions and H_2O groups can be removed from the structure through the system of pores. The minimum and maximum sections of the two eight-membered channels are about 3 and 5 Å, respectively; the analogous sections are about 1 and 6.5 Å in the ten-membered channel, the bottleneck corresponding to two facing TiO_6 octahedra (Fig. 2b). Calculation of the free sections was done by subtracting 2.7 Å (*i.e.*, twice the radius of O^{2-}) from the appropriate O...O distances in the channel cross-sections (McCusker *et al.* 2003).

Conclusions

As for bornemanite (Ferraris *et al.* 2001), kalifersite (Ferraris *et al.* 1998), nafertisite (Ferraris *et al.* 1996), and tungusite (Ferraris *et al.* 1995), the concepts of modular mineralogy (Merlino 1997, Ferraris *et al.* 2004) have been applied to obtain a model of the structure of seidite-(Ce) by comparing chemical composition, cell parameters and diffraction features of the unknown structure with the corresponding quantities of the fully characterized mineral miserite (Scott 1976). Qualitative application of the concepts of modular crystallography has been very effective in modeling the structure of the new titanosilicate seidite-(Ce). *A posteriori*, a mero-plesiotype modular connection with the rhodesite group has been established.

As in other titanosilicates, in particular heterophyllosilicates (Ferraris *et al.* 1996), a comparable crystal-chemical role of SiO_4 and TiO_6 polyhedra is evident in the structure of seidite-(Ce). This role is based both on dimensions (O...O distances) and bond strength. In fact, a (TiO_6) octahedron bears a formal negative charge, 8–, 4– or 2–, depending on whether it is isolated, shares four or six corners. Thus, a TiO_6 octahedron can supply bonds comparable to those supplied by $2(SiO_4)^{4-}$, $(SiO_4)^{4-}$ or an $(SiO_3)^{2-}$ group in a pyroxene-like chain. The introduction of TiO_6 octahedra in a silicate structure can lead to a framework structure, as in the formal transition miserite → seidite-(Ce) or in some heterophyllosilicates, *e.g.*, astrophyllite (Woodrow 1967). In the latter case, insertion of TiO_6 octahedra in a *TOT* layer proper of the layer silicates results in a framework structure, where *HOH* layers (Ferraris *et al.* 1996; *H* stands for "hetero" to indicate the substitution of silicate tetrahedra by TiO_6 octahedra in a *TOT* layer) are bridged by the octahedra. In heterophyllosilicates, the possibility of establishing tetragonal pyramidal coordination, instead of the usual octahedral coordination, adds further flexibility to a TiO_n polyhedron.

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