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FROM STRUCTURE TOPOLOGY TO CHEMICAL COMPOSITION. V. TITANIUM SILICATES: THE CRYSTAL CHEMISTRY OF NACARENIOBSITE-(Ce)

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Abstract

The crystal structure of nacareniobsite-(Ce), ideally $Na_3\,Ca_3\,REE\,Nb\,(Si_2O_7)_2\,OF_3$, *a* 7.468(2), *b* 5.689(1), *c* 18.891(4) Å, β 101.37(3)°, *V* 786.9(1) Å^3, space group $P2_1/c$, $Z = 2$, $D_{calc} = 3.539$ g.cm^{-3}, from Kvanefjeld in the Ilímaussaq alkaline complex, South Greenland, has been solved by direct methods and refined to $R_1 = 6.5\%$ on the basis of 1866 unique reflections $|F_o \geq 4\sigma F|$ collected on a Bruker *P*4 diffractometer with a CCD 4K Smart detector and Mo*K*α radiation from a crystal consisting of an epitactic intergrowth of nacareniobsite-(Ce) domains. An electron-microprobe analysis gave (wt.%): SiO_2 28.30, Nb_2O_5 12.01, TiO_2 2.24, Ta_2O_5 0.33, Ce_2O_3 10.55, La_2O_3 4.42, Nd_2O_3 4.34, Pr_2O_3 1.12, Sm_2O_3 0.64, Gd_2O_3 0.47, Y_2O_3 0.57, SrO 0.45, CaO 19.79 Na_2O 10.07, F 6.15, total 98.86. The empirical formula is $Na_{2.77}\,(Ca_{3.01}\,Sr_{0.04})_{\Sigma 3.05}\,(Ce_{0.55}\,La_{0.23}\,Nd_{0.22}\,Pr_{0.06}\,Sm_{0.03}\,Gd_{0.02}\,Y_{0.04})_{\Sigma 1.15}\,(Nb_{0.77}Ti^{4+}{}_{0.24}Ta_{0.01})_{\Sigma 1.02}\,(Si_2O_7)_2\,(O_{1.24}\,F_{0.76})_{\Sigma 2.00}\,F_2$, Z = 2, calculated on a basis of 18 (O + F) *apfu*. Nacareniobsite-(Ce) belongs to a group of titanium disilicate minerals containing the TS block, which consists of HOH sheets (H: heteropolyhedral sheet, O: trioctahedral sheet). In the O sheet, there are two octahedrally coordinated sites: the $M^O(1)$ site is primarily occupied by Nb with minor Ti^{4+} and trace Ta, giving ideally 1 Nb *apfu*, $\langle M^O(1)–O,F \rangle = 2.01$ Å , and the $M^O(3)$ site is occupied by Na, giving 2 Na *apfu*, $\langle M^O(3)–O,F \rangle = 2.41$ Å. The [8]-coordinated $M^O(2)$ site is occupied by Na with subordinate Ca, $\langle M^O(2)–O,F \rangle = 2.50$ Å. The M^O polyhedra each share six common edges to form a close-packed O sheet. The H sheet consists of (Si_2O_7) groups and M^H and A^P polyhedra. In the H sheet, there are two tetrahedrally coordinated sites occupied by Si with a grand <Si–O> distance of 1.625 Å. There are two [7]-coordinated sites, M^H and A^P, occupied by Ca and REE, giving in total $(Ca_3\,REE_{1.0})$, $\langle M^H–O,F \rangle = 2.46$ and $\langle A^P–O,F \rangle = 2.49$ Å, respectively. An H sheet is connected to an O sheet through vertices of (SiO_4) tetrahedra and M^H and A^P polyhedra. Within one TS block in nacareniobsite-(Ce), two (Si_2O_7) groups, one from each H sheet, link to the $M^O(2)$ polyhedron of the O sheet, and two H sheets are approximately related by a pseudo-mirror plane, m_z. In the structure of nacareniobsite-(Ce), TS blocks repeat along [001] and are connected through common vertices and edges of (SiO_4) tetrahedra and M^H and A^P polyhedra. Nacareniobsite-(Ce) has the same type of linkage of H and O sheets in the TS block as the Ti disilicate minerals of Group I: götzenite, hainite, seidozerite, grenmarite, mosandrite, rinkite, kochite and rosenbuschite. In the minerals of Group I, (Ti + Nb) equals 1 *apfu* and occurs in the O sheet of the TS block. Nacareniobsite-(Ce) is the only disilicate mineral with the TS block in which a pentavalent cation, Nb^{5+}, is dominant at one site in the O sheet. The topology of the crystal structure of nacareniobsite-(Ce) is identical to that of mosandrite [ideally $Na_2\,Ca_4\,REE\,Ti\,(Si_2O_7)_2\,O_2\,F_3$]. Nacareniobsite-(Ce) and mosandrite differ in the cations in the O sheet of the TS block: $\{^{[8]}Na\ ^{[6]}Na_2\ ^{[6]}Nb^{5+}\}$ in nacareniobsite-(Ce) and $\{^{[8]}Na\ ^{[6]}(NaCa)\ ^{[6]}Ti^{4+}\}$ in mosandrite. In nacareniobsite-(Ce), dominance of Nb^{5+} at the $M^O(1)$ site results in partial substitution of Na for Ca at the [6]-coordinated $M^O(3)$ site in the O sheet.

Keywords: nacareniobsite-(Ce), crystal structure, mosandrite, rinkite, Ilímaussaq alkaline complex, South Greenland.

Sommaire

Nous avons résolu la structure cristalline de la nacareniobsite-(Ce), de formule idéale $Na_3\,Ca_3\,REE\,Nb\,(Si_2O_7)_2\,OF_3$, *a* 7.468(2), *b* 5.689(1), *c* 18.891(4) Å, β 101.37(3)°, *V* 786.9(1) Å^3, groupe spatial $P2_1/c$, $Z = 2$, $D_{calc} = 3.539$ g.cm^{-3}, provenant de Kvanefjeld, complexe alcalin de Ilímaussaq, dans le sud du Groënland, par méthodes directes, et nous l'avons affiné jusqu'à un résidu R_1 de 6.5% en utilisant 1866 réflexions uniques $|F_o \geq 4\sigma F|$ prélevées avec un diffractomètre Bruker *P*4 muni d'un détecteur CCD 4K Smart et avec rayonnement Mo*K*α; le cristal consiste d'une intercroissance épitactique de domaines de nacareniobsite-(Ce). Une analyse avec une microsonde électronique a donné: SiO_2 28.30, Nb_2O_5 12.01, TiO_2 2.24, Ta_2O_5 0.33, Ce_2O_3 10.55, La_2O_3 4.42, Nd_2O_3 4.34, Pr_2O_3 1.12, Sm_2O_3 0.64, Gd_2O_3 0.47, Y_2O_3 0.57, SrO 0.45, CaO 19.79 Na_2O 10.07, F 6.15,

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pour un total de 98.86% (poids). La formule empirique est $Na_{2.77}(Ca_{3.01}Sr_{0.04})_{\Sigma 3.05}(Ce_{0.55}La_{0.23}Nd_{0.22}Pr_{0.06}Sm_{0.03}Gd_{0.02}Y_{0.04})_{\Sigma 1.15}(Nb_{0.77}Ti^{4+}_{0.24}Ta_{0.01})_{\Sigma 1.02}(Si_2O_7)_2(O_{1.24}F_{0.76})_{\Sigma 2.00}F_2$, $Z = 2$, calculée sur une base de 18 (O + F) *apfu*. La nacareniobsite-(Ce) fait partie d'une groupe de disilicates de titanium, minéraux qui contiennent le bloc TS, fait de couches HOH (H: couche hétéropolyédrique, O: couche trioctaédrique). Dans la couche O, il y a deux sites à coordinence octaédrique: le site $M^O(1)$ est surtout occupé par le Nb avec un peu de Ti^{4+} et des traces de Ta, pour donner idéalement 1 Nb *apfu*, $\langle M^O(1)\text{–}O,F\rangle = 2.01$ Å, tandis que le site $M^O(3)$ est occupé par Na, pour donner 2 Na *apfu*, $\langle M^O(3)\text{–}O,F\rangle = 2.41$ Å. Le site $M^O(2)$, à coordinence [8], est occupé par Na avec Ca subordonné, $\langle M^O(2)\text{–}O,F\rangle = 2.50$ Å. Les polyèdres M^O partagent chacun six arêtes communes pour former un feuillet O d'octaèdres à empilement compact. Le feuillet H est fait de groupes (Si_2O_7) et de polyèdres M^H et A^P. Dans ce feuillet, il y a deux sites à coordinence tétraédrique occupés par Si, avec une distance globale $\langle Si\text{–}O\rangle$ de 1.625 Å. Il y a aussi deux sites à coordinence [7], M^H et A^P, occupés par Ca et les terres rares (TR), pour donner en tout $(Ca_3TR_{1.0})$, $\langle M^H\text{–}O,F\rangle = 2.46$ et $\langle A^P\text{–}O,F\rangle = 2.49$ Å, respectivement. Un feuillet H est lié à un feuillet O par partage de sommets des tétraèdres (SiO_4) et des polyèdres M^H et A^P. A l'intérieur de chaque bloc TS de la nacareniobsite-(Ce), deux groupes (Si_2O_7), un contribué par chaque feuillet H, sont liés au polyèdre $M^O(2)$ du feuillet O, et deux feuillets H sont approximativement alignés pour obéir à une relation et un plan pseudo-miroir, m_z. Dans la structure de la nacareniobsite-(Ce), les blocs TS se répètent le long de [001] et sont connectés par plusieurs sommets et arêtes partagés impliquant les tétraèdres (SiO_4) et les polyèdres M^H et A^P. La nacareniobsite-(Ce) possède la même sorte de liaisons entre les couches H et O dans le bloc TS que les minéraux disilicatés de Ti du groupe I: götzenite, hainite, seidozerite, grenmarite, mosandrite, rinkite, kochite et rosenbuschite. Pour ces minéraux, (Ti + Nb) est égal à 1 *apfu* et situé dans le feuillet O du bloc TS. La nacareniobsite-(Ce) est le seul minéral ayant un cation pentavalent, Nb^{5+}, dans un site du feuillet O dans le bloc TS. La topologie de la structure de la nacareniobsite-(Ce) est identique à celle de la mosandrite [idéalement $Na_2Ca_4REE\,Ti(Si_2O_7)_2O_2F_3$]. La nacareniobsite-(Ce) et la mosandrite diffèrent par les cations dans le feuillet O du bloc TS: $\{^{[8]}Na\,^{[6]}Na_2\,^{[6]}Nb^{5+}\}$ dans la nacareniobsite-(Ce), $\{^{[8]}Na\,^{[6]}(NaCa)\,^{[6]}Ti^{4+}\}$ dans la mosandrite. Dans la nacareniobsite-(Ce), la dominance de Nb^{5+} au site $M^O(1)$ résulte de la substitution partielle de Na au Ca dans le site $M^O(3)$, à coordinence [6], dans le feuillet O.

(Traduit par la Rédaction)

Mots-clés: nacareniobsite-(Ce), structure cristalline, mosandrite, rinkite, complexe alcalin d'Ilímaussaq, Groënland du sud.

INTRODUCTION

Nacareniobsite-(Ce), ideally $Na_3Ca_3REE\,Nb(Si_2O_7)_2OF_3$, was described from the Ilímaussaq alkaline complex in South Greenland (Petersen *et al.* 1989). For nacareniobsite-(Ce), Petersen *et al.* (1989) reported a monoclinic unit-cell, *a* 18.901(5), *b* 5.683(3), *c* 7.462(2) Å, β 101.29(4)°, V 786.9(1) Å^3, $Z = 2$, $D_{calc} = 3.43$ g.cm^{-3}, possible space-group $P2_1/a$. They related nacareniobsite-(Ce) to rinkite, ideally $Na_2Ca_4REE\,Ti(Si_2O_7)_2OF_3$, by the substitution $Nb^{5+} + Na^+ \rightarrow Ti^{4+} + Ca^{2+}$. Originally, the crystal structure of rinkite was determined in space group $P1$ (Kheirov *et al.* 1963). The latest refinements of the structure of rinkite were done by Galli & Alberti (1971): *a* 7.437(2), *b* 5.664(2), *c* 18.843(3) Å, β 101.38(2)°, *V* 778.11 Å^3, space group $P2_1/c$, $Z = 2$, $D_{calc.} = 3.45$ g cm^{-3}, with an approximate formula $(Ti,Nb,Al,Zr)(Na,Ca)_3(Ca,Ce)_4(Si_2O_7)_2(O,F)_4$, and by Rastsvetaeva *et al.* (1991): *a* 5.679(3), *b* 7.412(3), *c* 18.835(6) Å, α 101.26(3)°, *V* 777.6 Å^3, space group $P2_1$, $Z = 2$, $D_{calc.} = 3.36$ g cm^{-3}, with the structural formula: $\{TiF(O,F)[Si_2O_7]_2\}\{Na(Na,Ca)_2F(O,F)\}\{(Ca,TR)_4\}$. Petersen *et al.* (1989) also compared nacareniobsite-(Ce) to mosandrite, which had been described by Slepnev (1957) as a Na-leached hydrated product of alteration of "rinkite-series minerals" on the basis of chemical analyses of mosandrite from Langesund. Moreover, Petersen *et al.* (1989) gave a back-scattered electron (BSE) image of mosandrite from Langesund showing "an intergrowth of minerals with slightly different mean atomic number", and reported chemical compositions of these phases in which CaO and Na_2O contents are much lower (CaO 17.82–5.07, Na_2O 4.40–0.69 wt%) than those expected in minerals of this structure type (CaO 28.48–19.92, Na_2O 10.75–9.38 wt%). The crystal structure of mosandrite, *a* 7.4184(8), *b* 5.6789(6), *c* 18.873(2) Å, β 101.410(2)°, *V* 779.35(5) Å^3, space group $P2_1/c$, from the type locality of Låven (Skådön), Langesundsfjorden, Larvik, Vestfold, Norway, was reported by Sokolova & Cámara (2008a); the crystal analyzed by them showed no apparent leaching of Ca or Na (CaO 27.06, Na_2O 7.59), and the idealized composition is $Na_2Ca_4REE\,Ti(Si_2O_7)_2OF_3$. Sokolova & Cámara (2008a) showed that Galli & Alberti (1971) and Rastsvetaeva *et al.* (1991) used different unit cells to describe the structure of rinkite (in addition to the non-conventional orientation of the monoclinic 2-fold axis parallel to **a** with $\alpha \neq 90$ and $\beta = 90°$), cells that are related by the transformation matrix $[0\ 1\ 0\ /\ \bar{1}\ 0\ 0\ /\ 1\ 0\ 1]$. Furthermore, Sokolova & Cámara (2008a) suggested that an epitactic intergrowth of mosandrite domains is possible, and that this mechanism may result in apparent loss of glide-plane symmetry in the mosandrite and related structures. However, the structure of nacareniobsite-(Ce) has not yet been reported. Here we provide results for crystals from the type locality of Ilimaussaq.

Background Information

Sokolova (2006) considered the structural hierarchy and stereochemistry for twenty-four titanium disilicate minerals containing the TS block. The central part of the block is a close-packed trioctahedral O sheet (Fig. 1a). There are two adjacent H sheets containing different polyhedra, including (Si_2O_7) groups (Fig. 1b). The M^H cations invariably occur in the plane of the H sheet, whereas A^P cations may occur in the H sheet or shifted from the plane of the H sheet toward the intermediate space between adjacent TS blocks. Two H sheets and an O sheet constitute the TS block (Fig. 1c). The TS block is characterized by a planar cell based on translation vectors, $\mathbf{t_1}$ and $\mathbf{t_2}$, with $t_1 \approx 5.5$ and $t_2 \approx 7$ Å and $\mathbf{t_1} \wedge \mathbf{t_2}$ close to 90° (shown in red in Figs. 1a, b). Sokolova (2006) wrote the following general formula for the TS block within the planar cell: $A^P_2\ B^P_2\ \mathbf{M^H_2\ M^O_4\ (Si_2O_7)_2\ X_{4+n}}$, where M^O represents cations of the O sheet, M^H represents cations of the H sheet, A^P, B^P are cations at the peripheral (*P*) sites, and $X_{4+n} = X^O_4 + X^P_{M2} + X^P_{A2}$; X^O_4 anions are common vertices of M^O octahedra and two M^H and two A^P polyhedra; they are the X^O_M and X^O_A anions (Figs. 1a, b), anions X^P_M (Fig. 1c) and X^P_A belong to the M^H and A^P polyhedra on the outside of the TS block [in the intermediate space (**I**) between two TS blocks]; n is the number of X^P anions: n = 0, 2, 4 depending on the coordination of the M^H site and the position of the A^P polyhedron relative to the adjacent TS block. The core part of the TS block, $\mathbf{M^H_2\ M^O_4\ (Si_2O_7)_2\ X_4}$, is shown in bold; the stoichiometry of this part of the TS block is invariant.

Sokolova (2006) established the relation between structure topology and chemical composition for these minerals and divided them into four groups, characterized by a different topology and stereochemistry of the TS block. Each group of structures has a different linkage of H and O sheets in the TS block and a different arrangement of Ti (= Ti + Nb) polyhedra. In Groups I, II III and IV, Ti equals 1, 2, 3 and 4 *apfu*, respectively. Sokolova (2006) listed seven minerals in Group I: götzenite, hainite, seidozerite, grenmarite, rinkite, kochite and rosenbuschite (Table 1). In Group I, Ti = 1 *apfu*, Ti (or Zr + Ti in grenmarite) occurs in the O sheet: 1 M^O = Ti (Fig. 2a), 3 M^O = Na, Ca and rarely Mn^{2+}; $^{[6],[7]}M^H = Zr^{4+}$,Ca + REE, Ca, Mn^{2+}; A^P = Na, Ca, Ca + REE. The (Si_2O_7) groups link to Na octahedra of the O sheet, and Na becomes [8]-coordinated (Fig. 2b). In Group I, the monovalent anions at the X^O_A and X^O_M sites are invariably F^-. Sokolova (2006) wrote the general formula for minerals of Group I as $A^P_2\ M^H_2\ M^O_4\ (Si_2O_7)_2\ X^O_4$ (see Table 1). As the crystal structure of nacareniobsite-(Ce) was not known, Sokolova (2006) did not include it in her scheme. However, Petersen *et al.* (1989) pointed out that nacareniobsite-(Ce) is closely related to rinkite. In nacareniobsite-(Ce), Nb is approximately equal to 1 *apfu*, indicating that it belongs to Group I and that Nb must occupy one unique site in the O sheet. Hence, nacareniobsite-(Ce) is the only disilicate mineral with the TS block in which a pentavalent cation (Nb^{5+}) is dominant at a distinct site in the O sheet. Following Sokolova (2006), further work on the Ti disilicate minerals includes revision of the crystal structure and chemical formula of delindeite (Sokolova & Cámara 2007) and bornemanite (Cámara & Sokolova 2007), the crystal chemistry of mosandrite (Sokolova & Cámara 2008a) and barytolamprophyllite (Sokolova & Cámara 2008b) and the present work on nacareniobsite-(Ce).

Experimental

The sample of nacareniobsite-(Ce) used in this work is from Kvanefjeld in the Ilímaussaq alkaline complex, South Greenland, and was obtained from Forrest Cureton.

TABLE 1. STRUCTURAL FORMULAE* AND UNIT-CELL PARAMETERS FOR GROUP-I MINERALS WITH THE TS BLOCK

Mineral	Structural formula			*a* (Å)	*b* (Å)	*c* (Å)	α(°)	β(°)	γ(°)	Sp. gr.	*Z*	Ref.
nacareniobsite-(Ce)	(Ca_3REE)	$\mathbf{Na_3Nb}$	$(Si_2O_7)_2OF_3$	7.468	5.688	18.892		101.40		$P2_1/c$	2	(1)
mosandrite	(Ca_3REE)	**Na(NaCa)Ti**	$(Si_2O_7)_2OF_3$	7.4184	5.6789	18.873		101.410		$P2_1/c$		(2)
rinkite	(Ca_3REE)	**Na(NaCa)Ti**	$(Si_2O_7)_2OF_3$	7.437	5.664	18.843		101.38		$P2_1/c$	2	(3)
rinkite	(Ca_3REE)	**Na(NaCa)Ti**	$(Si_2O_7)_2OF_3$	5.679	7.412	18.835	101.26			$P2_1$	2	(4)
götzenite	Ca_2Ca_2	$\mathbf{NaCa_2Ti}$	$(Si_2O_7)_2OF_3$	9.6192	5.7249	7.3307	89.981	101.132	100.639	$P\bar{1}$	1	(5)
hainite	Ca_3(Y,REE)	**Na(NaCa)Ti**	$(Si_2O_7)_2OF_3$	9.6079	5.7135	7.3198	89.916	101.077	100.828	$P\bar{1}$	1	(6)
seidozerite	Na_2Zr_2	$\mathbf{Na_2\,MnTi}$	$(Si_2O_7)_2O_2F_2$	5.5558	7.0752	18.406		102.713		$P2/c$	1	(7)
grenmarite	$Na_2\,Zr_2$	$\mathbf{Na_2MnZr}$	$(Si_2O_7)_2O_2\,F_2$	5.608	7.139	18.575		102.60		$P2/c$	1	(8)
kochite	Ca_2MnZr	$\mathbf{Na_3Ti}$	$(Si_2O_7)_2OF_3$	10.032	11.333	7.202	90.192	100.334	111.551	$P\bar{1}$	1	(9)
rosenbuschite	$Ca_4Ca_2Zr_2$	$\mathbf{Na_2Na_4TiZr}$	$(Si_2O_7)_4O_2F_6$	10.137	11.398	7.2717	90.216	100.308	111.868	$P\bar{1}$	1	(10)

* The structural formulae are written in the form of $A^P_2\ M^H_2\ M^O_4\ (Si_2O_7)_2\ X^O_4$ in accord with Sokolova (2006), M^O_4 (= cations of the O sheet) shown in bold. References (the latest reference on the structure is the first entry in the numbered list of references): (1) this work, (2) Sokolova & Cámara (2008a), (3) Galli & Alberti (1971), (4) Rastsvetaeva *et al.* (1991), Simonov & Belov (1968), (5) Christiansen *et al.* (2003a), Cannillo *et al.* (1972), (6) Christiansen *et al.* (2003a), Rastsvetaeva *et al.* (1995), (7) Christiansen *et al.* (2003a), Simonov & Belov (1960), Skszat & Simonov (1966), Pushcharovskii *et al.* (2002), (8) Bellezza *et al.* (2004), (9) Christiansen *et al.* (2003b), (10) Christiansen *et al.* (2003a), Shibaeva *et al.* (1964).

Electron-microprobe analysis

A single crystal of nacareniobsite-(Ce) previously used for structure solution was analyzed with a Cameca SX–100 electron-microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, a beam size of 20 μm and count times on peak and background of 2 and 10 s, respectively. The following standards were used for *K* or *L* X-ray lines: topaz: F, jadeite: Na, diopside: Si, Ca, $BaNaNbO_4$: Nb, $CePO_{4:}$: Ce, $LaPO_4$: La, $NdPO_4$: Nd, $PrPO_4$: Pr, $SmPO_4$: Sm, $GdPO_4$: Gd, titanite: Ti, $SrTiO_3$: Sr, YPO_4: Y, $MnNb_2Ta_2O_{11}$: Ta. Data were reduced using the $\phi(\rho Z)$ procedure of Pouchou & Pichoir (1985). The chemical composition of nacareniobsite-(Ce) is given in Table 2 and is the mean of 10 determinations. The empirical formula (Table 2) was calculated on the basis of 18 anions (O + F): $Na_{2.77}\,(Ca_{3.01}\,Sr_{0.04})_{\Sigma 3.05}\,(Ce_{0.55}\,La_{0.23}\,Nd_{0.22}\,Pr_{0.06}\,Sm_{0.03}\,Gd_{0.02}\,Y_{0.04})_{\Sigma 1.15}\,(Nb_{0.77}Ti^{4+}_{0.24}Ta_{0.01})_{\Sigma 1.02}\,(Si_2O_7)_2\,(O_{1.24}\,F_{0.76})_{\Sigma 2.00}\,F_2$,

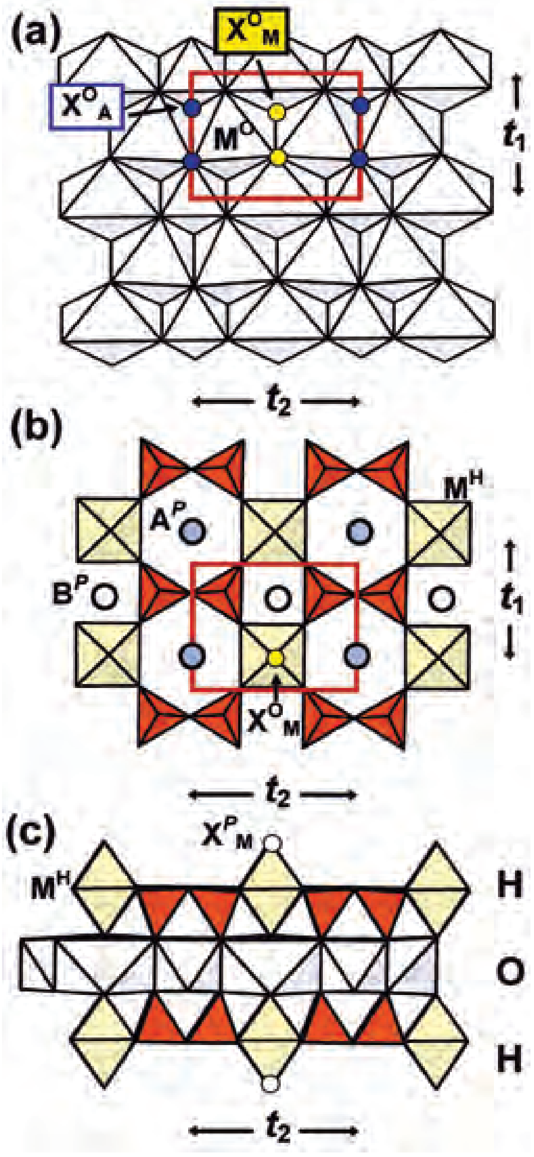

FIG. 1. Titanium silicate (TS) block; general view of (a) the sheet of octahedra (O sheet), and (b) the heteropolyhedral sheet (H sheet), linkage of O and H sheets viewed down the t_1 translation (c). M^O and M^H octahedra are white and yellow, A^P and B^P atoms are shown as blue and white circles, (SiO_4) tetrahedra are orange, X^O_M, X^O_A and X^P_M anions are shown as small yellow, blue and white circles, and the planar cell with translations $t_1 \approx 5.5$ Å and $t_2 \approx 7$ Å is shown in red.

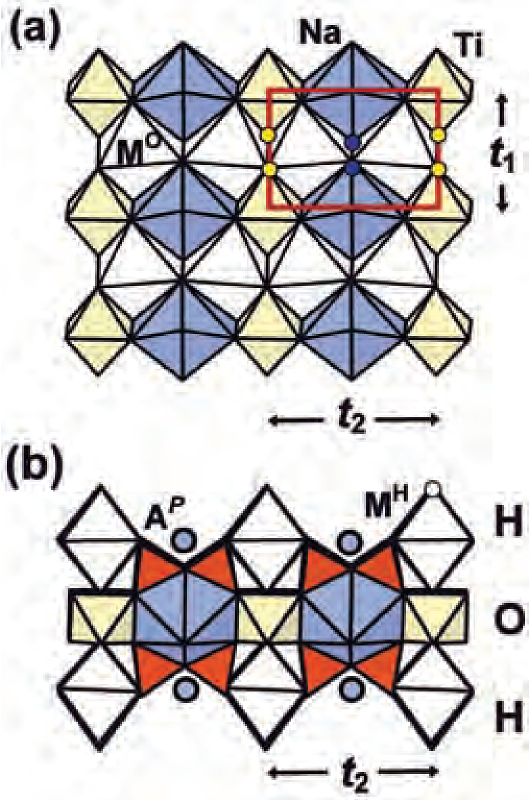

FIG. 2. The TS block in Group I: general view of the O sheet (a), linkage of O and H sheets viewed down the t_1 translation (b). $^{[8]}$Na polyhedra and Ti octahedra in the O sheet are navy blue and yellow, unspecified M^O octahedra and M^H polyhedra are white, (SiO_4) tetrahedra are orange, A^P atoms and X^O_M, X^O_A and X^P_M anions are shown as large navy blue circles and small yellow, blue and white circles; the planar cell is shown in red.

Z = 2, and the end-member composition is Na_3 Ca_3 REE Nb $(Si_2O_7)_2$ OF_3. The chemical composition, the empirical formula and the end-member formula are in close agreement with those of Petersen *et al.* (1989) (Table 2).

CRYSTAL STRUCTURE

A single crystal of nacareniobsite-(Ce) was mounted on a Bruker *P*4 automated four-circle diffractometer equipped with graphite-filtered Mo*K*α X-radiation and a Smart 4K CCD detector. The intensities of 9115 reflections with $-10 < h < 10$, $-8 < k < 8$, $-26 < l < 26$ were collected to 59.99° 2θ using 30 s per 0.2° frame, and an empirical absorption-correction (SADABS, Sheldrick 1998) was applied. The X-ray data were integrated on three different cells, of orthorhombic, monoclinic and triclinic symmetry, respectively, and processed with SADABS as both centric and acentric. Note that for all three symmetries, all reflections were indexed on the assigned cell. The refined unit-cell parameters were obtained from ~7400–7600 reflections with $I > 10\sigma I$. The solution and refinement of the crystal structure were done in orthorhombic, monoclinic and triclinic symmetries. The best structure model was found for monoclinic symmetry (Table 2). As there are very few observed reflections at high 2θ, refinement of the structure was done for $2\theta \leq 55°$. We observed 68 (h 0 l) reflections with $l = 2n + 1$ (33 of them $> 3\sigma I$) (total number of reflections 9115) violating the c_y glide plane. Note that for rinkite, Galli & Alberti (1971) did not observe any violation of systematic absences characteristic for the c_y glide plane and refined the structure in space group $P2_1/c$, whereas Rastsvetaeva *et al.* (1991) refined the structure in space group $P2_1$ and stated that the lower symmetry was chosen owing to observed *extinction laws.*

TABLE 2. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*) OF NACARENIOBSITE-(Ce)

Sample*	(1)	(2)		(1)	(2)
SiO_2	28.30	29.63	Si	4.01	4.00
Nb_2O_5	12.01	11.61	Σ	4.01	4.08
TiO_2	2.24	2.79			
Ta_2O_5	0.33	0.34	Nb	0.77	0.72
Ce_2O_3	10.55	10.32	Ti^{4+}	0.24	0.20
La_2O_3	4.42	4.09	Ta	0.01	0.01
Nd_2O_3	4.34	4.19	$\Sigma M^O(1)$	1.02	1.02
Pr_2O_3	1.12	1.42			
Sm_2O_3	0.64	0.81	Na	2.77	2.67
Gd_2O_3	0.47	–	Ca	0.20	0.07
Dy_2O_3	–	0.05	$\Sigma[M^O(2)+M^O(3)]$	2.97	2.74
Y_2O_3	0.57	0.78			
CaO	19.79	19.92	Ca	2.81	2.87
SrO	0.45	0.27	**REE^{3+},Y	1.15	1.11
Na_2O	10.07	10.01	Sr	0.04	0.02
F	6.15	6.87	$\Sigma(M^H+A^P)$	4.00	4.00
O=F	–2.59	–2.89			
Total	98.86	100.21	F	2.76	2.99

* (1) this work; (2) holotype nacareniobsite-(Ce) from Petersen *et al.* (1989): Al_2O_3 < 0.05, ZrO_2 < 0.10 wt.%. ** REE^{3+},Y = (1) 0.55Ce + 0.23La + 0.22Na + 0.06Pr + 0.03Sm +0.02Gd + 0.04Y; (2) 0.52Ce + 0.21La + 0.21Nd + 0.07Pr + 0.04Sm + 0.00Dy + 0.06Y.

In their work on the structure of mosandrite, Sokolova & Cámara (2008a) suggested that the epitactic growth of crystals of this structure type is possible, with the result that in a "crystal" of mosandrite, layers of mosandrite in a different orientation (relative to that required by the space-group symmetry and unit-cell orientation of the primary crystal) may occur owing to matching of the unit cells in two different orientations. As they noted, such an intergrowth will result in apparent violation of c-glide symmetry due to the layers in a second orientation. We suggest that this is the origin of the $h0l$ reflections with $h + l = 2n + 1$ that seem to violate the c glide of the structure. We may deal with this situation by incorporating a second component of the crystal into the refinement, a component that is related to the first by the transformation matrix $[\bar{1}\ 0\ 0\ /\ 0\ \bar{1}\ 0\ /\ 1\ 0\ 1]$.

Scattering curves for neutral atoms were taken from the International Tables for X-ray Crystallography (1992), and the occupancies of the five sites were refined with the following curves: M^H and A^P sites: Ce; $M^O(1)$ site: Nb; $M^O(2)$ and $M^O(3)$ sites: Na. Solution and refinement of the structure were done with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 1997). Refinement ignoring the second component resulted in a structure in which the mean displacements of several atoms had a negative sign, the range of Si–O distances exceeded normal values, and the variations in Si–O distances were unrelated to bond topology. Inclusion of the second component in the refinement resulted in convergence to an R_1 value of 6.5% and a GoF of 1.182 in space group $P2_1/c$, giving a structure that is well-behaved in all respects and that consists of ~50% of each orientation.

Details of the data collection and structure refinement are given in Table 3, final atom parameters are given in Table 4, selected interatomic distances and angles in Table 5, refined site-scattering values and

TABLE 3. MISCELLANEOUS DATA CONCERNING THE STRUCTURE REFINEMENT OF NACARENIOBSITE-(Ce)

Unit-cell parameters	*a* 7.468(2), *b* 5.689(1), *c* 18.891(4) Å β 101.37(3)°, *V* 786.9(1) $Å^3$
Space group, *Z*	$P2_1/c$, 2
Absorption coefficient	5.70 mm^{-1}
F(000)	795.4
D_{calc}	3.539 g/cm^3
Crystal size (mm)	0.015 × 0.18 ×0.23
Radiation/ filter	Mo*K*α/graphite
2θ range for data collection	55.00°
R(int) %	2.4
Reflections collected	9115
Independent reflections	1904
$F_o > 4\sigma F$ reflections	1866
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$
Goodness of fit on F^2	1.182
Final $R_{(obs)}$ (%)	6.5 [$F_o > 4\sigma F$]
R indices (all data) (%)	R_1 = 6.6, wR_2 = 17.1, Go*F* = 1.182

TABLE 4. FINAL POSITIONS AND DISPLACEMENT PARAMETERS (Å) OF ATOMS IN NACARENIOBSITE-(Ce)

Atoms	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M^H	0.0957(3)	0.6593(3)	0.19209(16)	0.0163(10)	0.0135(8)	0.0192(12)	0.0039(6)	0.0079(13)	0.0062(6)	0.0157(7)
A^P	0.5974(3)	0.6618(3)	0.1897(2)	0.0153(13)	0.0179(11)	0.011(3)	0.0037(8)	0.0085(14)	0.0067(6)	0.0139(17)
$M^O(1)$	0	0	0	0.0069(8)	0.0382(11)	0.0153(8)	–0.0243(8)	–0.0011(11)	0.0037(11)	0.0206(5)
$M^O(2)$	½	0	0	0.032(3)	0.050(6)	0.052(6)	0.005(5)	–0.018(8)	0.003(5)	0.049(3)
$M^O(3)$	0.7467(6)	0.5005(9)	–0.0003(2)	0.039(3)	0.028(2)	0.036(2)	0.0101(17)	0.010(4)	0.016(3)	0.0338(14)
Si(1)	0.3466(6)	0.1544(6)	0.14010(17)	0.034(3)	0.0094(15)	0.010(14)	0.004(1)	0.0004(15)	0.009(2)	0.0183(9)
Si(2)	0.7832(4)	0.1534(6)	0.13833(17)	0.0000(14)	0.0070(13)	0.0133(13)	0.0023(11)	0.0009(10)	0.0080(14)	0.0068(7)
O(1)	0.2191(13)	0.149(2)	0.0624(5)	0.024(5)	0.031(6)	0.013(4)	0.003(4)	–0.010(3)	0.001(5)	0.025(2)
O(2)	0.8329(12)	0.1416(18)	0.0586(5)	0.030(5)	0.018(4)	0.013(4)	0.007(3)	0.003(3)	0.009(4)	0.021(2)
O(3)	0.3380(16)	0.3937(15)	0.1838(4)	0.012(4)	0.019(4)	0.023(4)	–0.006(3)	–0.007(6)	0.010(5)	0.0195(19)
O(4)	0.8455(15)	0.3948(15)	0.1809(4)	0.010(4)	0.018(4)	0.024(4)	–0.010(3)	–0.010(5)	0.007(5)	0.0192(18)
O(5)	0.3347(14)	0.9297(14)	0.1913(4)	0.013(4)	0.018(4)	0.012(3)	0.007(3)	0.006(4)	0.011(4)	0.0139(17)
O(6)	0.8510(15)	0.9313(14)	0.1894(4)	0.021(4)	0.012(4)	0.011(3)	0.004(3)	0.009(5)	0.003(5)	0.0140(16)
O(7)	0.5551(14)	0.147(2)	0.1196(5)	0.016(4)	0.053(6)	0.029(4)	–0.006(4)	0.012(4)	0.005(6)	0.032(2)
X^O_M	0.0202(15)	0.7058(14)	0.0617(4)	0.012(4)	0.021(4)	0.018(3)	–0.002(3)	0.006(4)	0.014(4)	0.0168(16)
F	0.5207(16)	0.6624(13)	0.0638(4)	0.027(4)	0.030(4)	0.012(3)	–0.000(3)	0.014(4)	–0.008(4)	0.0218(16)
A^P(A)	0.606(5)	0.650(6)	0.212(4)	0.05(0)						
A^P(B)	0.593(6)	0.679(6)	0.167(4)	0.05(0)						
M^H(A)	0.078(6)	0.692(7)	0.170(3)	0.05(0)						
M^O(2A)	0.55(4)	–0.01(4)	–0.003(8)	0.05(0)						

TABLE 5. INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR NACARENIOBSITE-(Ce)

Si(1) – O(1)	1.586(9)		Si(2) – O(6)a	1.610(8)
Si(1) – O(3)	1.600(9)		Si(2) – O(4)	1.613(9)
Si(1) – O(5)a	1.616(8)		Si(2) – O(2)	1.623(9)
Si(1) – O(7)	1.677(10)		Si(2) – O(7)	1.671(11)
<Si(1) – O>	1.620		<Si(2) – O>	1.629
Si(1) – O(7) – Si(2)	154.9(6) [205.1(6)]*			
$^{[7]}M^H$ – O(5)	2.36(1)		$^{[7]}A^P$ – F	2.335(8)
$^{[7]}M^H$ – O(4)b	2.38(1)		$^{[7]}A^P$ – O(4)	2.43(1)
$^{[7]}M^H$ – O(6)b	2.39(1)		$^{[7]}A^P$ – O(6)	2.44(1)
$^{[7]}M^H$ – O(3)	2.39(1)		$^{[7]}A^P$ – O(3)	2.45(1)
$^{[7]}M^H$ – X^O_M	2.431(8)		$^{[7]}A^P$ – O(5)	2.489(9)
$^{[7]}M^H$ – O(6)c	2.551(8)		$^{[7]}A^P$ – O(5)c	2.570(9)
$^{[7]}M^H$ – O(4)d	2.707(9)		$^{[7]}A^P$ – O(3)d	2.688(9)
<M^H – φ**>	2.46		<A^P – φ>	2.49
$^{[6]}M^O(1)$ – O(2)b	1.994(9)	×2	$^{[6]}M^O(3)$ – Fe	2.31(1)
$^{[6]}M^O(1)$ – O(1)	2.01(1)	×2	$^{[6]}M^O(3)$ – O(2)	2.35(1)
$^{[6]}M^O(1)$ – X^O_Ma	2.028(8)	×2	$^{[6]}M^O(3)$ – O(1)e	2.35(1)
<$M^O(1)$ – φ>	2.01		$^{[6]}M^O(3)$ – X^O_Mf	2.44(1)
			$^{[6]}M^O(3)$ – F	2.44(1)
$^{[8]}M^O(2)$ – Fa	2.256(7)	×2	$^{[6]}M^O(3)$ – X^O_Me	2.560(9)
$^{[8]}M^O(2)$ – O(7)	2.369(9)	×2	<$M^O(3)$ – φ>	2.41
$^{[8]}M^O(2)$ – O(2)	2.64(1)	×2		
$^{[8]}M^O(2)$ – O(1)	2.73(1)	×2		
<$M^O(2)$ – φ>	2.50			

* a reflex angle toward the O sheet; ** φ: unspecified anion.
a: *x*, *y* – 1, *z*; b: *x* – 1, *y*, *z*; c: –*x* + 1, *y* – 2, –*z* + 2; d: –*x* + 1, *y* + 2, –*z* + 2;
e: –*x* + 1, –*y* + 1, –*z*; f: *x* + 1, *y*, *z*.

assigned populations for selected sites in Table 6, and bond-valence values in Table 7. A structure-factor table may be obtained from the Depository of Unpublished Data, on the MAC website [document Nacareniobsite CM46_1333].

DESCRIPTION OF THE STRUCTURE

Nacareniobsite-(Ce) belongs to Group I of the titanium disilicate minerals with a TS block (Sokolova 2006). We will describe nacareniobsite-(Ce) and compare it to mosandrite, as the topologies of the structures are identical.

Cation sites

The O sheet: In the O sheet, there are two octahedrally coordinated sites, $M^O(1)$ and $M^O(3)$, and one [8]-coordinated $M^O(2)$ site. The $M^O(1)$ site is coordinated by four O atoms and two (O,F) [= X^O_M in the terminology of Sokolova (2006)] anions and is primarily occupied by Nb with minor Ti^{4+} and trace of Ta, *i.e.* ideally Nb^{5+}, $\langle M^O(1)–\phi \rangle = 2.01$ Å (Table 5, ϕ: unspecified anion). In mosandrite, Ti is dominant at this particular site (Sokolova & Cámara 2008a). The $M^O(3)$ site is coordinated by four O and two F atoms and is occupied by Na, giving 2 Na *apfu*, $\langle M^O(3)–\phi \rangle = 2.41$ Å (Table 5). The $M^O(2)$ site is coordinated by six O and two F atoms and is occupied by 0.8 Na + 0.2 Ca with $\langle M^O(2)–\phi \rangle = 2.50$ Å (Table 5). Our initial refinement gave 31.2 and 18.2 *epfu* at the $M^O(1)$ and $M^O(2)$ sites, respectively, whereas the corresponding values derived from the results of electron-microprobe analysis are 36.8 and 12.8 *epfu*. For the final cycles of refinement, the site-scattering values at the $M^O(1)$ and $M^O(2)$ sites were fixed at values intermediate between those of the refinement of the structure and the chemical-analytical results (Table 6). In nacareniobsite-(Ce), the alkali sites of the O sheet, $M^O(2)$ and $M^O(3)$, sum to $Na_{2.8}Ca_{0.2}$, *i.e.*,

TABLE 6. REFINED SITE-SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR NACARENIOBSITE-(Ce)

Site	Site-scattering	Site population ***	Calculated site-scattering	<X–φ>$_{calc}$* Å	<X–φ>$_{obs}$* Å
$^{[6]}M^O(1)$	34.4	0.75 Nb + 0.24 Ti + 0.01 Ta 0.87 Ti + 0.08 Nb + 0.05 Zr	36.8	2.00	2.01 1.99
$^{[8]}M^O(2)$	15.6	0.80 Na + 0.20 Ca 1.00 Na	12.8	2.53	2.50 2.50
$^{[6]}M^O(3)$	27.8(5)	1.60 Na + 0.40 Ca 0.99 Na + 0.85 Ca + 0.16 □	25.6	2.37	2.41 2.38
$^{[7]}M^H$	62(1)	1.40 Ca + 0.60 REE ** 1.35 Ca + 0.65 REE^{3+}	62.7	2.44	2.46 2.45
$^{[7]}A^P$	57(3)	0.91 Ca + 0.55 REE + 0.50 Na + 0.04 Sr 1.63 Ca + 0.35 REE^{3+} + 0.02 Sr	57.0	2.45	2.48 2.48

* ionic radii from Shannon (1976); φ: unspecified anion.
** REE^{3+} (total 1.15 *apfu* with 0.55 Ce + 0.23 La + 0.22 Nd + 0.06 Pr + 0.03 Sm + 0.02 Gd + 0.04 Y); mean scattering curve of 57.78 *el* and ionic radius of $^{[7]}Ce^{3+}$.
*** second line gives site-populations and mean bond-lengths for the corresponding sites in mosandrite (Sokolova & Cámara 2008a).

ideally Na_3 with a total charge of +3. In mosandrite, the corresponding sites sum to ($Na_{1.99}Ca_{0.85}\square_{0.16}$), *i.e.*, ideally Na_2Ca with a total charge of +4.

The H sheet: In the H sheet, there are two tetrahedrally coordinated sites occupied by Si with a grand <Si–O> distance of 1.625 Å. There are two [7]-coordinated sites, M^H and A^P, occupied by Ca and REE^{3+} approximately in the ratio 3:1 (Table 6). The scattering at the A^P site is slightly lower than at the M^H site, and consequently less REE^{3+} and all Sr was assigned to the A^P site. The M^H site is coordinated by six O atoms and an X^O_M anion, and the A^P site is coordinated by six O atoms and one F atom. In mosandrite, the M^H and A^P sites are also [7]-coordinated and are occupied by Ca and REE^{3+}, approximately in the ratio 3:1 (Sokolova & Cámara 2008a).

TABLE 7. BOND-VALENCE* (*vu*) TABLE FOR NACARENIOBSITE-(Ce)

	Si(1)	Si(2)	M^H	A^P	$M^O(1)$	$M^O(2)$	$M^O(3)$	Σ
O(1)	1.12				$0.73^{\times2}\downarrow$	$0.12^{\times2}\downarrow$	0.25	2.22
O(2)		1.02			$0.76^{\times2}\downarrow$	$0.15^{\times2}\downarrow$	0.25	2.18
O(3)	1.08		0.36	0.30 0.17				1.91
O(4)		1.05	0.37 0.18	0.31				1.91
O(5)	1.04		0.39	0.27 0.23				1.93
O(6)		1.05	0.36 0.25	0.30				1.96
O(7)	0.89	0.90				$0.24^{\times2}\downarrow$		2.03
X^O_M			0.30		$0.62^{\times2}\downarrow$		0.18 0.15	1.25
F				0.29		$0.22^{\times2}\downarrow$	0.20 0.15	0.86
Total	4.13	4.02	2.21	1.87	4.22	1.46	1.18	
Aggregate charge	4.00	4.00	2.30	2.03	4.76	1.20	1.20	

* bond-valence parameters of Brown (1981).

Anion considerations

In the structure of nacareniobsite-(Ce), there are nine anion sites. Analysis of incident bond-valence sums at these anions (Table 7) indicates that seven sites are occupied by O atoms [O(1)–(O(7)], the X^O_A site (= F) is occupied by F (less than 1 valence unit, *vu*), and the X^O_M site is statistically occupied by O and F with a bond-valence sum of 1.25 *vu*. The environment of the X^O_A and X^O_M anions is shown in Figure 3a. We can calculate the content of F at the X^O_M site as the difference between the total F content, 2.76 *apfu* (Table 2), and the F content at the X^O_A site, 2 *apfu*: 0.76 *apfu*. Therefore, the X^O_M site is occupied by ($O_{1.24}$ $F_{0.76}$) *apfu* in our crystal. The two sites, X^O_M and X^O_A, sum to ($O_{1.24}$ $F_{0.76}$) + F_2, ideally OF_3. In mosandrite, the two corresponding anion sites are occupied by ($F_{0.75}O_{0.25}$) (Sokolova & Cámara 2008a), also ideally OF_3.

Structure topology

The M^O polyhedra each share six common edges to form a sheet of close-packed octahedra; this O sheet forms the central part of the TS block (Fig. 3a). Two outer parts of the block are H sheets of (Si_2O_7) groups and [7]-coordinated M^H and A^P polyhedra (Fig. 3b). Two H sheets are connected to a sheet of octahedra *via* common vertices of (SiO_4) tetrahedra and M^H and A^P

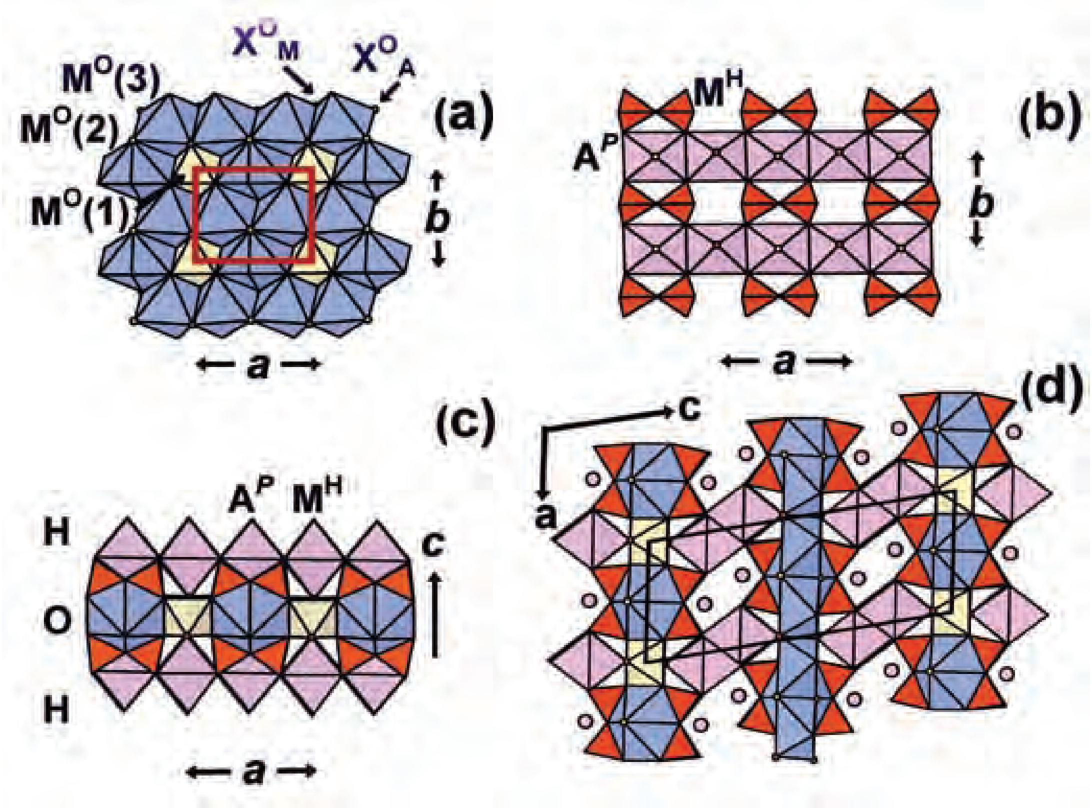

FIG. 3. The crystal structure of nacareniobsite-(Ce): the O sheet of the TS block viewed down [0 0 1]. The planar cell is shown in red (a); the H sheet of the TS block viewed down [0 0 1]; the TS block viewed down [0 1 0] (c); general view of the crystal structure projected onto (010) (d). (SiO_4) tetrahedra are orange, Nb octahedra are yellow, Na-dominant and Ca-dominant polyhedra are navy blue and pink, and F (= X^{O}_{A}) and X^{O}_{M} anions are shown as yellow and orange circles.

polyhedra (Fig. 3c). Within the TS block of nacareniobsite-(Ce), two [Si_2O_7] groups, one from each H sheet, link to the $M^{O}(2)$ polyhedron of the O sheet, and two H sheets are approximately related by a pseudo-mirror-plane, m_z (Fig. 3c). In the structure of nacareniobsite-(Ce), TS blocks are connected through common vertices of (Si_2O_7) groups and M^{H} and A^{P} polyhedra (Fig. 3d). The TS blocks repeat along the **c** direction (Fig. 3d). There are two unique TS blocks per unit cell in the crystal structure of nacareniobsite-(Ce).

Structural formulae of nacareniobsite-(Ce) and mosandrite

We can write the structural formulae of the form A^{P}_{2} M^{H}_{2} M^{O}_{4} $(Si_2O_7)_2$ X^{O}_{4} for these two minerals in terms of the components of their TS blocks in accord with Sokolova (2006): O sheet [= 4 M^{O} 4 X^{O}] + 2H sheets [= 2 M^{H} $(Si_2O_7)_2$] + 2 A^{P} cations. The structural formula for nacareniobsite-(Ce) is $^{[8]}$Na Na_2 Nb $(O,F)_2$ F_2 + $^{[7]}$($Ca_{1.5}$ $REE_{0.5}$) $(Si_2O_7)_2$ + $^{[7]}$($Ca_{1.5}$ $REE_{0.5}$) = ($Ca_{1.5}$ $REE_{0.5}$) ($Ca_{1.5}$ $REE_{0.5}$) Na Na_2 Nb $(Si_2O_7)_2$ $(O,F)_2$ F_2 or, in a compact form: Ca_3REE Na_3 Nb $(Si_2O_7)_2$ OF_3. The structural formula for mosandrite is $^{[8]}$Na (NaCa) Ti $(O,F)_2$ F_2 + $^{[7]}$($Ca_{1.5}$ $REE_{0.5}$) $(Si_2O_7)_2$ + $^{[7]}$($Ca_{1.5}$ $REE_{0.5}$) = ($Ca_{1.5}$ $REE_{0.5}$) ($Ca_{1.5}$ $REE_{0.5}$) Na Na_2 Nb $(Si_2O_7)_2$ $(O,F)_2$ F_2 or, in a compact form: Ca_3REE Na_2 Ca Ti $(Si_2O_7)_2$ OF_3. We can write the end-member formulae of nacareniobsite-(Ce) and mosandrite in the following way: nacareniobsite-(Ce), Na_3 Ca_3 REE Nb $(Si_2O_7)_2$ OF_3, and mosandrite, Na_2 Ca_4 REE Ti $(Si_2O_7)_2$ OF_3 (see Table 1). Mosandrite and nacareniobsite-(Ce) are related by the substitution $Nb^{5+} + Na^{+} \rightarrow Ti^{4+} + Ca^{2+}$ (Petersen *et al.* 1989). This substitution occurs in the O sheet of the TS block, where the cations are Na_3 Nb and Na (NaCa) Ti in nacareniobsite-(Ce) and mosandrite, respectively. Note that in nacareniobsite-(Ce) and mosandrite: (1) the $M^{O}(1)$ site is occupied primarily by Nb and Ti; (2) the $M^{O}(2)$ site is occupied primarily by Na, and (3) the $M^{O}(3)$ site is statistically occupied by Na and Ca in the ratio 1:1. The occurrence of the $[Na_3 Nb]$ cluster in the O sheet of nacareniobsite-(Ce) is in accord with conclusions of Sokolova (2006) on the possible substitution of M^{5+} (primarily Nb^{5+}) for Ti^{4+} in the O sheet. She proposed that this substitution can occur in Group I, giving rise to the cluster (3 Na + M^{5+}) in the O sheet. This is exactly the case in nacareniobsite-(Ce).

SUMMARY

The structure topologies of nacareniobsite-(Ce) and mosandrite are identical. Nacareniobsite-(Ce) and mosandrite are isotypic and isostructural. Nacareniobsite-(Ce) is the only mineral in Group I of the Ti disilicate minerals to contain a pentavalent cation in the O sheet of the TS block.

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