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Microporous titanosilicates – Synthesis and structural characterization of a new orthorhombic-type labuntsovite

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Abstract: The crystal structure of a new orthorhombic-type labuntsovite with composition $Na_{5.36}Ti_4(Si_4O_{12})_2(O_{0.34}OH_{0.66})_4 \cdot 10.31H_2O$, obtained as side product of hydrothermal runs devoted to the synthesis of rhodesite-type microporous silicates, has been solved and refined in the space group *Cmmm* (a = 7.278, b = 14.134, c = 7.118 Å; Z = 1) with X-ray single-crystal diffraction data collected by a Bruker-AXS Smart Apex diffractometer equipped with a CCD area detector. The crystal structure shows the overall features known for the heteropolyhedral framework (tetrahedral/octahedral) structures of the labuntsovite-group minerals, like systems of channels and disorder. The simpler chemical composition of the synthetic compound, which does not show isomorphous replacements, allows a detailed discussion of the zeolite-like disorder in the channels, which is related to the charge of the framework $[Ti_4(Si_4O_{12})_2(OH_{4-x}O_x)]^{(4+x)-}$ and to the system of hydrogen bonding. The different space group *Pbam* shown by the two known natural labuntsovites (nenadkevichite and korobitsynite) is attributed to the presence in the natural samples of the Nb → Ti substitution.

Key-words: labuntsovite group, zeolite-like structure, nenadkevichite, korobitsynite, microporous titanosilicates, hydrothermal synthesis.

Introduction

The labuntsovite group (Chukanov *et al*., 2002; 2003) includes hydrous titanium and niobium alkali silicates represented by the general formula $A_4B_4[C_{4-2x}(H_2O,OH)_{2x}]D_x[M_8(Si_4O_{12})_4(OH,O)_8]\cdot nH_2O$. In this formula A and B represent mainly alkalis; C and D represent several types of cations, but the corresponding crystallographic sites exclude each other because the $C - D$ distance is about 2 Å only; M represents mainly Ti and Nb. If the site D is occupied by cations, to a maximum of $x = 2$, $2x$ oxygen atoms (belonging either to H_2O molecules or OH groups) occur in C to complete the octahedral coordination of D. In the crystal structure, chains of corner-sharing M octahedra are linked by Si tetrahedra to form a heteropolyhedral framework crossed by various kinds of channels and cavities (Fig. 1). Consequently, the labuntsovite-group minerals show zeolitic-like properties (Chukanov & Pekov, 2005) and belong to the growing family of micro- and mesoporous mineral phases (Ferraris & Merlino, 2005).

Among the about thirty known members of the labuntsovite-group minerals (Chukanov *et al*., 2003), most are monoclinic and only two members are orthorhombic: nenadkevichite (Perrault *et al*., 1973) and korobitsynite (Pekov *et al*., 1999; Niedermayr *et al*., 2002). In comparison to the orthorhombic members (a ~ 7.4, b ~ 14.2, c ~ 7.1 Å), the monoclinic members show a larger unit cell with a doubled a and, in some cases, also a doubled c (Chukanov *et al*., 2002); however, being β ~ 117°, the latter direction cannot correspond to that of the orthorhombic c parameter. The chains of M oc-

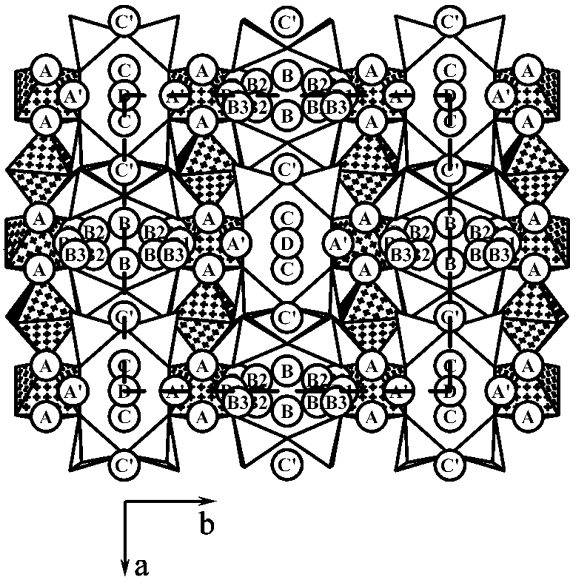

Fig. 1. Projection along [001] of the crystal structure of tsepinite-Ca to show the sites A, B, C, D within the channels of a monoclinic labuntsovite. (Ti, Nb) octahedra are dotted.

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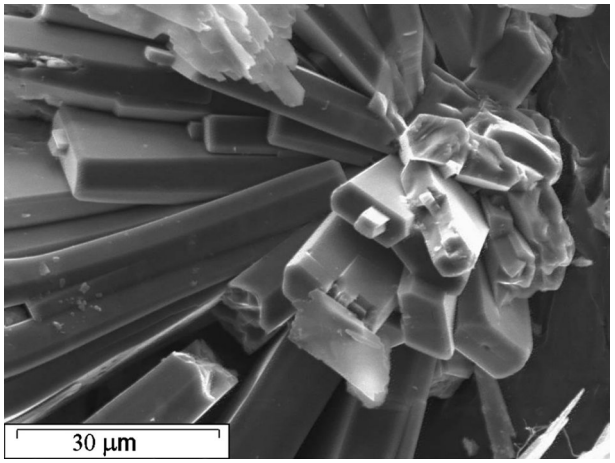

Fig. 2. SEM image of TR01.

tahedra are straight in the orthorhombic members, because of symmetry, but tend to bend in the monoclinic members even if in some cases, like tsepinite-Ca (Pekov *et al.*, 2003), they are quite straight (Fig. 1). The substantial difference between monoclinic and orthorhombic structures is related to the value of the *a* parameter along which the chains of *M* octahedra run. In fact, because of the halving of *a*, in the orthorhombic structures, contrary to the monoclinic structures, all the large channels that run along [001] are crystallographically equivalent. Consequently, in the orthorhombic members some of the sites corresponding to *A*, *B*, *C* and *D* (Fig. 1) coalesce and the general formula of these members has been given as $A_6M_4(Si_4O_{12})_2(OH,O)_4{\cdot}nH_2O$ (Chukanov *et al.*, 2002). In nenadkevichite [*M* = Nb > Ti; $(Na_{3.76}K_{0.24}Ca_{0.11}Mn_{0.03})(Nb_{2.76}Ti_{1.18})(Si_4O_{12})_2(O_{2.80}OH_{1.20}){\cdot}8H_2O$; *a* = 7.408, *b* = 14.198, *c* = 7.148 Å; Perrault *et al.*, 1973] and korobitsynite [*M* = Ti > Nb; $Na_{5.76}(Ti_{2.80}Nb_{1.04}Zr_{0.04}Fe_{0.04})(Si_4O_{12})_2(O_{2.40}OH_{1.60}){\cdot}{\sim}4H_2O$; *a* = 7.349, *b* = 14.164, *c* = 7.130 Å; Rastsvetaeva *et al.*, 1997] *A* corresponds to two independent sites which are partially occupied by Na in 8- and 9-fold coordination. The crystal structures of both minerals have been refined in the space group *Pbam*.

Microporous heteropolyhedral structures (*i.e.*, containing interlinked tetrahedra and octahedra) like those of labuntsovites are potentially of technological interest; thus, Rocha *et al*. (1996a and b) (see also Rocha & Anderson, 2000) synthesised a series of nenadkevichite analogues with various Nb/Ti molar ratios. Isostructurality of these analogues with nenadkevichite was affirmed on the basis of X-ray powder diffraction patterns only.

In this paper we describe the crystal structure of a synthetic compound that corresponds to a Ti-pure korobitsynite in composition, but shows space group *Cmmm* instead of *Pbam*; the two structure types of orthorhombic labuntsovites are compared and discussed.

Experimental

Synthesis and characterization

We have obtained, together with an unidentified Ce and K silicate, a labuntsovite showing composition $Na_{5.36}Ti_4(Si_4O_{12})_2(O_{0.34}OH_{0.66})_4{\cdot}10.31H_2O$ (hereafter TR01) as side product of hydrothermal runs devoted to the synthesis of rhodesite-type microporous silicates (*cf.* Ferraris & Gula, 2005). TR01 was synthesized using a mixture with composition: $1SiO_2 : 0.108\ TiO_2 : 0.77\ Na_2O : 0.125\ K_2O : 0.090$

Table 1. Crystal data and structure refinement for TR01

Identification code	TR01
Formula	$Na_{5.36}\,Ti_4(Si_4O_{12})_2\,(OH_{0.66}\,O_{0.34}){\cdot}10.31H_2O$
Formula weight	1175.95
Temperature	293(2) K
Wavelength	0.71073 Å
Space group	*Cmmm*
Unit cell dimensions	$a = 7.278(1)$, $b = 14.134(2)$, $c = 7.118(1)$ Å
Volume	732.2(2) Å^3
Z	1
Density (calculated)	2.667 Mg/m^3
Absorption coefficient	1.612 mm^{-1}
F(000)	589
Crystal size (mm)	0.080 x 0.050 x 0.015
θ range for data collection	2.4 to 30.0°.
Frames (φ values)/ω scan width	840 x 3 (0, 120, 240°)/0.2°
Index ranges	$-10 \le h \le 10$, $-19 \le k \le 19$, $-10 \le l \le 10$
Reflections collected	8417
Independent reflections	643 [R(int) = 0.066]
$\lvert F_O \rvert > 4\sigma(\lvert F_O \rvert)$	494
Refinement method	Weighted full-matrix least-squares on F^2 anisotropic
Data / restraints / parameters	643 / 0 / 68
Goodness-of-fit on F^2	1.06
Final R indices [I > 2 σ(I)]	R1 = 0.060, wR2 = 0.120
R indices (all data)	R1 = 0.079, wR2 = 0.125
Largest diff. peak and hole	0.97 and –0.69 e.Å^{-3}

Table 2. Atomic coordinates (*xyz*) and equivalent isotropic displacement parameters [*U(eq)* $Å^2$ x 10^3] for TR01. *U(eq)* is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Occupancy	x	y	z	U(eq)
Ti1	1	¼	1/4	1/2	20(1)
Na1	0.24(1)	0.2832(17)	0.2659(14)	0	26(5)
Na2	0.68(2)	–0.2081(13)	0	1/2	57(3)
Na3	0.17(2)	–0.445(8)	1/2	0	7(3)
Si1	1	0	0.3888(1)	0.2250(2)	12(1)
O1	1	0	0.3800(6)	0	37(2)
O2	1	0	1/2	0.2763(11)	39(2)
O3	1	0.1837(4)	0.3417(3)	0.3041(5)	34(1)
O4	1	0	0.2000(4)	1/2	17(1)
OW1	0.87(6)	0	0	0.2710(3)	128(11)
OW2	0.54(6)	0	0.124(4)	–0.1760(10)	28(5)
OW3	0.31(4)	0.063(3)	0.1611(13)	0	36(8)

Ce_2O_3 : 0.040 SrO : 0.008 CaO : 0.005 BaO : 45 H_2O. A gel with this composition was prepared by adding to a strongly alkaline gel, obtained by dissolving fumed silica in a NaOH and KOH solution, a solution of titanium isopropoxide in ethanol and, subsequently, solutions of cerium nitrate, strontium nitrate, calcium nitrate and barium nitrate; additions were made under vigorous stirring. Static crystallization was carried out in a 25-ml Teflon-lined stainless-steel autoclave at 503 K under autogenous pressure for duration of 8 days.

Powder X-ray diffraction data were collected on a Siemens diffractometer using CuK_α ($\lambda = 1.5418$ Å) radiation. A careful examination by SEM (Fig. 2), combined with EDS analysis was carried out on a Cambridge S-360 microscope. The morphology of the crystals shown in Fig. 2 is very similar to that reported for natural orthorhombic labuntsovites (Chukanov *et al*., 2003).

Single-crystal X-ray diffractometry

Single crystal X-ray diffraction data have been collected on a Bruker-AXS Smart Apex diffractometer equipped with a CCD area detector and operated at 50 kV and 35 mA; graphite-monochromatized MoK_α radiation. Information on data collection and structure refinement is given in Table 1. Three-dimensional data were integrated and corrected for Lorentz, polarisation and background effects using the SAINT+ software version 6.45a (® Bruker AXS). Raw intensity data were corrected for absorption using SADABS (Sheldrick, 1996). The following orthorhombic unit-cell parameters have been obtained by least-squares refinement of the position of all collected reflections: $a = 7.278(2)$, $b = 14.134(2)$, $c = 7.118(1)$ Å.

Structure determination and refinement

The crystal structure of TR01 has been solved in *Cmmm* space group by direct methods and anisotropically refined (SHELX 97; Sheldrick, 1997) to R = 0.06 for 494 observed independent reflection with $|F_o| > \sigma(|F_o|)$. OW2, OW1 and Na3 show large mean square atomic displacements *U* along the [100] direction (0.67, 0.21 and 0.14 $Å^2$, in the order). However, attempts to split the positions of these atoms failed, presumably because the splitting of sites which already are partially occupied reduces the weight of the individual site contributions in the least-squares procedure.

Table 3. Selected bond lengths (Å) for TR01

Ti1-O4 x 2	1.952(2)	Si1-O3 x 2	1.596(3)
Ti1-O3 x 4	1.964(3)	Si1-O1	1.607(2)
		Si1-O2	1.614(2)
Na1-OW3	2.18(2)	Na2-OW1 x 2	2.226(2)
Na1-OW3	2.29(2)	Na2-O2 x 2	2.655(9)
Na1-O3 x 2	2.522(1)	Na2-O3 x 4	2.752(5)
Na1-OW2 x 2	2.54(7)		
Na1-O1	2.60(2)	Na3-OW1 x 2	1.97(2)
Na1-O1	2.617(2)	Na3-OW2 x 4	2.19(3)
Na1-O3 x 2	2.656(1)	Na3-OW3 x 2	2.278(2)
Na1-OW3	2.946(2)	Na3-OW3 x 2	2.43(3)

Tables 2 and 3 report the atom parameters and the main bond lengths, respectively. As far as possible, the labelling of the atoms corresponds to that used for the crystal structures of nenadkevichite and korobitsynite.

The crystal structure

As found in general for labuntsovites (see Introduction), the titanosilicate framework of TR01 consists of chains of Ti octahedra, running along the [100] direction, that are joined together by square rings of silica tetrahedra (Fig. 3a) to form a heteropolyhedral framework of composition $[Ti_4(Si_4O_{12})_2(OH_{4-x}O_x)]^{(4+x)-}$. The $(OH_{4-x}O_x)^{(4+x)-}$ anion is bound to Ti , but not to Si and corresponds to the corner O4 which is shared by two Ti-octahedra to form the mentioned chains. The maximum of positive charge available for the extra-framework cations is 8 when $x = 4$ and reduces up to 4 ($x = 0$) if Ti^{4+} is progressively substituted by Nb^{5+}, as in natural orthorhombic labuntsovites.

A wide eight-membered channel (ch1) delimited by four tetrahedra and four octahedra develops along [001] (Fig. 3a). It shows an effective width of 5.5x3.0 Å as calculated, according to McCusker *et al*. (2003), by subtracting the ionic diameter of O^{2-} (2.7 Å) to the longest and shortest O···O distances across the channel. The ch1 channel hosts, in two partially occupied sites [Wyckoff positions 4*h* (occupancy 0.68) and 4*g* (occupancy 0.17)], the Na2 and Na3 cations which, on the whole, account for 3.42 Na atoms per formula unit (*apfu*). A further 1.94 *apfu* of Na is hosted in a 8*p* site (Na1, occupancy 0.24) within a smaller six-membered channel (ch2) that is delimited by four tetrahedra and two octahedra, runs along [100] (Fig. 3b) and does not cross ch1. The latter channel is instead crossed at the position of Na2 by a second six-membered channel (ch3), which too is delimited by four tetrahedra and two octahedra and runs along the [100] direction as ch2 (Fig. 3b). A third six-membered channel (ch4) is again delimited by four tetrahedra and two octahedra, runs along [010] (Fig. 3c) and intersects ch2 at the position of Na1. In conclusion, the large channel ch1 is intersected by ch3; ch2 and ch4 intersect each other.

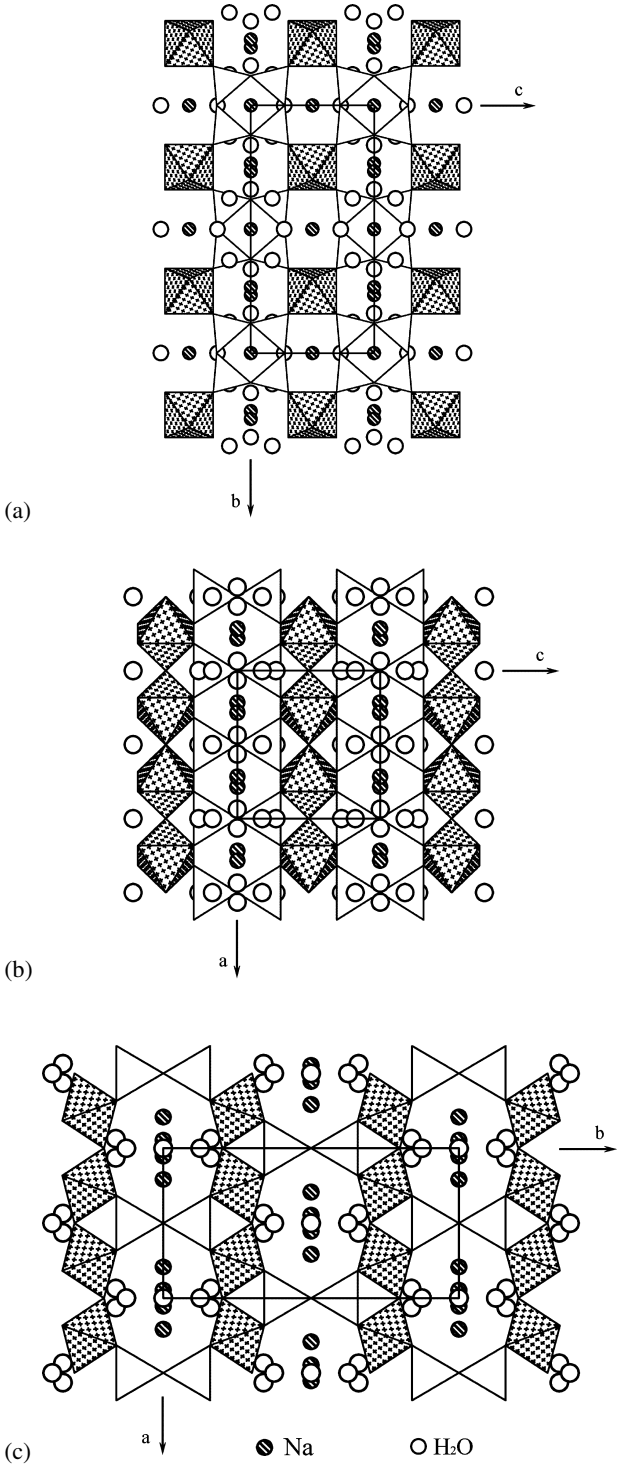

Fig. 3. Projections along [100] (a), [010] (b) and [001] (c) of the crystal structure of TR01. Ti octahedra are dotted.

All three water molecules, for a total of 10.31 H_2O molecules pfu, are located within the large channel ch1 (Fig.3a) as follows: 3.49 in 4*h* (OW1, occupancy 0.87); 4.32 in 8*n* (OW2, occupancy 0.54); 2.50 in 8*p* (OW3, occupancy 0.31). OW2 and OW3 cannot occur at the same time to avoid distances as short as 1.42 Å between them.

In conclusion, the crystal-chemical formula of TR01 is $(Na_{5.36})Ti_4(Si_4O_{12})_2(OH_{0.\ 66}O_{0.34})_4 \cdot 10.31H_2O$. The atomic position labelled O4 in the Tables 2 and 3 corresponds to $(OH_{0.66}O_{0.34})$ and carries a negative charge -1.34 which, according to the Pauling second rule, is what is needed to balance the positive charge +4/3 received via the two Ti-O4 bonds.

Coordination polyhedra

The coordination environment of the three crystallographically independent Na atoms can be described as follows (Table 3) up to the distance Na-O = 3 Å.

Na1, with occupancy 0.24, is surrounded by eleven oxygen atoms: 2 O1 and 4 O3 belong to the frameworks; 2 OW2 and 3 OW3 belong to the disordered H_2O molecules. Taking into account the occupancies and that OW2 and OW3 cannot occur at the same time, in practice the coordination number of Na1 is eight with the Na1-O distance in a range from 2.18 to 2.94 Å. A short Na1-OW3 = 1.52 Å distance (not given in Table 3) can be locally avoided because both Na1 and OW3 show occupancy lower that 0.5.

Na2, with occupancy 0.68, is surrounded by six oxygen atoms of the frameworks and by two OW1 oxygen atoms with occupancy 0.87; therefore, in practice Na2 has coordination number 8 and the Na2-O distance is in a range from 2.226 to 2.752 Å.

Na3, with occupancy 0.17, is surrounded by two OW1, four OW2 and four OW3 atoms; OW2 and OW3 cannot occur at the same time. Likely, when the Na3 site is occupied, 5-6 OW atoms occur around it with the Na3-O distance in a range from 1.97 to 2.43 Å. Apparently Na3-OW1 = 1.97 Å is too short, but it must be taken into account that for both Na3 and OW1 the large component of the atomic displacements along the [100] (see above) is indicative of disorder, such that locally the Na3-OW1 distance can be longer than 2 Å.

The coordination polyhedron of Ti is practically an ideal octahedron, whereas both in nenadkevichite (Perrault *et al.*, 1973) and korobitsynite (Rastsvetaeva *et al.*, 1997) the corresponding polyhedron shows, in the order, the following anomalous bonds: Nb-O = 1.78 and 2.20 Å; Ti-O = 1.79 and 2.16 Å.

Bond valence and hydrogen bonding

The disorder present in the structure of TR01 does not allow a straightforward calculation of the bond valence. However, clearly OW1, OW2 and OW3, being coordinated only by Na (Table 3), represent oxygen atoms of H_2O molecules; besides, as proved above, 2/3 of O4 belong to an OH group. The analysis of the O…O distances that involve OW1, OW2, OW3 and O4 allows establishing the following system of hydrogen bonding.

The distances O4…OW2 = 2.551 Å and O4…OW1 = 3.265 Å are indicative, in the order, of a very strong and a very weak hydrogen bond both donated by O4, *i.e.* the $OH_{0.\ 66}$ $O_{0.34}$ group bound to Ti. On its turn, the water molecule to which the oxygen atom OW2 belongs is donor of a strong hydrogen bond to O3 (OW2…O3 = 2.528 Å), which is the

most under-bonded tetrahedral oxygen atom. In fact, it is bound only once to Si and once to Ti, whereas the other two tetrahedral oxygen atoms (O1 and O2) bridge two tetrahedra and thus are bound twice to Si. Likely, O3 is acceptor of a second hydrogen bond from OW3 (OW3…O3 = 2.839 Å) at least when Na3 is absent, being the same OW3…O3 edge of the coordination polyhedron of Na3.

Presumably, other weak hydrogen bonds with O…O distances longer than, but close to, 3 Å may occur between the water molecules, at least when locally, in absence of Na, these distances do not correspond to edges of an Na coordination polyhedron.

The short OW2…O3 = 2.528 Å distance is very unusual for a hydrogen bond donated by a water molecule (Chiari & Ferraris, 1982); as discussed by Ferraris *et al*. (1986), in a survey of water molecules donating short hydrogen bonds, it can occur because in its turn OW2 is acceptor of the short hydrogen bond O4…OW2 = 2.551 Å. The bond valence transferred by each of the two short hydrogen bonds is $s \sim 0.34$ as calculated by the equation $s = [(O\ldots O)/2.17]^{-8.2} + 0.06$ proposed by Ferraris & Ivaldi (1988).

Discussion

Ideal composition and endemic disorder of orthorhombic labuntsovites

Taking into account that

(i) the position 8*p* of Na1 is close to a twofold axis and can by be occupied 50 % at maximum to avoid Na…Na distances as short as 0.66 Å;

(ii) the position 4*h* of Na2 can be fully occupied;

(iii) the position 4*g* of Na3 is close to an inversion centre and can be occupied at 50 % maximum to avoid Na…Na distances as short as 0.78 Å;

(iv) the positions 4*h* of OW1 and 8*n* of OW2 can be fully occupied, but the presence of OW2 excludes that of OW3 in 8*p* to avoid OW2…OW3 distances as short as 1.42 Å; a maximum amount of 10 Na atoms and 12 H_2O molecules pfu can in principle occur as guests within the framework of TR01. However, the following considerations lead to conclude that the theoretical maximum amount of guests never can be accepted by the host framework.

The disorder of the extra-framework content (Na atoms and H_2O molecules) is typical of a zeolitic-like structure with a low binding capacity of the framework anions. In the framework $[Ti_4(Si_4O_{12})_2(OH_{4-x}O_x)]^{(4+x)-}$ of TR01 the negative charge is concentrated on the $(OH_{4-x}O_x)^{(4+x)-}$ group which corresponds to O4 and is shared by two Ti octahedra. To contribute to the formation of Na-O coordination bonds, the (4+x)- negative charges must be distributed among the Na^+ cations, a function typically played by the hydrogen bonds. As we have seen above, O4 acts as donor of hydrogen bonds to two water molecules, such that these can form coordination bonds with the Na^+ cations. It turns out that necessarily in the formula of the framework $x < 4$ and the number of Na^+ cations is constrained to be not higher than 8, a value which can be reached only for $x = 4$. Therefore, even in the alike case of $O4 = O^{2-}$ only, it would be impossible to insert in the channels of TR01 the maximum number of 10 Na that, on purely crystallographic basis, are allowed. In conclusion, the partial occupancy affecting the extra-framework content is a consequence of the chemical composition of the framework and could be likely overcome by the introduction of lower charge cations, e.g. by an Al → Si substitution.

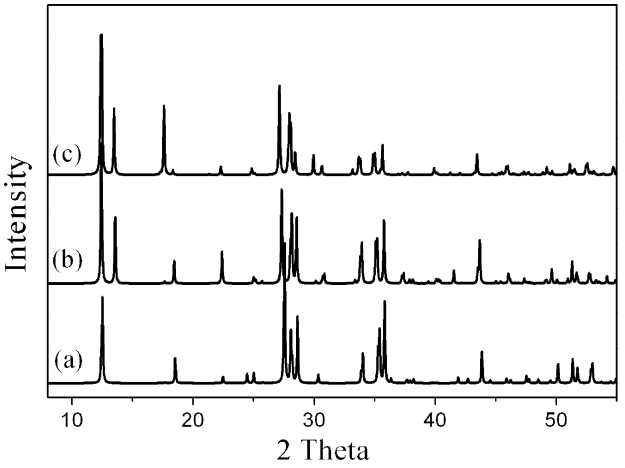

Fig. 4. Calculated X-ray powder diffraction patterns of TR01 (a), korobitsynite (b) and nenadkevichite (c).

Conclusions

On the whole, the crystal structures of the two natural orthorhombic labuntsovites, nenadkevichite and korobitsynite, which have been refined in the space group *Pbam*, and of the present synthetic TR01 orthorhombic labuntsovite, refined in the space group *Cmmm*, are quite similar, as shown also by their calculated X-ray powder diffraction patterns (Fig. 4). In particular, the *Pbam* structures are based on an almost *C* centred lattice, as proved by the weakness of the *hkl* reflections with $h + k = 2n + 1$. Actually, only the intensity of very few reflections of this type approaches 10 % of the maximum calculated value.

The switching from a *P* to a *C l*attice is mainly related to the locking, in TR01, of the Ti atom in a special position which constrains the coordination octahedron. Likely in the two natural orthorhombic labuntsovites (nenadkevichite and korobitsynite) the Nb → Ti substitution does not allow the same constrains. Interestingly, a nenadkevichite sample with a very low Ti content (Ti/Nb = 0.065) shows an "anomalous" infrared spectrum (Chukanov *et al*., 2003) that could be indicative of a *Cmmm* instead of *Pbam* symmetry; no samples of Nb-poor korobitsynite are instead known. The effect of the position of Ti on the symmetry of the structure was already mentioned by Perrault *et al*. (1973). The same authors quoted also some results showing *C* and *F* orthorhombic lattices; most likely the corresponding diffraction patterns were obtained from twinned monoclinic crystals, a non rare event carefully analysed for gjerdingenite-Fe (Raade *et al*., 2002).

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