Tsepinite–Ca, $(Ca,K,Na,\square)_2(Ti,Nb)_2(Si_4O_{12})$ $(OH,O)_2 \cdot 4H_2O$, a new mineral of the labuntsovite group from the Khibiny alkaline massif, Kola Peninsula – Novel disordered sites in the vuoriyarvite-type structure

Igor V. Pekov, Moscow, **Nikita V. Chukanov,** Chernogolovka,
Giovanni Ferraris, Angela Gula, Torino, **Dmitry Yu. Pushcharovsky,**
and **Aleksandr E. Zadov,** Moscow

With 2 figures and 6 tables

Abstract: Tsepinite–Ca, ideally $(Ca,K,Na,\square)_2(Ti,Nb)_2(Si_4O_{12})(OH,O)_2 \cdot 4H_2O$ (Z = 4), is a new mineral species of the labuntsovite group (vuoriyarvite subgroup) found in the abandoned Lovchorrite mine, Hackman Valley, Yukspor Mountain, Khibiny massif, Kola Peninsula, Russia. It occurs in the hydrothermally altered zone of a large aegirine–nepheline–potassic feldspar pegmatite and is associated mainly with microcline, aegirine, natrolite, kentbrooksite, kupletskite, Mn-rich lamprophyllite, fluorapatite, catapleiite, ancylite–(Ce), ancylite–(La), fluorapophyllite, leucophanite, chabazite–Ca. The new mineral is late hydrothermal and occurs in cavities after leaching of rinkite, the probable source of Ti, Nb and Ca. Tsepinite–Ca forms coarse long-prismatic to needle-shaped and usually split crystals which are transparent, colourless to white and pale brownish, up to $0.2 \times 0.6 \times 5$ mm in size and form aggregates up to 1 cm in size. The streak is white and the lustre is vitreous. Tsepinite–Ca is brittle, shows uneven fracture and no cleavage. Its Mohs' hardness is 5; $D_{meas.}$ = 2.73(1), $D_{calc.}$ = 2.72 g/cm³. Biaxial (+), $2V_{meas.}$ = 30 ± 10°, $2V_{calc.}$ = 36°; α = 1.666(2), β = 1.676(2), γ = 1.780(4). Dispersion is very weak: $r <$ v. Non-pleochroic; the orientation is Y = b. The strongest IR bands (cm⁻¹) are at 3260, 1103, 946, 673, 455. Electron microprobe analysis (H₂O by TGA) gave: Na₂O

1.32, K_2O 2.23, CaO 5.29, SrO 3.01, BaO 3.52, MnO 0.16, FeO 0.04, ZnO 0.12, Al_2O_3 0.04, SiO_2 41.06, TiO_2 21.95, Nb_2O_5 9.08, H_2O 13.30, total 101.12 wt.%. The empirical formula, based on Si + Al = 8 and OH/O ratio from charge balance (Z = 2), is $(Ca_{1.10}K_{0.55}Na_{0.50}Sr_{0.34}Ba_{0.27}Mn_{0.03}Zn_{0.02}Fe_{0.01})_{\Sigma2.82}(Ti_{3.21}Nb_{0.80})_{\Sigma4.01}(Si_{7.99}Al_{0.01})_{\Sigma8}O_{24}[(OH)_{2.58}O_{1.42}]_{\Sigma4}\cdot7.35H_2O$. The strongest lines of the X-ray powder pattern [d in Å (I) (hkl)] are: 7.02(60)(020, 001), 6.38(40)(20–1, 200), 3.53(45) (131); 3.16(100)(041, 022), 2.62(45)(20–3, 202), 2.51(85)(44–1, 40–3, 042), 1.718 (50)(46–3, 461, 44–4, 442, 081). X-ray single crystal diffraction showed tsepinite–Ca is monoclinic, space group $C2/m$, with a = 14.484(4), b = 14.191(4), c = 7.907(2) Å, β = 117.26(2)°, V = 1445(1) Å^3. The structure, refined to R 0.11 for 1559 observed reflections, is based on a framework consisting of corrugated chains of [(Ti,Nb)(O, OH)] octahedra connected by (Si_4O_{12}) rings. The larger cations are dominated by Ca and, together with the H_2O molecules, are distributed, within zeolite-like cages, on several split sites, including a C' site which is novel for this type of structure. According to the chemical analysis and the refined structure, the crystal-chemical formula is (Z = 1): $\{(Na_{1.40}K_{1.11}(H_2O)_{0.35}\square_{1.14})_{\Sigma4}[Ba_{0.35}(H_2O)_{3.65}]_{\Sigma4}\}$ $\{[Ca_{0.52}Sr_{0.40}(H_2O)_{2.60}\square_{0.48}]_{\Sigma4}[Ba_{0.19}(H_2O)_{3.81}]_{\Sigma4}\}\{[Sr_{0.28}(H_2O)_{3.72}]_{\Sigma4}[Ca_{0.84}\square_{3.16}]_{\Sigma4}\}$ $(Ca_{0.85}Mn_{0.05}Fe_{0.01}Zn_{0.03}\square_{1.06})_{\Sigma2}[Ti_{6.4}Nb_{1.60}]_{\Sigma8}(Si_{15.98}Al_{0.02}O_{48})[O_{3.12}(OH)_{4.88}]_{\Sigma8}$. The role of Ca in the structure of the vuoriyarvite subgroup and the genesis of tsepinite–Ca are discussed. The mineral was named by analogy with tsepinite–Na and tsepinite–K. Both the mineral and its name have been approved by the CNMMN–IMA. Type specimen is deposited at the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow.

Introduction

The minerals of the labuntsovite group are zeolite-like titano- and niobosilicates with a unique structure motif and have been intensively investigated in the last ten years (cf. CHUKANOV et al. 2002). As a result, now it is known that these minerals are characterised by a very wide range of chemical composition and significant structural modifications of a basic structure. More than 20 mineral species have been described which, according to their different structures, belong to subgroups on the basis of the nomenclature recently approved for the labuntsovite group by the IMA Commission on New Minerals and Mineral Names (CHUKANOV et al. 2002). Minerals of the labuntsovite group have been already described in 14 alkaline massifs

and in the Green River formation (Wyoming, USA), proving that they are not so rare as it was deemed earlier. Sometimes labuntsovite-like minerals form large segregations (tens of kg) and, according to our data, can behave as a major concentrator of Ti, Nb, Ba and Zn in the hydrothermalites connected with the agpaitic nepheline syenites (Khibiny and Lovozero massifs at Kola Peninsula) and carbonatites (Kovdor massif at Kola, Vyoriyarvi massif in Northern Karelia).

The minerals of the labuntsovite group are represented by the general formula $A_4B_4[C_{4-2x}(H_2O,OH)_{2x}]D_x[M_8(Si_4O_{12})_4(O,OH)_8] \cdot nH_2O$ ($0 < x < 1$, $n \sim 8$) where A and B are mainly alkalis; C and D sites can contain several types of cations (and anions), but exclude each other their distance being ~ 2 Å; M = Ti, Nb. The basic structure consists of a framework built up by chains of (Ti, Nb)–octahedra, which are linked by 4-membered rings of Si–tetrahedra to form a complex anion $[M_8(Si_4O_{12})_4(O,OH)_8]^{n-}$. The A, B, C and D sites occupy zeolite-like channels and cages; the octahedral D site is usually considered a part of the framework. Both monoclinic and orthorhombic members are known. In the orthorhombic case ($a \sim 7.5$, $b \sim 14.2$, $c \sim 7$ Å), the octahedral chains are straight and only two main extra-framework sites with 8- and 9-fold coordination occur. The monoclinic members ($a \sim 14.2$, $b \sim 13.8$, $c \sim 7.8$ Å) show double a and in some cases also double c. They contain a site A, which corresponds to the 9-fold site in the orthorhombic structure, and three sites B, C and D, which correspond to the 8-fold orthorhombic site. Because of the deformation of the framework and, in particular, of the zig-zag octahedral chains, the D site becomes larger in the monoclinic structures. Relative to the A site, the B site is larger and normally is filled by K; C = K, Ba, Sr, and H_2O when D is occupied by cations; D = Fe, Mg, Mn, Zn, rarely Ca. Splitting of the extra-framework sites is often observed, especially in members of the vuoriyarvite and close-related kuzmenkoite subgroup (cf. ORGANOVA et al. 1976, RASTSVETAEVA et al. 1994 and 1997, CHUKANOV et al. 1999, RAADE et al. 2002).

The high degree of cation selectivity and isomorphism, which takes place in all sites except the tetrahedral ones (Si), has attracted the attention of materials scientists searching for new microporous materials; labuntsovite-like (Ti, Nb)–silicate with a zeolite behaviour were recently synthesised and investigated in their properties (for a review see ROCHA & ANDERSON 2000). Recent results (PEKOV et al. 2002 c) show that the exchange properties of minerals of the labuntsovite group depend on structural features, like presence/absence of the D octahedron and cation ordering, and are particularly

evident in the vuoriyarvite subgroup. Unlike the fine-grained and often heterogeneous synthetic compounds, minerals of the labuntsovite group offer large crystals with a wide range of composition which are suitable for single-crystal methods of investigation and research on different properties including technologically important ones.

Tsepinite–Ca, a new mineral of the labuntsovite group was found in Khibiny alkaline massif at Kola Peninsula, Russia. It is the Ca-dominant analogue of tsepinite–Na (SHLYUKOVA et al. 2001) and tsepinite–K (CHUKANOV et al. 2003) and a member of the vuoriyarvite subgroup (Table 1). It was named according to the approved nomenclature for labuntsovite-group minerals (CHUKANOV et al. 2002): root-name was given (SHLYUKOVA et al. 2001) after A. I. TSEPIN (born 1946), a specialist in electron probe analysis who first obtained microprobe data for minerals of the labuntsovite group; the –Ca modifier shows the prevailing extraframework cation. Both mineral and name have been approved by the IMA Commission on New Minerals and Mineral Names (1st August 2002; IMA code 2002-020). The type specimen is deposited at the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow (registration no. 2877/1).

Occurrence and general appearance

Tsepinite–Ca was collected by one of the authors (IVP), in Summer 2000, at the underground works of the abandoned Lovchorrite mine which is situated in the upper part of Hackman Valley, Mount Yukspor, southern segment of the Khibiny massif. It was found in the hydrothermally altered zone of a large (>50 m long and up to 2 m thick in bulges) pegmatite vein crosscutting gneiss-like nepheline syenite. The outer parts of the vein consist of common minerals for this type of pegmatite: potassic feldspar, nepheline, aegirine and arfvedsonite with subordinate amounts of sodalite, albite, rinkite (mainly represented by its microcrystalline glue-like variety, the so-called "lovchorrite"), eudialyte, astrophyllite and fluorapatite. A lenticular cavernous polymineral nest (about $3 \times 3 \times 1$ m in size), situated within a large bulge, mainly consists of white to pale-yellowish coarse-grained microcline which, in the cavities crossing the massive body, also appears as thick-tabular and prismatic crystals up to 10–15 cm in size. Microcline is in parageneses with aggregates consisting of black needle-shaped aegirine, kupletskite, kentbrooksite, leucophanite and fluorapatite. The late hydrothermal assemblage contains crystals of natrolite, aegirine, kentbrooksite,

Table 1. Comparative data for minerals of the vuoriyarvite subgroup and the close related paratsepinite-Ba.

Mineral	Vuoriyarvite-K	Tsepinite-Na	Tsepinite-K	Tsepinite-Ca	Paratsepinite-Ba
Formula	$(K,Na)_2(Nb,Ti)_2$ $(Si_4O_{12})(O,OH)_2 \cdot 4H_2O$	$(Na,H_3O,K)_2(Ti,Nb)_2$ $(Si_4O_{12})(OH,O)_2 \cdot 3H_2O$	$(K,Ba,Na)_2(Ti,Nb)_2$ $(Si_4O_{12})(OH,O)_2 \cdot 3H_2O$	$(Ca,K,Na,\square)_2(Ti,Nb)_2$ $(Si_4O_{12})(OH,O)_2 \cdot 4H_2O$	$(Ba,Na,K)_{2-x}(Ti,Nb)_2$ $(Si_4O_{12})(OH,O)_2 \cdot 4H_2O$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Cm	Cm	Cm	$C2/m$	$C2/m$
Unit cell data					
a, Å	14.629	14.604	14.327	14.484	14.551
b, Å	14.164	14.274	13.802	14.191	14.001
c, Å	7.859	7.933	7.783	7.907	15.702
β, °	117.9	117.40	116.95	117.26	117.58
V, Å³	1446	1468	1372	1445	2835
Z	4	4	4	4	8
D_{meas}, g/cm³	2.95	2.74	2.88	2.73	2.88
Optical data					
α	1.649	1.655–1.658	1.689	1.666	1.667
β	1.655	1.661–1.668	1.700	1.676	1.674
γ	1.759	1.770	1.775	1.780	1.770
Optical sign, 2 V	$+20°$	$+19–31°$	$+35°$	$+30°$	$+30°$
Strongest lines in the X-ray powder pattern d, Å (I)	7.10 (9) 4.98 (6) 3.262 (10) 3.151 (8) 2.956 (6) 2.549 (4) 1.723 (4)	7.01 (4) 6.46 (10) 3.954 (3) 3.236 (10) 3.179 (3) 3.160 (4) 2.531 (3)	6.87 (10) 4.85 (5) 3.95 (5) 3.20 (6) 3.05 (8) 3.00 (6) 2.56 (9)	7.02 (6) 6.38 (4) 3.53 (4.5) 3.16 (10) 2.62 (4.5) 2.51 (8.5) 1.718 (5)	7.11 (10) 4.08 (8) 3.95 (10) 3.24 (9) 3.11 (8) 2.50 (7) 2.403 (8)
References	SUBBOTIN et al. 1998	SHLYUKOVA et al. 2001 RASTSVETAEVA et al. 2000	CHUKANOV et al. 2003 ROZENBERG et al. 2002 b	This work	CHUKANOV et al. 2003

kupletskite, Mn-rich lamprophyllite, fluorapatite, catapleiite, lorenzenite, vinogradovite, titanite, fluorapophyllite, tsepinite–Ca, ancylite–(Ce), and ancylite–(La), crusts of tainiolite and chabazite–Ca, and calcite which occurs in numerous cavities. Loose brown-black Mn oxides form pseudomorphs after Mn-bearing pectolite.

Tsepinite–Ca is mainly associated with natrolite and ancylite–(Ce) within specific cavities formed after leaching of pseudohexagonal prismatic rinkite crystals (up to $12 \times 1 \times 1$ cm in size). The new mineral forms coarse long-prismatic to needle-shaped crystals up to $0.2 \times 0.6 \times 5$ mm in size. The crystals are usually split and longitudinally streaked; they combine both in sheaf-like clusters up to 2×6 mm large and chaotic open-worked aggregates up to 1 cm as maximum dimension. The crystals are poorly terminated and, by analogy with tsepinite–Na, their major forms are probably {100} and {001}.

Physical and optical properties

Tsepinite–Ca is transparent, colourless to white and pale brownish. The streak is white and lustre is vitreous. Non-fluorescent in UV light. Brittle, cleavage is not observed, fracture uneven. Mohs' hardness 5. The density measured using heavy liquids is 2.73(1) g/cm^3, the calculated density is 2.72 g/cm^3. Tsepinite–Ca is biaxial (+), $2V_{meas} = 30 \pm 10°$, $2V_{calc} = 36°$; $\alpha = 1.666(2)$, $\beta = 1.676(2)$, $\gamma = 1.780(4)$. Dispersion is very weak: $r < v$. Under the microscope, the mineral is colourless, non-pleochroic; the orientation is $Y = b$.

IR-spectroscopy

The IR spectrum of tsepinite–Ca (Fig. 1) is similar to the spectra of tsepinite–Na and tsepinite–K. Absorption bands (in cm^{-1}, frequencies of the strongest bands are underlined, sh = shoulder, br = broad) are: <u>3260</u>br, 1645, 1610, <u>1103</u>, <u>946</u>, 745 sh, <u>673</u>, 572, 530 sh, <u>455</u>, 425 sh.

Among the monoclinic minerals of the labuntsovite group, the IR spectra of the members of the vuoriyarvite subgroup are characterized by very broad and poorly resolved bands. Actually, each observed band corresponds to the overlapping of narrower bands each one originated by coherent domains where the same type of occupancy in the disordered sites occurs. In fact, as discussed below, the crystal structure of tsepinite–Ca and, in gen-
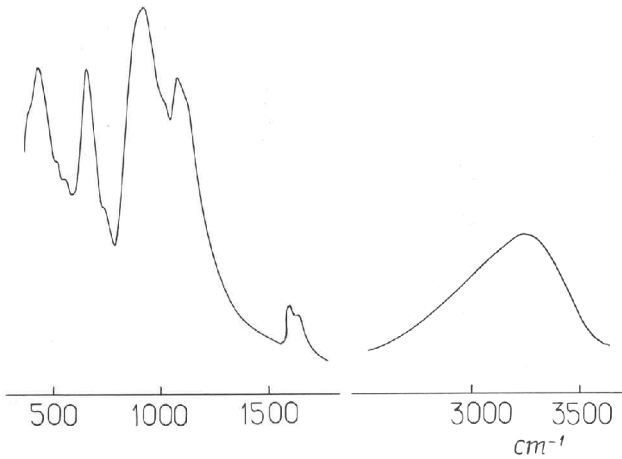
Fig. 1. IR spectrum of tsepinite–Ca.

eral, of the vuoriyarvite subgroup minerals is characterized by a large number of extra-framework (multiple split) sites which are randomly occupied by different cations, H_2O molecules and vacancies. The same situation is observed for minerals of the close-related kuzmenkoite subgroup which are characterized by high ($>50\%$) occupancy of the D site.

As it was shown elsewhere (RASTSVETAEVA & CHUKANOV 2002), in the basis of a first-order perturbation theory the active IR frequency ν of the Ti(Nb)–O stretching vibration in octahedral chains linearly depends on the percent occupancy x of the linking D octahedra. For the labuntsovite-group minerals, ν is higher or lower than $680\,cm^{-1}$ for x larger or smaller than 50% respectively. For tsepinite–Ca, the value of $673\,cm^{-1}$ gives to $x = 27 \pm 5\%$, which reasonably matches the value found by crystal structure determination (see below). Thus, a member of the vuoriyarvite subgroup can be reliably identified through the general broadening of its IR bands and the shift towards lower frequencies ($<680\,cm^{-1}$) of its Ti(Nb)–O stretching frequency. A characteristic feature of tsepinite–Ca relative to most of the vuoriyarvite subgroup minerals is the shift toward low-frequencies (towards $3260\,cm^{-1}$ instead of the usually observed range $3330–3370\,cm^{-1}$) of the O–H stretching vibrations. That should mean presence of stronger hydrogen bonds established by the H_2O molecules.

Chemical composition

The cation composition of tsepinite–Ca was obtained by a Camebax SX 50 electron microprobe operating at 15 kV and 30 nA estimated beam-current. The electron beam was rastered over $10 \times 10\,\mu m^2$ to minimise sample damage. Standards were: albite (Na, Al), orthoclase (K), amphibole (Ca, Fe, Si), $SrSO_4$ (Sr), $BaSO_4$ (Ba), $MnTiO_3$ (Mn, Ti), ZnO (Zn), and $LiNbO_3$ (Nb). The average value of 10 analyses (wt.%, ranges in brackets) is: Na_2O 1.32 (1.0–1.8), K_2O 2.23 (2.0–2.6), CaO 5.29 (4.6–6.3), SrO 3.01 (2.3–3.3),
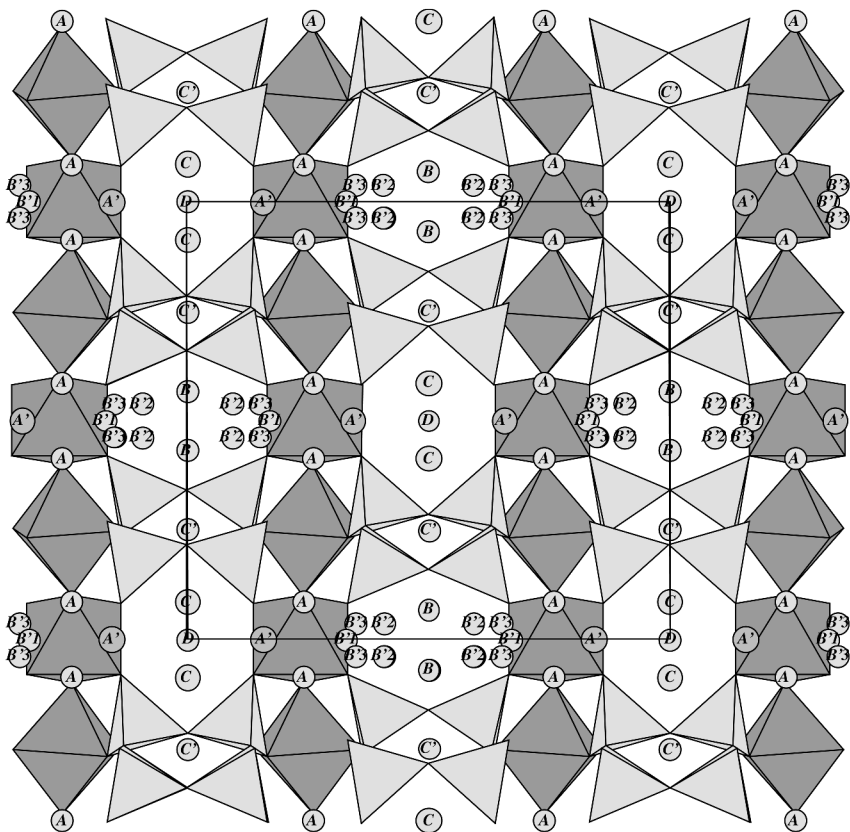
Fig. 2. Crystal structure of tsepinite–Ca seen along [001]. The extra-framework sites are shown with their labels (see text); *A, B'2* and *B'3* are close to a mirror plane and, at random, only 50% maximum of the shown positions are occupied.

Table 2. Experimental and refinement conditions, and crystal data for tsepinite-Ca.

Simplified chemical formula	$(Ca, K, Na, \square)_2(Ti, Nb)_2(Si_4O_{12})(OH, O)_2 \cdot 4H_2O$
Radiation and wavelength, Å	MoK_α; 0.71069
μ, mm^{-1}	2.95
Diffractometer; monochrom.	Siemens $P4$; graphite
Space group; Z	$C2/m$; 4
Unit-cell dimensions, Å	$a = 14.484\,(4)$, $b = 14.191\,(4)$, $c = 7.907(2)$, $\beta = 117.26\,(2)^\circ$
Unit-cell volume, Å^3	1445 (1)
D (calc.), g/cm^3	2.72
D (meas.), g/cm^3	2.73 (1)
Crystal size, mm	$0.25 \times 0.06 \times 0.02$
Index ranges	$-0 \leq h \leq 20$, $-19 \leq k \leq 19$, $-10 \leq l \leq 9$
Check reflections	4 every 100 reflections
Collected reflections	4321
Indep. reflect. with $I > 2\sigma\,(I)$	1559; $R_{int} = 0.1(1)$
Refinement method	full-matrix least-squares on F^2
Weights	$1/[\sigma(Fo)^2 + (0.085P)^2 + (67.6P)]$, $P = [\max(Fo)^2 + 2(Fc)^2]$
R(F), R(F^2), Goof	0.11; 0.30; 1.11
Number of refined parameters	154
Largest residues (e/Å^3)	1.94; -1.35

BaO 3.52 (1.1–6.4), MnO 0.16 (0.0–0.3), FeO 0.04 (0.0–0.1), ZnO 0.12 (0.0–0.4), Al$_2$O$_3$ 0.04 (0.0–0.1), SiO$_2$ 41.06 (40.1–43.6), TiO$_2$ 21.95 (21.4–23.3), Nb$_2$O$_5$ 9.08 (8.3–9.5), H$_2$O 13.30 (thermogravimetric analysis), total 101.12. The Mg, *REE*, Zr, Ta and F contents were found to be below the detection limits, i.e. <0.01–0.05 %.

The empirical formula, based on Si + Al = 8 and OH/O ratio from charge balance, is $(Ca_{1.10}K_{0.55}Na_{0.50}Sr_{0.34}Ba_{0.27}Mn_{0.03}Zn_{0.02}Fe_{0.01})_{\Sigma 2.82}(Ti_{3.21}Nb_{0.80})_{\Sigma 4.01}(Si_{7.99}Al_{0.01})_{\Sigma 8}O_{24}[(OH)_{2.58}O_{1.42}]_{\Sigma 4} \cdot 7.35H_2O$ with $Z = 2$. The idealised formula of tsepinite–Ca is $(Ca,K,Na,\square)_2(Ti,Nb)_2(Si_4O_{12})(OH,O)_2 \cdot 4H_2O$ ($Z=4$) which, for CaK$_{0.5}$Na$_{0.5}$Ti$_2$Si$_4$O$_{12}$O(OH)$\cdot$4H$_2$O), requires: Na$_2$O 2.69, K$_2$O 4.09, CaO 9.73, SiO$_2$ 41.69, TiO$_2$ 27.73, H$_2$O 14.07, total 100.00 wt.%. The compatibility index (1–Kp/Kc) is 0.026 and 0.021 if D_{meas} and D_{calc} is used, respectively, i.e. excellent according to MANDARINO (1981).

X-ray crystallography

Single-crystal diffraction data for tsepinite–Ca were collected on a Siemens $P4$ diffractometer; information on data collection and structure refinement

Table 3. X-ray powder data of tsepinite-Ca.

I_{obs}	d_{obs}, Å	d_{calc}, Å	h	k	l						
60	7.02	7.096	0	2	0						
		7.029	0	0	1						
40	6.38	6.438	2	0	−1	2	0	0			
25	5.01	4.993	0	2	1						
5	4.85	4.917	1	1	1						
		4.768	2	2	−1						
10	3.88	3.934	2	0	−2	2	0	1			
45	3.53	3.512	1	3	1						
100	3.16	3.167	0	4	1						
		3.149	0	2	2						
20	2.97	2.985	1	1	2						
30	2.93	2.932	4	2	−2						
		2.931	4	2	0						
30	2.78	2.824	5	1	−1						
		2.772	1	5	0						
45	2.62	2.621	2	0	−3	2	0	2			
85	2.51	2.534	4	4	−1						
		2.522	4	0	−3						
		2.497	0	4	2						
5	2.39	2.438	3	5	−1						
		2.379	6	0	−2	6	0	−1			
10	2.35	2.367	3	5	0						
		2.365	0	6	0						
25	2.25	2.244	3	5	−2						
		2.242	0	6	1						
25	2.05	2.089	3	5	1						
		2.056	4	4	−3						
		2.055	4	4	1						
20	1.953	1.962	0	6	2						
		1.955	0	4	3						
10	1.885	1.896	4	2	−4	4	2	2			
20	1.806	1.811	8	0	−2						
5	1.763	1.767	3	5	2						
		1.757	0	0	4						
50	1.718	1.725	4	6	−3	4	6	1			
		1.720	4	4	−4	4	4	2	0	8	1
10	1.659	1.664	0	6	3						
10	1.637	1.632	1	1	4						
10	1.572	1.572	8	4	−3	8	4	−1			
		1.570	8	2	−4	8	2	0			
40	1.450	1.451	4	8	−3	4	8	1			
30	1.307	1.307	0	4	5						

Indices $h\,k\,l$ are chosen taking into account I_{calc} obtained from the structural data.

Table 4. Atom coordinates, number of electrons per site (e_{ref}) when refined, and equivalent displacement factors U_{eq} (Å^2). Estimated standard deviation in parentheses.

Site*	x	y	z	e_{ref}	U_{eq}**
Si1	0.2004 (2)	0.1114 (2)	0.7911 (4)	–	0.0174 (7)
Si2	0.6887 (2)	0.8894 (2)	0.7648 (4)	–	0.0171 (7)
M1 (Ti vs Nb)	0	0.7583 (2)	1/2	25.5 (3)	0.027 (1)
M2 (Ti vs Nb)	3/4	3/4	1/2	25.2 (3)	0.033 (1)
A (K)	0.4134 (9)	0.7401 (9)	−0.000 (2)	5.5 (3)	0.049 (4)
A' (K vs O)	1/2	0.657 (3)	0	12.1 (3)	0.23 (2)
B (Ca)	0.432 (2)	0	0.700 (3)	10.5 (3)	0.15 (1)
B'1 (O)	1/2	0.829 (3)	0	6.8 (3)	0.12 (2)
B'2 (O)	0.462 (3)	0.907 (4)	−0.149 (6)	1.2 (3)	0.02 (1)
B'3 (O)	0.462 (2)	0.849 (2)	−0.153 (4)	1.9 (3)	0.02 (1)
C (Sr vs O)	0.086 (2)	0	0.330 (2)	10.2 (3)	0.10 (1)
C' (Ca)	0.251 (1)	0	0.501 (2)	3.9 (2)	0.015 (4)
D (Ca)	0	0	1/2	9.0 (1)	0.024 (3)
O1	0.9001 (6)	0.7605 (6)	0.602 (1)	–	0.023 (2)
O2	0.9194 (7)	0.8626 (7)	0.326 (2)	–	0.040 (3)
O3	0.2482 (8)	0.8605 (7)	0.342 (1)	–	0.037 (2)
O4	0.2694 (7)	0.8334 (8)	0.709 (1)	–	0.037 (2)
O5	0.4190 (7)	0.8331 (7)	0.308 (2)	–	0.044 (3)
O6	0.340 (1)	0	0.254 (2)	–	0.049 (4)
O7	0.2418 (8)	0.8689 (6)	0.014 (1)	–	0.037 (2)
O8	0.215 (2)	0	0.762 (2)	–	0.045 (4)

* When the site is labelled by a non-chemical symbol, the scattering curve used in the refinement is indicated in parentheses.
** Isotropic U (Å^2) for C', B'2 and B'3.

is given in Table 2. The mineral is monoclinic, space group $C2/m$. The unit cell dimensions were refined from the coordinates of 22 single-crystal reflections and are: a = 14.484(4), b = 14.191(4), c = 7.907(2) Å, β = 117.26 (2)°, V = 1445(1) Å^3. The X-ray powder pattern of tsepinite–Ca given in Table 3 was obtained using an RKG 86 mm camera and Mn-filtered FeKα-radiation. This pattern is close to those of other members of the vuoriyarvite subgroup.

Table 5. Number of electrons per site according to the refinement (e_{ref}) and the atomic content per cell assigned to the sites (e_{ass}).

Site*	e_{ref}**	e_{ass}	Content of the site per cell
A (8)	5.5 (3)	4.9	$[Na_{1.40}K_{1.11}(H_2O)_{0.35}\square_{1.14}]_{\Sigma 4}$
A' (4)	12.1 (3)	12.2	$[Ba_{0.35}(H_2O)_{3.65}]_{\Sigma 4}$
B (4)	10.5 (3)	11.6	$[Ca_{0.52}Sr_{0.40}(H_2O)_{2.6}\square_{0.48}]_{\Sigma 4}$
B' (4 + 8 + 8)	9.9 (3)	10.3	$[Ba_{0.19}(H_2O)_{3.81}]_{\Sigma 4}$
C (4)	10.2 (3)	10.1	$[Sr_{0.28}(H_2O)_{3.72}]_{\Sigma 4}$
C' (4)	3.9 (2)	4.2	$(Ca_{0.84}\square_{3.16})_{\Sigma 4}$
D (2)	9.0 (1)	9.7	$(Ca_{0.85}Mn_{0.05}Fe_{0.01}Zn_{0.03}\square_{1.06})_{\Sigma 2}$
$M1 + M2$ (4 + 4)	50.6 (3)	51.6	$(Ti_{6.40}Nb_{1.60})_{\Sigma 8}$

* The multiplicity of the site (Wykoff position) is given in parentheses. Because of closeness, the ideal multiplicity indicated as 8 for A and B' reduces to 4.

** Estimated standard deviation in parentheses.

Crystal structure

Starting from the coordinates of the framework atoms, the crystal structure (Fig. 2) has been completed by Fourier methods and anisotropically (except some disordered site as shown in Table 4) refined (SHELX–97; SHELDRICK 1997; Table 2) in the space group $C2/m$. Attempts to refine the structure either in the Cm or $C2$ space group and to introduce twinning by merohedry failed. The high value of R (0.11 for 1559 observed reflections) is related to the low quality of the available crystals and to structural disorder in the extra-framework sites that is typical of the vuoriyarvite subgroup, as discussed below. Disorder is also responsible of the quite high displacement factors shown by some atom position as usual in this type of structures. The space group $C2/m$ showed by the average structure, unlike tsepinite–Na and tsepinite–K refined in Cm, is presumably favoured by a slightly different distribution of the extra-framework cations and water molecules in the zeolite-like channels and the degree and extent of long range order. The same situation takes place in the kuzmenkoite subgroup of the labuntsovite group (see CHUKANOV et al. 2002). Structural parameters, occupancies of sites and bond lengths are given in Tables 4, 5 and 6 respectively.

With respect to the labuntsovite-type structure described in the Introduction, the main features of the structure of tsepinite–Ca are as follows.

a) The sites usually occupied by H_2O in labuntsovites and labelled $W1$ and $W2$ in literature, have an electron content higher than 8 (Table 4) and

Table 6. Selected bond lengths (Å) for tsepinite-Ca. Estimated standard deviations in parentheses. For the content of the sites *A, A′, B, B′, C, C′,* and *M* see Table 5.

Si1–O2	1.591 (9)	Si2–O3	1.560 (1)	*B*– *B′* 2×2	1.70 (2)
O7	1.601 (9)	O7	1.598 (9)	*B′* 3×2	2.39 (3)
O4	1.62 (1)	O5	1.606 (9)	O6	3.14 (3)
O8	1.626 (5)	O6	1.612 (5)	O6	3.16 (3)
Average	1.610 (6)	Average	1.594 (5)	*B′* 1×2	3.21 (4)
				O5×2	3.22 (2)
*M*1–O5×2	1.934 (9)	*M*2–O4×2	1.948 (9)	O4×2	3.36 (2)
O1×2	1.951 (7)	O1×2	1.948 (7)	O8	3.39 (4)
O2×2	1.992 (9)	O3×2	1.995 (9)	*B′* 2×2	3.43 (4)
Average	1.959 (4)	Average	1.964 (4)	O3×2	3.48 (3)
C– O3×2	3.03 (2)	*A*– *A′*	1.72 (3)	*B′* 1–*A*×2	1.78 (4)
O8	3.05 (2)	*B′* 1	1.78 (4)	*A′*	2.45 (7)
O2×2	3.10 (2)	*B′* 3	2.25 (3)	O4×2	3.068 (9)
A′×2	3.21 (3)	*B′* 3	2.26 (3)	O1×2	3.08 (2)
O2×2	3.38 (2)	O4	2.64 (2)	O5×2	3.15 (1)
O1×2	3.43 (2)	O7	2.69 (2)	*B*×2	3.21 (4)
		O5	2.74 (2)		
C′– O3×2	2.34 (1)	*B′* 2	2.87 (5)	*B′* 2–*B*	1.70 (2)
O8	2.34 (2)	*B′* 2	2.88 (5)	O4	2.70 (5)
B	2.36 (3)	O2	2.93 (2)	O5	2.75 (5)
O6	2.78 (2)	O3	3.00 (2)	*A*	2.87 (5)
O4×2	2.82 (1)	O1	3.06 (2)	*A*	2.88 (5)
		O1	3.07 (2)	O1	2.95 (5)
D– *C*×2	2.22 (2)	O7	3.13 (2)		
O2×4	2.36 (1)			*B′* 3–*A*	2.25 (3)
Average	2.310 (7)	*A′*– *A*×2	1.72 (3)	*A*	2.26 (3)
		B′ 1	2.45 (7)	O1	2.31 (3)
		B′ 3×2	2.93 (5)	*B*	2.39 (3)
		O1×2	3.04 (2)	O4	2.50 (3)
				O5	2.53 (3)
				A′	2.93 (5)

therefore cannot contain only oxygen atoms. The *W*2 (on the mirror plane) and *W*1 (see below for splitting) sites being, in the order, close to *A* [*A*–W2 = 1.72(3) Å] and *B* [*B*–W1 = 1.70(5) Å] are here labelled *A′* and *B′*, respectively. Note that in gjerdingenite–Fe (Raade et al. 2002) *W*1

has been labelled B' being the A site empty, as in all members of the kuz-menkoite subgroup. The A' site corresponds to the site which has been labelled $A2$ in some labuntsovites refined in the space group Cm (ROZEN-BERG et al. 2002 a, ROZENBERG et al. 2002 c).

b) The B' site ($W1$) is split on three positions (Table 4): $B'1$ has multiplicity 4, being on the mirror plane; $B'2$ and $B'3$ are in general position with ideal multiplicity 8 which is reduced to 4 because of closeness to the mirror plane [$B'2–B'2 = 2.10(9)$ Å; $B'3–B'3 = 2.15(6)$ Å] and consequent maximum occupancy of 50 %. Further, because of their closeness [$B'1–B'2 = 1.52(6)$ Å; $B'1–B'3 = 1.11(3)$ Å; $B'2–B'3 = 0.82(5)$ Å] only one out of three B' sites can be occupied at the same time; consequently, on the whole, the multiplicity of B' is lowered to 4.

c) In the known structures of the labuntsovite group, for the first time a site surrounded by six oxygen atoms (Table 6) appears between the C and B sites within the [001] channel. This site is close to C [$C–C' = 2.13(3)$ Å; $B–C' = 2.37(3)$ Å] and is named C'.

d) The D site has by far more electrons (Table 5) than those allowed by the chemical elements (Fe, Mn, Zn in the present case) which usually are put in this site according to crystal-chemical considerations. By comparison with karupmøllerite–Ca (YAMNOVA et al. 2000, PEKOV et al. 2002 a), Ca is taken as further cation partially occupying the C' and D sites [see also RASTSVETAEVA & CHUKANOV (2002)].
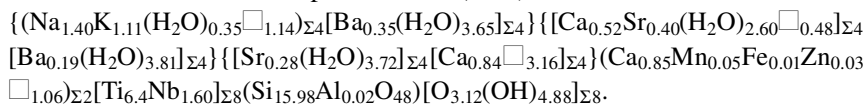
Taking into account the number of split sites and their maximum occupancy, for the present purposes the general formula of the labuntsovite-type minerals given in the Introduction is re-written as $\{A_4A'_4\}\{B_4B'_4\}\{C'_y C_{4-2x}(H_2O,OH)_{2x}\}D_z[M_8(Si_4O_{12})_4(OH,O)_8]$ [$z \leq x$; y is constraint by the content of C and B (see below)]. The distribution of cations and H_2O molecules in the sites to obtain a crystal-chemical formula (Table 5), must take into account the following arguments.

1. The content of refined electrons in the sites (Tables 4 and 5).

2. Crystal-chemical considerations, like ionic radii and coordination number.

3. The A' site must be fully occupied by H_2O molecules plus cations to account for its number of electrons (Table 4).

4. The A site is sufficiently distant from the framework oxygen atoms (Table 6) to contain either cation or H_2O molecules. Because of closeness to the mirror plane [$A–A = 2.51(2)$ Å] the A site is at maximum 50 % statistically occupied, if only cations occur in it. In case that some H_2O mole-

cules stay in it, an O…O distance of 2.51(2) Å is suitable for hydrogen bonding (CHIARI & FERRARIS 1982). Note that, in the present labuntsovite-group mineral, the IR spectrum indicates the presence of shorter than usual hydrogen bonds. The short distance $A–A' = 1.72(3)$ Å excludes the simultaneous presence of both cations and H_2O molecules in the two sites. One can assume instead a simultaneous presence of a cation in one site and H_2O in the other, on the reasonable hypothesis that, as indicated by the high displacement factors (Table 4), cations and H_2O molecules occupy substantially different (even if close) positions within their coordination sphere. On the whole, the content of H_2O molecules in the A site cannot be higher than that of cations in the A' site because, as said above, the latter site is fully occupied. Similar considerations can be applied to the short distances $A–B'$ (Table 6). In particular, being the B' site only partially occupied, the simultaneous occupancy of the A and B' sites can be locally arranged such to avoid unreasonable cation-cation and oxygen-oxygen distances.

5. The B' and C sites show distances (Table 6) which are suitable for O…O hydrogen bonding, thus they can contain either cations or H_2O. The same situation holds for the B site except for the short distances $B–B'3$, 2.39(3) Å, and $B–B'2$, 1.70(5) Å; however, vacancies, cations, and H_2O can be locally distributed in the B and B' sites such to avoid short O…O contacts.

6. The C' and D sites cannot contain H_2O because they are too close to at least one framework oxygen atom (Table 6). Because of short distances, C' can be occupied only if both B and C do not contain cations.

7. The number z of cations in D (multiplicity 2) cannot be higher than the number of oxygens in C (multiplicity 4).

Taking into account the described constraints and the chemical analysis, Table 5 shows the distribution of cations and H_2O molecules in the crystallographic sites with mixed occupancy. According to the data of Table 5 and the general formula with split sites, which has been given above, the crystal-chemical formula of tsepinite–Ca is ($Z=1$):

$\{(Na_{1.40}K_{1.11}(H_2O)_{0.35}\square_{1.14})_{\Sigma4}[Ba_{0.35}(H_2O)_{3.65}]_{\Sigma4}\}\{[Ca_{0.52}Sr_{0.40}(H_2O)_{2.60}\square_{0.48}]_{\Sigma4}$ $[Ba_{0.19}(H_2O)_{3.81}]_{\Sigma4}\}\{[Sr_{0.28}(H_2O)_{3.72}]_{\Sigma4}[Ca_{0.84}\square_{3.16}]_{\Sigma4}\}(Ca_{0.85}Mn_{0.05}Fe_{0.01}Zn_{0.03}$ $\square_{1.06})_{\Sigma2}[Ti_{6.4}Nb_{1.60}]_{\Sigma8}(Si_{15.98}Al_{0.02}O_{48})[O_{3.12}(OH)_{4.88}]_{\Sigma8}$.

Strictly speaking, the given crystal-chemical formula is not completely constrained by the available constraints, however only minor alternatives can be expected if the experimental chemical composition and electron con-

tents of the sites must be satisfied. In particular, the crystal-chemical composition fully agrees with the chemical analysis except minor discrepancies for Na_2O (1.83 against 1.32 %) and H_2O (12.63 against 13.30 %). However, both the alkalis and water have large mobility in the minerals of the labuntsovite group because of the zeolite-like channels. Due to the large disorder affecting the structure, bond-valence calculations are not straightforward. Anyway, it is easy to see that O1, the only framework oxygen not bonded to Si (Table 6), is the most underbonded oxygen atom. Consequently, as in other minerals of the labuntsovite group (e.g. gjerdingenite–Fe; RAADE et al. 2002), O1 represents the about 5 hydroxyls per formula unit shown in the crystal-chemical formula of tsepinite–Ca. In some cases, [RASTSVE-TAEVA et al. 2000; see RASTSVETAEVA & CHUKANOV (2002) for a review, including IR spectra] a presence of $(H_3O)^+$ has been supposed in extra-framework sites. However, so far no direct proofs of such presence have been published. On the other side, in tsepinite–Ca the underbonded O1 can represent enough OH to satisfy the charge balance.

Discussion

In accordance with the accepted nomenclature for labuntsovite-group minerals (CHUKANOV et al. 2002), tsepinite–Ca is a member of the vuoriyarvite subgroup because of two major criteria: 1) the D site is mainly vacant, i.e. the number of vacancies is larger than the sum of the cations; 2) the extra-framework cations occupy numerous (>3) cation-deficient sites in the zeolite-like channels. However, tsepinite–Ca is peculiar in the vuoriyarvite subgroup and among the other described tsepinites, because of the presence in its structure of the so far unreported extra-framework C' site. This peculiarity and, in general, the unusually high number of split sites, is presumably related to the high content of Ca in tsepinite–Ca (see below). A future discovery of members with higher occupancy of C' might lead to a subdivision of the vuoriyarvite subgroup to emphasise the role of the split sites, in particular of C'.

Ca in the D site was firstly reported for the so-called "monoclinic nenadkevichite" (ORGANOVA et al. 1976). Like tsepinites, recently described karupmøllerite–Ca, $(Na,Ca,K)_2Ca(Nb,Ti)_4(Si_4O_{12})_2(O,OH)_4 \cdot 7H_2O$, which is a member of the labuntsovite group highly enriched in Ca, contains Ca in both the framework D site (significantly prevails in it) and in the extra-framework B site (YAMNOVA et al. 2000, PEKOV et al. 2002 a). The structural

role of Ca in the labuntsovite-group minerals is thus double: it can be a species-forming cation both in the framework (D site) and extra-framework sites. This possibility makes Ca peculiar among all other cations which occur only in either framework (tetrahedra – Si; M octahedra in chains – Ti and Nb; D linking octahedron – Mn, Fe, Mg, Zn) or extra-framework sites (Na, K, Ba, Sr). Thanks to the intermediate value of its ionic radius, as in other mineral groups, also in the labuntsovite group Ca^{2+} can replace both the usual bivalent smaller D cations (Mn^{2+}, Fe^{2+}, Mg^{2+} and Zn^{2+}) and the typical extra-framework larger cations, Ba^{2+} and Sr^{2+}. Among labuntsovite-type minerals, tsepinites, which represent the Ti-dominant members of the vuoriyarvite subgroup, are the most important concentrators of Ca. In tsepinites, most of Ca occurs in the zeolite-like channels and is usually distributed among several partially occupied and split sites (Table 5). Instead, in the gutkovaite subgroup members, which are characterised by a strict ordering of the extra-framework cations, all Ca is concentrated in the $A1$ site. This latter site is either completely occupied by Ca in gutkovaite–Mn, $CaK_2Mn(Ti,Nb)_4(Si_4O_{12})_2(O,OH)_4 \cdot 5H_2O$ (PEKOV et al. 2002 b), or by Ca and Na in alsakharovite–Zn, $(Na,Ca)SrKZn(Ti,Nb)_4[Si_4O_{12}]_2(O,OH)_4 \cdot 7H_2O$ (PEKOV et al. 2003).

Tsepinite–Ca mainly occurs in cavities after leaching of rinkite from which can inherit some chemical constituents. According to our and KOSTY-LEVA-LABUNTSOVA et al. (1978) data, the major constituents of fresh rinkite from the pegmatites of Hackman Valley are in the following ranges (wt.%): Na_2O 5–7, CaO 24–28, SrO 1–4, REE_2O_3 13–17, SiO_2 27–30, TiO_2 8–12, Nb_2O_5 2–4, F 5–7. In a previous occasion we observed both replacement of several titanoan and/or niobian minerals by labuntsovite-group members and crystallisation of the labuntsovites in cavities originated by the leaching of the former minerals. The observed proto-phases were usually lomonosovite/murmanite, vuonnemite/epistolite and sometimes lorenzenite, lamprophyllite, astrophyllite, loparite, and pyrochlore. The inheritance by labuntsovites of low-mobile constituents, which come from the proto-minerals, is a usual phenomenon. For example, it has been reported for pseudomorphs of both Nb-dominant members after vuonnemite, $Na_5Nb_3Ti(Si_2O_7)_3O_2F_2 \cdot 2Na_3PO_4$, and Ti-dominant members after lomonosovite, $Na_2Ti_2Si_2O_9 \cdot Na_3PO_4$, and typically occurs in many pegmatites of Lovozero and Khibiny massifs, Kola, and Ilímaussaq complex, South Greenland (PEKOV et al. 2002 a). Instead, Zn–enriched labuntsovites were formed only close to cavities after complete or partial leaching of sphalerite (PEKOV et al. in press).

Apparently, tsepinite – Ca inherits Si, Ti (with Nb) and Ca (with Sr) from rinkite whereas closely associated ancylite – (Ce) accumulates *REE*. In conclusion, the dominance of Ca among the extraframework cations in tsepinite – Ca is a result of its formation after leaching of the Ca-bearing mineral rinkite.

Acknowledgements

References

CHIARI, G. & FERRARIS, G. (1982): The water molecule in crystalline hydrates studied by neutron diffraction. – Acta Cryst. **B 38:** 2331–2341.

CHUKANOV, N. V., PEKOV, I. V., RASTSVETAEVA, R. K. & NEKRASOV, A. N. (1999): Labuntsovite: solid solutions and features of the crystal structure. – Can. Miner. **37:** 901–910.

CHUKANOV, N. V., PEKOV, I. V. & KHOMYAKOV, A. P. (2002): Recommended nomenclature for labuntsovite group minerals. – Eur. J. Miner. **14:** 166–173.

CHUKANOV, N. V., PEKOV, I. V., ZADOV, A. E., ROZENBERG, K. A., RASTSVETAEVA, R. K. & KRIVOVICHEV, S. V. (2003): New minerals tsepinite – K and paratsepinite – Ba and their relationship with other members of the labuntsovite group. – Zapiski VMO **132** (1): 38–51 (in Russian).

KOSTYLEVA-LABUNTSOVA, E. E., BORUTSKIY, B. E., SOKOLOVA, M. N., SHLYUKOVA, Z. V., DORFMAN, M. D., DUDKIN, O. B. & KOZYREVA, L. V. (1978): The Mineralogy of the Khibiny Massif. Vol. 2. Nauka Publishing, Moscow, 586 pp. (in Russian).

MANDARINO, J. A. (1981): The Gladstone-Dale relationship. VI. The compatibility concept and its application. – Can. Miner. **19:** 441–450.

ORGANOVA, N. I., SHLYUKOVA, Z. V., ZABAVNIKOVA, N. I., PLATONOV, A. N. & RUDNITSKAYA, E. S. (1976): On crystal chemistry of labuntsovite and nenadkevichite. – Izvestiya AN SSSR, ser. geol. **2:** 98–116 (in Russian).

PEKOV, I. V., CHUKANOV, N. V., PETERSEN, O. V., ZADOV, A. E., YAMNOVA, N. A., KABALOV, Y. K. & SCHNEIDER, J. (2002 a): Karupmøllerite–Ca, $(Na,Ca,K)_2Ca(Nb,Ti)_4(Si_4O_{12})_2(O,OH)_4 \cdot 7H_2O$, a new mineral of the labuntsovite group from the Ilímaussaq alkaline complex, South Greenland. – N. Jb. Miner. Mh. **2002:** 433–444.

PEKOV, I. V., CHUKANOV, N. V., RASTSVETAEVA, R. K., ZADOV, A. E. & KONONKOVA, N. N. (2002 b): Gutkovaite–Mn, $CaK_2Mn(Ti,Nb)_4(Si_4O_{12})_2(O,OH)_4 \cdot 5H_2O$, a new mineral of the labuntsovite group from the Khibiny alkaline massif, Kola Peninsula. – Zapiski VMO **131** (2): 54–60 (in Russian).

PEKOV, I. V., TURCHKOVA, A. G., KONONKOVA, N. N. & CHUKANOV, N. V. (2002 c): A study of cation-exchange properties of labuntsovite group minerals. I. Experiment in water solutions under the normal conditions. – Materials of All-Russian Conference "Alkaline Magmatism of the Earth". Moscow, 76 (in Russian).

PEKOV, I. V., CHUKANOV, N. V., ZADOV, A. E., ROZENBERG, K. A. & RASTSVETAEVA, R. K. (2003): Alsakharovite–Zn, $NaSrKZn(Ti,Nb)_4[Si_4O_{12}]_2(O,OH)_4 \cdot 7H_2O$, a new mineral of the labuntsovite group from the Lovozero alkaline massif, Kola Peninsula. – Zapiski VMO **132** (1): 52–58 (in Russian).

RAADE, G., FERRARIS, G., GULA, A. & IVALDI, G. (2002): Gjerdingenite–Fe from Norway, a new mineral species in the labuntsovite group: description, crystal structure and twinning. – Can. Miner. **40:** 1583–1594.

RASTSVETAEVA, R. K., TAMAZYAN, R. A., PUSHCHAROVSKY, D. YU. & NADEZHINA, T. N. (1994): Crystal structure and microtwinning of K-rich nenadkevichite. – Eur. J. Miner. **6:** 503–509.

RASTSVETAEVA, R. K., CHUKANOV, N. V. & PEKOV, I. V. (1997): Crystal structure of new mineral – Analogue of labuntsovite with high ordering of potassium and barium. – Dokl. Chem. **357:** 244–247.

RASTSVETAEVA, R. K., ORGANOVA, N. I., ROZHDESTVENSKAYA, I. V., SHLYUKOVA, Z. V. & CHUKANOV, N. V. (2000): Crystal structure of oxonium mineral of the nenadkevichite–labuntsovite group from Khibina massif. – Dokl. Chem. **371:** 52–56.

RASTSVETAEVA, R. K. & CHUKANOV, N. V. (2002): X-ray diffraction and IR spectroscopy study of labuntsovite-group minerals. – Crystallogr. Reports **47:** 939–945.

ROCHA, A. & ANDERSON, M. W. (2000): Microporous titanosilicates and other novel mixed octahedral-tetrahedral framework oxides. – Eur. J. Inorg. Chem.: 801–818.

ROZENBERG, K. A., RASTSVETAEVA, R. K., PEKOV, I. V. & CHUKANOV, N. V. (2002 a): New zinc-rich representative of the labuntsovite group: Crystal structure and microtwinning. – Dokl. Chem. **383:** 110–113.

Rozenberg, K. A., Rastsvetaeva, R. K., Chukanov, N. V. & Pekov, I. V. (2002 b): Crystal structure of the new mineral tsepinite – K. – Dokl. Chem. **386:** 246 – 250.

Rozenberg, K. A., Rastsvetaeva, R. K., Chukanov, N. V. & Subbotin, V. V. (2002 c): Acentric niobium-rich analogue of labuntsovite – Fe: Crystal structure and microtwinning. – Crystallogr. Reports **47:** 408 – 411.

Sheldrick, G. M. (1997): SHELX – 97: Program for the solution and refinement of crystal structures. – Siemens Energy and Automation, Madison, WI.

Shlyukova, Z. V., Chukanov, N. V., Pekov, I. V., Rastsvetaeva, R. K., Organova, N. I. & Zadov, A. E. (2001): Tsepinite – Na, $(Na,H_3O,K,Sr,Ba)_2(Ti,Nb)_2[Si_4O_{12}](OH,O)_2 \cdot 3H_2O$, a new labuntsovite group mineral. – Zapiski VMO **130** (3): 43 – 50 (in Russian).

Subbotin, V. V., Voloshin, A. V., Pakhomovskii, Ya. A., Bakhchisaraitsev, A. Yu., Pushcharovsky, D. Yu., Rastsvetaeva, R. K. & Nadezhina, T. N. (1998): Vuoriyarvite, $(K,Na)_2(Nb,Ti)_2Si_4O_{12}(O,OH)_2 \cdot 4H_2O$, a new mineral from carbonatites of Vuoriyarvi, Kola Peninsula. – Doklady RAN **358:** 517 – 519 (in Russian).

Yamnova, N. A., Pekov, I. V., Kabalov, Yu. K., Schneider, J. & Chukanov, N. V. (2000): Crystal structure of a new Ca, Nb-representative of the labuntsovite group. – Dokl. Chem. **375:** 263 – 266.

Authors' addresses:

I. V. Pekov, D. Yu. Pushcharovsky, Faculty of Geology, Moscow State University, Vorobievy Gory, 119899 Moscow, Russia.

N. V. Chukanov, Institute of Problems of Chemical Physics, 142432 Chernogolovka, Moscow Oblast, Russia.

G. Ferraris, A. Gula, Department of Mineralogy and Petrology (University of Torino), and Institute of Geosciences and Georesources (CNR), Via Valperga Caluso 35, I-10125 Torino, Italy.

A. E. Zadov, NPO Regenerator, Skladochnaya ul. 6, 127018 Moscow, Russia.

Correspondence author: G. Ferraris E-mail: giovanni.ferraris@unito.it