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TSEPINITE-Sr*, (Sr,Ba,K)(Ti,Nb)₂(Si₄O₁₂)(OH,O)₂·3H₂O, A NEW MINERAL OF THE LABUNTSOVITE GROUP

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Tsepinite-Sr is a new mineral of the labuntsovite group (the vuoriyarvite subgroup); it is an analogue of tsepinite-Na, tsepinite-K, and tsepinite-Ca, with predominance of Sr among the extra-framework cations. Tsepinite-Sr has been found in hydrothermal paragenesis in cavities of nepheline-syenite pegmatite at the Mt. Eveslogchorr in the Khibiny massif, Kola Peninsula, Russia. It is associated with microcline, albite, natrolite, analcime, aegirine, eudialyte, lefite, vuoriyarvite-K, tsepinite-Ca, kuzmenkoite-Zn, paratsepinite-Ba, takanelite, etc. The mineral forms coarse-prismatic crystals up to 0.2 x 0.4 x 2 mm in size and crusts up to 4 x 5 mm. It is translucent, colourless or white; the streak is white, and the lustre is vitreous. The mineral is brittle, without cleavage; the fracture is uneven. The Mohs' hardness is ~5. The measured density is 2.67(2), and the calculated density is 2.63 g/cm³. The mineral is optically biaxial, positive; $N_p = 1.649(2)$, $N_m = 1.651(2)$, $N_o = 1.770(4)$; $2V_{meas} = 20(5)^\circ$, $2V_{calc} = 16^\circ$. Chemical composition is as follows (the electron microprobe data, H₂O by TGA, wt %): Na₂O 0.61, K₂O 1.30, CaO 0.92, SrO 5.12, BaO 4.27, MgO 0.01, MnO 0.05, FeO 0.08, ZnO 0.26, Al₂O₃ 0.18, SiO₂ 41.89, TiO₂ 18.49, Nb₂O₅ 16.07, H₂O 11.14, total 100.39. The empirical formula calculated on (Si,Al)₄O₁₂(O,OH)₂ is as follows: (Sr_{0.28}Ba_{0.16}K_{0.16}Na_{0.11}Ca_{0.05}Zn_{0.02})_{0.82}(Ti_{1.32}Nb_{0.68}Fe_{0.01})_{2.02}(Si_{3.99}Al_{0.02})₄O₁₂[(OH)_{1.89}O_{0.11}]₂·2.59H₂O. The ideal formula is (Sr,Ba,K)(Ti,Nb)₂(Si₄O₁₂)(OH,O)₂·3H₂O (Z = 4). The mineral is monoclinic; space group Cm. The unit cell parameters (from the single crystal data) are as follows: a = 14.490(3), b = 14.23(1), c = 7.881(3) Å, β = 117.28(2)°, V = 1444(1) Å³. The strongest lines on the X-ray powder pattern are as follows (d, Å - I (hkl)): 7.10-90 (020, 001); 6.45-50 (200, 20-1); 5.01-40 (021); 3.230-100 (42-1, 400, 40-2); 3.135-80 (022, 041, 24-1); 2.510-80 (44-1, 401, 40-3, 042), 1.728-50 (461, 46-3, 081, 442, 44-4), 1.570-45 (84-1, 820, 84-3, 190, 82-4). The IR spectrum is given. The type specimen is deposited in the Fersman Mineralogical Museum RAS, Moscow.

3 tables, 1 figure, 12 references..

At present, the labuntsovite group minerals are the most studied natural zeolite-like titan- and niobosilicates. In the recent decade, they were being studied the most actively, that has resulted not only in the discovery of more than 20 new mineral species of this group and the disclosure of the wide distribution of its members in derivatives of alkaline complexes but also the revelation of a number of the important regularities concerning to crystal chemistry, properties, and genesis of microporous silicates with heteropolyhedral (mixed) frameworks in whole. We have established the nomenclature of the labuntsovite group approved by the IMA Commission on New Minerals and Mineral Names (CNMMN) (Chukanov *et al.*, 2002), and slightly later the data on these minerals was summarized in a special monograph (Chukanov *et al.*, 2003b). The members of the labuntsovite group are characterized by wide variations of the framework configuration, symmetry, cation

order, and chemical compositions: each of 11 cations, excepting Si, i.e. Ti, Nb, Mn, Fe, Mg, Zn, Na, K, Ba, Sr, Ca, can be practically absent in the mineral composition or play a species-forming role, dominating in the respective structural site. The members of this group significantly excel the most of synthetic titan- and niobosilicates in their own diversity and perfection of crystals; therefore, the study of the crystal structures and properties of these minerals is of a great practical interest today. On the other hand, features of crystal chemistry of the labuntsovite group members are the important typomorphic signs reflecting conditions of mineral formation in alkaline pegmatites and hydrothermalites.

The unique framework of heteropolyhedral type is a basis of all labuntsovite-like structures. It is formed by the infinite chains of the M octahedra occupied by Ti and Nb atoms. In two other directions, the octahedra are connected with each other by the [Si₄O₁₂] rings. Some mon-

*It was approved by the IMA KNMMN on May 3, 2004.

Table 1. Comparative characteristic of the vuoriyarvite sub-group minerals

Mineral	Vuoriyarvite-K	Tsepinite-Na	Tsepinite-K	Tsepinite-Ca	Tsepinite-Sr
Formula	(K,Na) ₂ (Nb,Ti) ₂ (Si ₄ O ₁₂)(OH) ₂ ·4H ₂ O	(Na,H ₃ O,K) ₂ (Ti,Nb) ₂ (Si ₄ O ₁₂)(OH) ₂ ·3H ₂ O	(K,Ba,Na) ₂ (Ti,Nb) ₂ (Si ₄ O ₁₂)(OH) ₂ ·3H ₂ O	(Ca,K,Na) ₂ (Ti,Nb) ₂ (Si ₄ O ₁₂)(OH) ₂ ·4H ₂ O	(Sr,Ba,K)(Ti,Nb) ₂ (Si ₄ O ₁₂)(OH) ₂ ·3H ₂ O
Symmetry	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Cm</i>	<i>Cm</i>	<i>Cm</i>	<i>C2/m</i>	<i>Cm</i>
<i>a</i> , Å	14.629	14.604	14.327	14.484	14.49
<i>b</i> , Å	14.164	14.274	13.802	14.191	14.216
<i>c</i> , Å	7.859	7.933	7.783	7.907	7.88
β°	117.9	117.40	116.95	117.26	117.1
<i>V</i> , Å ³	1446	1468	1372	1445	1445
Z	4	4	4	4	4
D _{exp} , g/cm ³	2.95	2.74	2.88	2.73	2.67
n _p	1.649	1.655-1.658	1.689	1.666	1.649
n _m	1.655	1.661-1.668	1.700	1.676	1.652
n _q	1.759	1.770	1.7752	1.780	1.770
2V	+ 20°	+ 20 – 30°	+ 35°	+ 30°	+ 20°
Reference	Subbotin <i>et al.</i> , 1998	Shlyukova <i>et al.</i> , 2001	Chukanov <i>et al.</i> , 2003b	Pekov <i>et al.</i> , 2003	Present work

oclinic members of the group also contain the additional D octahedra occupied by Mn, Fe, Zn, Mg, rarely Ca, atoms. The bonds between the Si tetrahedra and the M octahedra are realized by the joint O vertices; the M octahedra are connected among themselves by the joint (O,OH) vertices, whereas with the D octahedra they are united by the joint O edges. The framework contains zeolite-like channels, in which are the large alkaline and alkaline-earth cations and the water molecules; the presence of vacancies is typical for the extra-framework sites (A, B, and C). These features and a set of the extra-framework cations (Na, K, Ca, Sr, and Ba), which is equal for the labuntsovite group members and the «true», i.e. aluminosilicate, zeolites, bring together these two groups of minerals.

The labuntsovite group unites the orthorhombic and monoclinic minerals with a general formula A₄B₄C_{4-2x}[D_x(H₂O)_{2x}][M₈(O,OH)₈](Si₄O₁₂)₄·4-12H₂O, where x=0-2. Eight structural types of the labuntsovite-like minerals are known; they differ in topology of the framework, symmetry, and unit cell dimensions; eight subgroups are distinguished in the labuntsovite group respectively. Among monoclinic members of the group, the members of the vuoriyarvite group are characterized by the most disordered and «friable» crystal structures. In them, the «linking» D octahedra are vacant, and the Ti and Nb atoms are strongly displaced from the centres of the M octahedra from the direction of one of the bridge vertices. The characteristic feature of the vuoriyarvite group minerals, which distinguishes them from the most of other members of the labuntsovite group, is the

large number of the extra-framework sites of cations and the water molecules; many of them are brought together to the distances excluding their simultaneous occupation; as a result vacancies prevail in most of these sites. Because of that, in the vuoriyarvite subgroup, the mineral species are distinguished like in zeolites: all extra-framework sites (without subdivision into A, B, and C) are united, and the cation, prevailing over each other, is considered as a species-forming cation. This cation is entered in the suffix-modifier. In the vuoriyarvite subgroup, only niobium member, vuoriyarvite-K, and three titanium members: tsepinite-Na, tsepinite-K, and tsepinite-Ca, were known till now (Chukanov *et al.*, 2002, 2003b).

In the present work, a new titanium member of the vuoriyarvite subgroup is described; it belongs to the tsepinite series, in which strontium predominates among extra-framework cations (Table 1). According to accepted nomenclature, it was named tsepinite-Sr. The new mineral and its name were approved by the IMA CNMMN on May 3, 2004. The holotype specimen is deposited in the Fersman Mineralogical Museum RAS, Moscow (the registration number is 3169/1).

Occurrences and general appearance

The holotype of tsepinite-Sr was found in a pegmatite uncovered in the right bank of the Astrofillitovyi (Astrophyllite) stream on the south slope of the Mt. Eveslogchorr in south-

east part of the Khibiny alkaline massif, Kola Peninsula, Russia. This pegmatite lens (up to 1 m thick) occurs in gneiss-like nepheline syenite. Like the most of pegmatites connected with nepheline syenites of the Khibiny massif, this pegmatite is composed mainly by microcline and aegirine, with subordinate amounts of nepheline, albite, and eudialyte; astrophyllite, lorenzenite, epididymite, mangan-neptunite, and belovite-(Ce) are usual here. In the pegmatite, especially in its cavernous core, the low-temperature hydrothermal mineralization is widespread. The whole parts are composed by late drusy albite, natrolite, analcime. Eudialyte is intensively replaced by catapleite; abundant Mn-pectolite (or serandite?) is entirely altered to brown-black aggregates of takanelite. In cavities, leifite, thorite, vino-gradovite, ancylite-(Ce), and barite occur; solid bituminous matters exude. The typical feature of this pegmatite is the diversity of late hydrothermal minerals of the labuntsovite group represented by members of the structural types with a low order of the extra-framework cations: vuoriyarvite, paratsepinite, and kuzmenkoite subgroup minerals. The zinc member of the group, kuzmenkoite-Zn, has been found here for the first time beyond the bounds of the Lovozero massif (Pekov *et al.*, 2004), also tsepinite-Na, tsepinite-K, tsepinite-Ca, tsepinite-Sr, and paratsepinite-Ba occur. Vuoriyarvite-K is the most widespread; it mainly composes fine-grained pseudomorphs after the well-shaped lamellar crystals of vuonnemite (up to 1 cm) in the pegmatite core. It forms also individual crystals on the surface of these pseudomorphs and in the cavities near them. Undoubtedly, at this place, vuonnemite was the source of Nb and Ti for vuoriyarvite-K. The other members of the labuntsovite group, indistinguishable from each other by sight here, mainly crystallize later than vuoriyarvite-K on the surface of pseudomorphs after vuonnemite or in the cavities on albite, microcline, and natrolite.

Tsepinite-Sr is one of the most rare minerals of the pegmatite. It occurs as coarse-prismatic, usually split crystals up to 0.2 x 0.4 x 2 mm in size. Sometimes they form crusts up to 4 x 5 mm and up to 0.3 mm thick, on the surface of vuoriyarvite pseudomorphs after vuonnemite. The crystals of new mineral are elongated on [010]. Their prism zone is formed mainly by faces {100} and {001}; these crystals are not well-terminated.

Tsepinite-Sr was found also in two other pegmatites of the Khibiny-Lovozero complex, both remarkable for diversity of the labuntso-

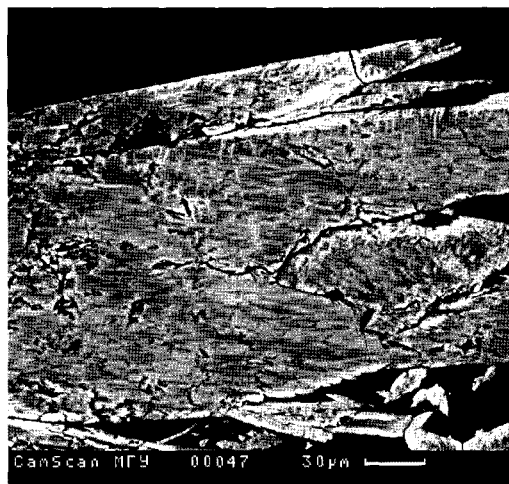


Figure 1. Crystals of tsepinite-Sr with Ba-enriched (light parts) margin zones. Mt. Eveslogchorr, Khibiny. Image in reflected electrons

vite group members (Chukanov *et al.*, 2003b). At the Mt. Khibinpakhkchorr, Khibiny, tsepinite-Sr forms zones in the white short-prismatic crystals of tsepinite-Na up to 1 mm in size (Shlyukova *et al.*, 2001); these crystals epitaxially overgrow the orange crystals of labuntsovite in the cavities of khibinite pegmatite. In the cavities of pegmatite No. 45, occurring in poikilitic feldspathoid syenites at the Mt. Lepkhe-Nel'm in the Lovozero massif, tsepinite-Sr forms light beige prismatic crystals (up to 3 mm long) overgrowing on lamprophyllite and eudialyte.

Physical properties

Tsepinite-Sr from the Mt. Eveslogchorr is colourless and white, translucent to transparent, has the white streak and vitreous lustre. It is not fluorescent in ultraviolet light. The Mohs' hardness is ~ 5. The mineral is brittle; the cleavage was not observed; the fracture is uneven. The density measured by heavy liquids is 2.67(2), the calculated density is 2.63(1) g/cm³.

The new mineral is optically biaxial, positive; $N_p = 1.649(2)$, $N_m = 1.651(2)$, $N_g = 1.770(4)$; $2V_{\text{meas}} = 20(5)^\circ$, $2V_{\text{calc}} = 16^\circ$. The dispersion is very weak, $r < v$. Tsepinite-Sr is colourless under microscope, no pleochroism. The orientation is $Y = b$.

The Gladstone-Dale compatibility (Mandarino, 1981) is 0.004 for the experimental density and -0.010 for the calculated density, i.e. «superior» in both cases.

Таблица 2. Химический состав цепинита-Sr

№ an.	1	2	wt. %			6
			3	4	5	
Na ₂ O	0.61	0.55	0.69	0.77	2.22	1.26
K ₂ O	1.30	1.71	1.65	2.30	1.25	1.81
CaO	0.92	0.85	1.39	1.36	2.11	1.03
SrO	5.12	5.57	4.89	5.67	8.64	4.66
BaO	4.27	0.81	5.25	2.06	1.62	2.15
MgO	0.01	bdl	0.01	0.01	bdl	bdl
MnO	0.05	0.11	bdl	bdl	bdl	0.06
FeO	0.08	0.05	0.05	bdl	bdl	0.16
ZnO	0.26	bdl	0.56	0.95	bdl	0.64
Al ₂ O ₃	0.18	0.03	0.27	0.11	0.17	0.12
SiO ₂	41.89	45.46	42.28	43.15	43.24	43.74
TiO ₂	18.49	18.85	17.48	20.58	20.71	19.21
Nb ₂ O ₅	16.07	19.27	17.95	14.93	13.50	14.51
H ₂ O	11.14	n.d.	n.d.	n.d.	n.d.	n.d.
Total	100.39	93.26	92.47	91.89	93.46	89.35
Formula coefficients, calculation on (Si + Al) = 4						
Na	0.11	0.09	0.13	0.14	0.40	0.22
K	0.16	0.19	0.20	0.27	0.15	0.21
Ca	0.09	0.08	0.14	0.13	0.21	0.10
Sr	0.28	0.28	0.27	0.30	0.46	0.25
Ba	0.16	0.03	0.19	0.07	0.06	0.08
Mn	—	0.01	—	—	—	—
Zn	0.02	—	0.04	0.06	—	0.04
Σ A	0.82	0.68	0.97	0.97	1.28	0.90
Fe	0.01	—	—	—	—	0.01
Ti	1.32	1.25	1.23	1.43	1.43	1.32
Nb	0.69	0.77	0.76	0.62	0.56	0.60
Σ M	2.02	2.02	1.99	2.05	1.99	1.93
Al	0.02	—	0.03	0.01	0.02	0.01
Si	3.98	4.00	3.97	3.99	3.98	3.99

Note:

1-4 – Mt. Eveslogchorr, Khibiny (including 1 – holotype); 5 – Mt. Khibinpakhkchorr, Khibiny; 6 – Mt. Lepkhe-Nel'm, Lovozero;

bdl – below detection limits of electron microprobe method (contents of REE, Zr, Ta, F are bdl in all analyses);

n.d. – content of water was not detected.

A – extra-framework cations: Na, K, Ca, Sr, Ba, Mn, Zn;

M-cations: Ti, Nb, Fe.

The IR spectrum of the new mineral is close to spectra of other members of the vuoriyarvite subgroup. The absorption bands are as follows (cm⁻¹; frequencies of the most intensive bands are underlined; sh – shoulder, w – wide band): 3545, 3475, 3290w, 1665, 1605, 1537, 1135sh, 1120, 949, 935sh, 760sh, 675, 610sh, 450. The low-frequency position of a band corresponding to stretching vibrations (Ti,Nb)-O (675 cm⁻¹) confirms that the D octahedron is significantly vacant (Chukanov *et al.*, 2003b). Tsepinite-Sr is only mineral of the labuntsovite group, in which IR spectrum are more than two well-distin-

guished bands in the range of bending vibrations of the water molecules, i.e. bands at 1665, 1605, and 1537 cm⁻¹. Undoubtedly, this phenomenon is connected with unusually great amount of non-equivalent sites of H₂O in zeolite channels (Rozenberg *et al.*, 2003).

Chemical composition

Chemical composition of the new mineral (Table 2) was studied by the electron microprobe method; the water content was detected by thermogravimetric procedure. The empirical formula of the holotype calculated on (Si,Al)₄O₁₂(O,OH)₂ is as follows: (Sr_{0.28}Ba_{0.16}K_{0.16}Na_{0.11}Ca_{0.09}Zn_{0.02})_{0.82}(Ti_{1.32}Nb_{0.69}Fe_{0.01})_{2.02}(Si_{3.98}Al_{0.02})₄O₁₂[(OH)_{1.89}O_{0.11}]₂·2.59H₂O. The O/OH ratio is calculated by the charge balance. The ideal formula (Z = 4) is: (Sr,Ba,K)(Ti,Nb)₂(Si₄O₁₂)(OH,O)₂·3H₂O.

In minerals of the tsepinite series, the ratios of the extra-framework alkaline and alkaline-earth cations vary widely. It is evident from Table 2 that tsepinite-Sr is represented by the varieties enriched by Ba, Na, or K. At the same time, the samples from different localities are quite close to each other by the Ti/Nb ratio and the low content of the small bivalent cations (Mn, Zn, Fe, Mg).

The significant variations of composition of the extra-framework cations are usual within a single crystal. On the Figure, it is evidence that peripheral parts of the tsepinite-Sr crystals from the Mt. Eveslogchorr are significantly enriched by barium. The «spotted» internal constitution is typical for many crystals from Lovozero: the parts with Na > Sr and Sr > Na are distributed irregular in them. At the same time, in the samples from the Mt. Eveslogchorr, the sharp phase bounds between the individuals of tsepinite-Sr and kuzmenkoite-Zn and also tsepinite-Sr and vuoriyarvite-K were observed. The latter pair of minerals is especially interesting, because its members belong to the same structural type. Probably, the distribution of the extra-framework cations between the niobium and titanium members of the group is caused by the charge restrictions, according to the isomorphous scheme: Nb⁵⁺ + K⁺ ↔ Ti⁴⁺ + A²⁺, where A²⁺ = Sr, Ba, Ca.

Tsepinite-Sr is the second member of the labuntsovite group, after alsakharovite-Zn, NaSrKZn(Ti,Nb)₄[Si₄O₁₂]₂(O,OH)₄·7H₂O (Pekov *et al.*, 2003b), in which strontium plays species-forming role. The highest content of strontium (8.6 wt % SrO) in the minerals of this group is detected in tsepinite-Sr from the Mt.

Table 3. Results of calculation of X-ray powder diagram of tsepinite-Sr.

I_{meas}	d_{meas} , Å	I_{calc}	d_{calc} , Å	hkl
90	7.10	100, 88	7.108, 7.015	020, 001
50	6.45	64, 73	6.450, 6.425	200, 20-1
40	5.01	72	4.993	021
5	4.78	6, 10	4.776, 4.766	220, 22-1
10	3.92	12, 10	3.937, 3.921	201, 20-2
100	3.230	45, 34, 33	3.228, 3.225, 3.213	42-1, 400, 40-2
80	3.135	47, 25, 26	3.145, 3.113, 3.110	022, 240, 24-1
3	3.015	2	3.021	311
20	2.945	11, 10	2.937, 2.927	420, 42-2
30	2.643	2, 6, 7, 6, 8	2.673, 2.638, 2.633, 2.621, 2.613	15-1, 241, 24-2, 202, 20-3
80	2.510	19, 11, 13, 37	2.537, 2.526, 2.514, 2.496	44-1, 401, 40-3, 042
5	2.156	4	2.150	600
5	2.091	1, 3	2.104, 2.093	511, 351
20	2.057	7, 4, 7, 2	2.059, 2.058, 2.052, 2.051	441, 620, 44-3, 62-3
10	1.961	8	1.963	062
15	1.813	12	1.811	80-2
10	1.781	13	1.777	080
10	1.755	1, 2, 7	1.755, 1.755, 1.754	82-2, 26-3, 004
50	1.728	7, 6, 3, 9, 10	1.728, 1.724, 1.723, 1.722, 1.717	461, 46-3, 081, 442, 44-4
5	1.675	1, 3	1.680, 1.678	66-1, 66-2
45	1.570	8, 3, 7, 1, 4	1.574, 1.572, 1.571, 1.568, 1.567	84-1, 820, 84-3, 190, 82-4
5	1.468	1, 3, 4	1.469, 1.468, 1.464	28-3, 840, 84-4
10	1.448	6, 6, 6, 1	1.453, 1.451, 1.445, 1.442	481, 48-3, 443, 10.0-2

Note: camera RKU-114.6, FeK α radiation, Mn filter. Indexes hkl are selected in accordance with I_{meas} values obtained from structural data.

Khibinpakhkchorr (an. 5 in Table 2). We should note that Sr as well as Ca is the most typical for members of the vuoriyarvite and gutkovaite subgroups; Sr is a usual minor admixture in minerals of the paratsepinite, organovaite, and kuzmenkoite subgroups; but this element is absolutely untypical for members of the labuntsovite sensu stricto, paralabuntsovite, and lemmleinite subgroups with more ordered distribution of the extra-framework cations.

X-ray data and crystal structure features

The X-ray study of a single crystal of tsepinite-Sr carried out by a diffractometer ENRAF NONIUS has obtained the monoclinic symmetry (space group Cm) and the following unit cell parameters: $a = 14.490(3)$, $b = 14.23(1)$, $c = 7.881(3)$ Å, $\beta = 117.28(2)^\circ$, $V = 1444(1)$ Å³ (Rozenberg *et al.*, 2003). The X-ray powder pattern of the new mineral (Table 3) is close to ones of other members of the tsepinite series. The unit cell parameters obtained from X-ray powder data are as follows: $a = 14.49(2)$, $b = 14.216(6)$, $c = 7.88(1)$ Å, $\beta = 117.1(1)^\circ$, $V = 1445(3)$ Å³.

The crystal structure of tsepinite-Sr studied on a single crystal is described in the work of K.A. Rozenberg with co-authors (2003). Its basis is the mixed framework, typical for the labuntsovite group minerals; it consists of the chains of the vertex-linked (Ti,Nb)O₆ octahedra and the fourfold rings of the SiO₄ tetrahedra, connecting them. The Sr, K, Ca, Na, and Ba atoms and the water molecules occupy 15 sites (instead 7-8 sites in the ordered members of the labuntsovite and lemmleinite groups and 12 sites in tsepinite-Na and vuoriyarvite-K) in the channels parallel to the coordinate axes. Five sites contain the cations, 7 – the water molecules, and 3 – the cations and water molecules together. Thus, tsepinite-Sr is one of the most cation-disordered members of the labuntsovite group. In the new mineral, the vacancies predominate in all extra-framework sites. It differs from tsepinite-Na not only by the prevalence of Sr among the extra-framework cations but also its distribution. In tsepinite-Sr, atoms of strontium is situated in three sites; in tsepinite-Na (Rastvetaeva *et al.*, 2000), first of these sites is also occupied by Sr, the second site - by Na, and the third site is vacant.

