STRUCTURE OF INORGANIC COMPOUNDS

Structure of the New Mineral Paratsepinite-Na and Its Place in the Labuntsovite Group

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Abstract—X-ray diffraction study of high-strontium Ti-nenadkevichite showed that it is a new mineral, which was given the name paratsepinite-Na, sp. gr. C2/m, a double value of the parameter c, and a different distribution of the non-framework cations in comparison with tsepinite-Na. In particular, strontium is located not only in the hexagonal window of the small channel, but also in three positions of the large channel. The characteristics of the mosaic blocks constituting the crystal are studied. It is assumed that polysynthetic twinning in these crystals and many other representatives of this family is associated with the phase transformation occurring in this hydrothermal mineral during its cooling after formation. The comparison of all the three structures of the vuoriyarvite subgroups of the labuntsovite group allows us to explain the disability of vuoriyarvite to absorb strontium from the aqueous solution by its smaller unit-cell volume and higher framework charge in comparison with those of tsepinites. © 2004 MAIK "Nauka/Interperiodica".

INTRODUCTION

Recently, an ever increasing interest in new microporous crystals that may absorb and retain harmful radioactive wastes resulted in numerous publications on possible use of mineral labuntsovite for this purpose [1]. The recent study of natural labuntsovites of different compositions in aqueous solutions at room temperature [2] showed that the highest absorption of Na, K, and Cs is observed in the minerals of the vuoriyarvite group, whereas Sr is absorbed only by tsepinite.

In the recent decade, Russian researchers achieved considerable progress in the structural and mineralogical study of the labuntsovite-nenadkevichite group. They also developed new nomenclature according to which all the 18 minerals of this group were divided into 8 subgroups [3].

The structures of the minerals of the labuntsovite group consist of the chains of Ti–Nb octahedra connected by four-member silicon–oxygen rings. The framework thus formed (Fig. 1) has a zeolite-like structure and two kinds of channels: those with a large diameter along the y axis and those with a small diameter

along the [101] and [101] directions.

The pseudoorthorhombic framework is negatively charged and its channels are filled with cations. The large channels are occupied by Na, K, and Ba, and, sometimes, also with Sr and Ca and water molecules. Some minerals of the labuntsovite group also contain oxonium ions [4]. Small channels are occupied by Mg, Fe, Zn, Na, Ca, and Sr ions. Similar to zeolites, the distribution of atoms over all or some positions may be both ordered and disordered and may or may not have vacancies.

The well-known minerals of the labuntsovite group are crystallized in one of four possible space groups: Pbam, Cm, C2/m, and I2/m. The first, orthorhombic, space group is characterized by the minimum unit-cell parameters $(a_p \sim 7, b_p \sim 7, c_p \sim 14 \text{ Å} (Fig. 1a)$. The mon-oclinic unit cells may be divided into three types: the C-cell with small dimensions $(a \sim 14, b \sim 14, c \sim 8 \text{ Å},$ $\beta' \sim 117^{\circ}$), the doubled C-cell ($a_{\rm m} \sim 14, b_{\rm m} \sim 14, c_{\rm m} \sim 16$ Å, $\beta'' \sim 117^{\circ}$), and the *I*-cell (*a* ~ 14, *b* ~ 14, *c* ~ 16 Å, β ~ 117°). It should be noted that the transition from the small c-cell to the large C-cell is caused not by doubling of the c parameter but, what is important, by the cell transformation described by the relationships \mathbf{a}_{m} = $-\mathbf{a}, \mathbf{b}_{m} = -\mathbf{b}$, and $\mathbf{c}_{m} = \mathbf{a} + 2\mathbf{c}$. The specific features of the diffraction pattern from labuntsovite with the doubled C-cell will be discussed later. The authors of the new nomenclature suggested to supply to the names of labuntsovites with the double cells the prefix "para-" in those cases where there exists a similar mineral with the conventional (not doubled) c parameter.

There are also other subgroups of the family having both para- and monoforms (e.g., kuzmenkoite and parakuzmenkoites [5]) and also minerals whose names have no prefix para- (e.g., organovaite-Zn and organovaite-Mn [6, 7]) because the latter have no varieties with the monoparameter c.



Fig. 1. Labuntsovite framework projected along the y axis (according to Rastsvetaeva) [4].

Earlier, we studied both mineralogically and structurally Ti-nenadkevichite from pegmatites of the Khibiny massif (mount Khibinpakhchorr) [8–10]. The microprobe analysis of these crystals epitaxially grown over the labuntsovite crystals ("caps") [10] showed not only the pronounced inhomogeneity in the distribution of the elements in both labuntsovite crystals and the caps, but also the presence of strontium "not seen" by the "wet" chemical analysis.

The structure determination of Sr-containing Tinenadkevichite (2.32% SrO) [4] allowed one to consider it as a new mineral tsepinite-Na [12]. The same pegmatites contained among small crystals of Tinenadkevichite epitaxially grown on labuntsovite also crystals with a high strontium content. One of these crystals with 8% SrO was selected for structure refinement, which is the subject of the present article, which allowed us to consider it as a new mineral: paratsepinite-Na. Its existence was confirmed by the Commission on New Minerals and Mineral Names of the International Mineralogical Association on March 12, 2003.

EXPERIMENT AND STRUCTURE REFINEMENT

The study of the chemical composition of paratsepinite-Na was performed on a CAMEBAX-MBX microprobe setup. The chemical formula of the crystal corresponds to the empirical formula

$$(Na_{3.68}Sr_{1.73}K_{0.76}Ca_{0.51}Ba_{0.16}Mn_{0.03}Zn_{0.03})_{\Sigma 7.99}(Ti_{5.03}Nb_{2.87}Fe_{0.09})_{\Sigma 7.99}$$

[Si_{15}_{92}Al_{0.08}O_{48}](O_{4.01}OH_{3.99})_{\Sigma 8.00} \cdot 7.75H_2O.

The X-ray diffraction experiment (Table 1) was performed at the University of Notre Dame, Indiana, USA. The set of diffraction-reflection intensities was obtained using a CCD detector (the exposure time of each pattern was 30 s). Altogether 1200 patterns were obtained by ω scanning at a step of 0.3°, which corresponds to the more than half of the diffraction sphere. The set of structure factors was obtained using the SAINT program with the introduction of all the necessary corrections. The absorption correction was introduced by the semiempirical method of pseudo ψ scanning with the use of 1276 reflections with $I > 15\sigma(I)$. The crystal shape was modeled by an ellipsoid. After averaging symmetrically equivalent reflections, the

 Table 1. Crystallographic characteristics and the refinement parameters for the paratsepinite-Na structure in the anisotropic approximation

Table 2.	Coordinates and	thermal	parameters	$(Å^2)$ of	structure
atoms					

<i>a</i> , Å	14.596(2)
<i>b</i> , Å	14.249(2)
<i>c</i> , Å	15.852(3)
β, deg	117.270(3)
<i>V</i> , Å ³	2930.55
Sp. gr., Z	<i>C</i> 2/ <i>m</i> , 4
Radiation, λ, Å	MoK _α , 0.70926
ρ_{calcd} , g/cm ³	2.76
Crystal dimensions, mm ³	$0.20 \times 0.35 \times 0.025$
Diffractometer	Bruker APEX 4K CCD
sinθ/λ	<1.245
Number of crystallographically independent reflections	$2164 F > 4\sigma(F)$
R	0.077

reliability factor was $R_{int} = 0.072$. The structure was refined in the anisotropic approximation up to $R_1 =$ 0.077 using 2164 reflections with $|F_{hkl}| \ge 4\sigma |F_{hkl}|$ with due regard for the pseudomerohedral twinning in the (001) plane. Twinning was taken into account using the SHELXTL program with the use of the twinning matrix [100/010/101]. The refined ratio of the twinning components was 0.75 : 0.25.

In order to confirm that doubling of the unit cell is not an auxiliary effect of twinning [13], the diffraction data were reindexed for a small C-cell. It turned out that about 600 reflections with $|F_{hkl}| \ge 4\sigma |F_{hkl}|$ cannot be adequately indexed within the frameworks of the small C-cell. The structure of the paratsepinite-Na was solved anew in the small unit cell and was refined in the sp. gr. C2/m up to R = 0.125 over 1518 reflections with $|F_{hkl}| \ge$ $4\sigma |F_{hkl}|$. All the attempts to refine the structure in the anisotropic approximation resulted in physically unreasonable thermal parameters, which usually indicates an inappropriate choice of the unit cell or the space group. The transition to the group Cm allowed us to refine the structure only to R = 0.154 and also deteriorated the thermal parameters. Thus, the unit-cell doubling is favored by the presence of about 600 strong reflections which could not be indexed in the small unit cell and the difficulties in structure refinement in this small unit cell. Thus, paratsepinite-Na really has the doubled unit cell, which determines its structural and mineralogical difference from tsepinite-Na. Structurally, doubling of the cell is explained by disorder of Sr²⁺ cations over the cavities of the titanium-silicate framework.

The high value of the R factor is explained, first and foremost, by the systematic broadening of some reflections and their approximate superposition.

Atom	x	у	z	$U_{\rm iso}$
Ti(1)	0.2497(2)	0.73996(6)	0.2502(2)	0.0271(4)
Ti(2)	0.5000(2)	0.2500(2)	0.2503(2)	0.0277(4)
Si(1)	0.6937(3)	0.3892(2)	0.3823(2)	0.0139(7)
Si(2)	0.3051(3)	0.1114(2)	0.1174(2)	0.0149(8)
Si(3)	0.6953(3)	0.3886(2)	0.8957(2)	0.0136(7)
Si(4)	0.8055(3)	0.3882(2)	0.6043(2)	0.0159(8)
O(1)	0.4011(6)	0.2607(4)	0.3015(5)	0.022(2)
O(2)	0.6716(1)	1/2	0.8829(8)	0.030(3)
O(3)	0.7420(7)	0.3597(5)	0.6587(6)	0.025(2)
O(4)	0.7354(7)	0.3630(4)	0.4932(6)	0.028(2)
O(5)	0.8263(10)	1/2	0.6128(8)	0.033(4)
O(6)	0.5745(7)	0.3588(5)	0.3281(6)	0.028(2)
O(7)	0.0988(5)	0.7411(5)	0.1983(4)	0.0148(14)
O(8)	0.5871(7)	0.3340(5)	0.8566(5)	0.028(2)
O(9)	0.9136(6)	0.3350(5)	0.6441(6)	0.025(2)
O(10)	0.7642(8)	0.3626(4)	0.0074(7)	0.035(2)
O(11)	0.7635(6)	0.3357(4)	0.3442(6)	0.020(2)
O(12)	0.7600(6)	0.3612(4)	0.8399(6)	0.018(2)
O(13)	0.2361(6)	0.1655(5)	0.1559(6)	0.023(2)
O(14)	0.4242(6)	0.1404(5)	0.1744(6)	0.025(2)
O(15)	0.2913(9)	0	0.1282(8)	0.028(3)
O(16)	0.7038(10)	1/2	0.3684(9)	0.037(4)
$H_2O(1)$	0.561(1)	1/2	0.665(1)	0.063(4)
$H_2O(2)$	0.930(1)	1/2	0.830(1)	0.051(4)
$H_2O(3)$	0.074(2)	0	0.151(1)	0.147(11)
$H_2O(4)$	0.0716(13)	1/2	0.6540(11)	0.107(6)
$H_2O(5)$	0.4099(4)	0.2587(4)	0.4964(4)	0.020(2)
$H_2O(6)$	-0.0889(4)	0.7435(3)	-0.0033(4)	0.0194(15)
K (1)	1/2	0.3194(16)	1/2	0.154(12)
K(2)	0	0.6136(15)	0	0.148(12)
Na(1)	0.2511(48)	0	0.2532(43)	0.026(8)
Na(2)	-0.0327(23)	0.8701(14)	-0.0574(17)	0.185(14)
Sr(1)	0.7490(7)	1/2	0.7485(6)	0.0168(9)
Sr(2)	0.4667(21)	0.1232(13)	0.4366(16)	0.199(14)

The final model included the coordinates of all the atoms and the anisotropic thermal parameters for all these atoms with the position occupancy 100% (Table 2). The cation coordination is indicated in Table 3.

COMPARISON OF THE STRUCTURES OF THE VUORIYARVITE SUBGROUP

Figure 2 shows the tsepinite-Na and paratsepinite-Na structures. Table 4 lists the data for each of the struc-

Posi- tion	Composition	c.n.	Bond lengths, Å		
			range	aver- age	
Ti (1)	0.6Ti + 0.4Nb	6	1.954(8)-1.988(7)	1.97	
Ti(2)	0.6Ti + 0.4Nb	6	1.959(8)-1.986(8)	1.97	
Si(1)	Si	4	1.597(8)–1.619(9)	1.61	
Si(2)	Si	4	1.595(9)–1.619(4)	1.61	
Si(3)	Si	4	1.609(8)-1.628(10)	1.62	
Si(4)	Si	4	1.581(8)-1.621(9)	1.60	
Sr (1)	0.2Sr + 0.2Ca	6	2.345(2)-2.438(2)	2.41	
Sr(2)	0.1Sr + 0.1Ca	7	2.17(2)-2.93(2)	2.60	
K(1)	0.2K + 0.05Ba	6	2.920(9)-3.411(10)	3.21	
K(2)	0.2K + 0.2Sr	7	2.27(5)-3.27(5)	2.67	
Na(1)	0.2Na	8	2.321(6)-2.77(6)	2.52	
Na(2)	0.6Na	6	2.27(2)-2.72(3)	2.53	
$H_2O(4)$	0.2Sr + 0.3 H ₂ O	6	2.46(2)-2.73(1)	2.60	

Table 3. Characteristics of coordination polyhedra

tures and for vuoriyarvite. It is obvious that the large channel in tsepinite-Na is less occupied than in paratsepinite-Na. The character of the disorder in these channels is somewhat contradictory. On the one hand, the doubling of one of the parameters indicates a higher order, whereas an increase in the number of isomorphously substituting components in most of the cation positions is a sign of a more pronounced disorder. The more disordered cation distribution results in cell doubling.

SPECIFIC FEATURES OF MOSAICITY AND A PROBABLE PHASE TRANSFORMATION IN TSEPINITE

The specific character of mosaicity in crystals gives the information on crystal genesis and is reflected in the crystal properties, including the characteristics of their diffraction patterns.

The mosaicity in labuntsovites was first observed by Bulakh and Evdokimov [14] who also assumed that the microblock structure of these crystals is the result of submicroscopic intergrowth of two solid phases with similar structures but different compositions. In light of

Table 4. Some structural characteristics of minerals of the vuorivarvite subgroup

	Paratsepinite-Na*	Tsepinite-Na**	Vuoriyarvite***
Sp. gr.	C2/m	Ст	Cm
Unit-cell parameters	a = 14.596, b = 14.249,	a = 14.604, b = 14.276,	a = 14.692, b = 14.164,
	$c = 15.952$ Å, $\beta = 117.27$	$c = 7.933$ Å, $\beta = 117.40$	$c = 7.859$ Å, $\beta = 117.87$
Unit-cell volume, Å ³	2948.9 (2 × 1474.5)	1468.2	1445.75
Twinning	(001)	(001), (-401)	(001), (-401)
Occupancy:			
Ti (1)	Ti _{0.6} Nb _{0.4}	Ti _{0.7} Nb _{0.3}	Ti _{0.4} Nb _{0.6}
Ti(2)	Ti _{0.6} Nb _{0.4}	Ti _{0.4} Nb _{0.6}	Ti _{0.5} Nb _{0.5}
Sr(1)	Sr _{0.2} Ca _{0.2} η _{0.6} ****	$Sr_{0.22} \square_{0.78}^{****}$	Na _{0.58} □ ^{****} _{0.42}
Sr(2)	Sr _{0.1} Ca _{0.1}		
К	$K_{0.2}Ba_{0.05}\eta_{0.75}$	$K_{0.6}\eta_{0.4}$	K _{0.49} η _{0.51}
Ba		$Ba_{0.08}\eta_{0.92}$	K _{0.44} η _{0.56}
Na(1)	Na _{0.2} n _{0.8} ****	Na _{0.47} □ ^{****} _{0.53}	Na _{0.49} □ ^{****} _{0.51}
Na(2) _P	Na _{0.6} n _{0.4}	Na _{0.62} □ ^{****}	$(H_2O)_{0.32}\Box_{0.68}^{****}$
Na(2) _O	$K_{0.2}Sr_{0.1}\eta_{0.7}$		
Na(3)	$Ca_{0.1}Sr_{0.1}\eta_{0.8}$		
Na(4)	Na _{0.6} η _{0.4}		
H ₂ O(4)	$(H_2O)_{0.3}, Sr_{0.2\eta_{0.5}}$		
H ₂ O		$(H_2O)_{0.2}\eta_{0.8}$	

* (Na, Sr, K, Ca, Ba)₁₀(Ti, Nb)₁₆[Si₄O₁₂]₈12H₂O. ** (H₃O, Na, K, Sr)_{7.5}(Ti, Nb)₈[Si₄O₁₂]₄₅H₂O. *** (K, Na)₈(Nb, Ti)₈[Si₄O₁₂₄6H₂O. *** The position between Ti(1) and Ti(2) is an analogue of the Na(1) position in the nenadkevichite and korobitsynite structures or the D position in labuntsovites with prevailing Ti components.





Fig. 2. (a) Tsepinite-Na and (b) paratsepinite-Na projected along the y axis.

the modern theories, the number of different phases can be even larger.

The structurally studied small paratsepinite-Na crystal was used to record the axial (h00) and (00l) reflections in the orthorhombic setting in order to perform profile analysis [15]. The experimental data obtained are shown in Fig. 3. The processing of these

data showed that the average sizes of the coherent-scattering regions along X and Z are 300 and 1100 Å, respectively. The stresses along the former axis are seven-fold higher than the stresses along the latter axis.

The schematic drawing of the image of a tsepinite crystal in an optical microscope may be found in [9]. The blocks of mosaics of the crystals grown from



Fig. 3. Profiles of the basic (h00) and (00l) reflections of the paratsepinite-Na crystal in the orthorhombic setting: (a) integral half-widths of the \Box --00l and \bullet --h00 reflections and \bullet --of the ruby standard, (b) reflections from the sample and the standard, (c) an example of the reflection decomposition into the $K_{\alpha 1}$ and $K_{\alpha 2}$ components.

hydrothermal solutions contain the information on the growth conditions and growth mechanism and also reflect the symmetry of a growing crystal. Thus, flattening of the coherent-scattering regions in the x_p direction in the layer grown mainly along the y axis may be explained by breaking of the bonds in the chain of T–Nb octahedra often linked by the hydroxyl groups which weaken bonding in comparison with the

Ti–O–Si bonds. The zero layer line of the paratsepinite-Na crystal recorded on the photographic film had diffuse (h00) and sharp (00l) reflections in full accordance with the shape of the coherent-scattering region.

Thus, the moderate-sized coherent-scattering region has the shape flattened along the X axis and intersects the structure normally to the direction of the elongation of the Ti–Nb octahedra. It is highly probable that the initial crystal growth starts with the formation of an individual blocks having orthorhombic symmetry and located with their side faces parallel to one another onto the (001) plane. Then, the "life" of tsepinite-Na and paratsepinite-Na may be considered as follows.

Small crystals grown from hydrothermal solutions have orthorhombic symmetry. All the positions between the chains of the Ti–Nb octahedra are filled as in korobitsynite. With lowering of the temperature, the crystals undergo a phase transition [16] as a result of which the orthorhombic symmetry changes to monoclinic. The resulting stresses give rise to a certain "discharge": polysynthetic twinning in the (001) or along (001) and ($\overline{4}01$) planes. Some atoms located between the octahedra migrate to larger channels. The structure at twin boundaries and inside these boundaries differs from the bulk structure. It is there that the atoms with small radii, and first of all Na atoms, may migrate [17].

The classical mineralogical example of such a transformation is albite which becomes twinned during the phase transition from monoclinic to triclinic modification.

The orthorhombic symmetry of the coherent-scattering regions confirms the assumption on the phase transformation. The distribution and redistribution of the framework cations takes place at the first stage of crystal growth. For non-framework cations, ordering processes may occur within their whole "life" and depend not only on the composition of the hydrothermal solution and its temperature, but also on the process kinetics.

Under certain conditions, the cations of one species may be localized within individual blocks. As a result, the order in such blocks may be higher than the average order over the whole diffracting volume.

The different space groups of the crystals from one pegmatite under similar conditions—Cm or C2/m—may be explained by the prevalence of one type of symmetry in the diffracting volume.

MAIN RESULTS

The paratsepinite-Na structure with the sp. gr. C2/m and the double c parameter is refined.

It is shown that the Na-tsepinite has two modifications with sp. gr. Cm and C2/m and with different values of the c parameter.

The polysynthetic microtwinning may be considered as a consequence of the phase transformation of the initial orthorhombic structure into the monoclinic one which is accompanied by the displacements of the nonframework cations and water molecules.

It is assumed that two varieties may coexist within one crystalline volume.

The processes described seem to be characteristic of most of the monoclinic labuntsovites; some other minerals of this family considered in this article are also polysynthetic twins and obey the same twinning laws.

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