

CHEMISTRY

Crystal Structure of a New Ca, Nb-Representative of the Labuntsovite Group

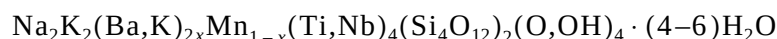
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Presented by Academician L.N. Kogarko June 7, 2000

Received June 21, 2000

The structures of monoclinic minerals of the labuntsovite group are based on the zeolite-like framework formed by corrugated chains of Ti(Nb) octahedra linked via shared vertices. The chains, in turn, are linked through four-membered silicon–oxygen rings and additional M^{II} octahedra, which are completely or

partially filled with small divalent cations $M^{2+} = \text{Mn, Fe, Mg, and Zn}$. The cavities of the framework are occupied by large alkali and alkaline-earth cations and water molecules. Three types of extraframework cationic positions (A^I , A^{II} , and A^{III}) are clearly distinguished by their size and location in the structures of labuntsovite



and the most closely related minerals to it [1–4]. The A^I and A^{II} positions are occupied exclusively by sodium and potassium atoms, respectively, and the A^{III} position is occupied by barium and potassium atoms. In labuntsovite-like structures, the distance between the A^{III} position and the adjacent M^{II} octahedral position is very short ($\sim 2.1 \text{ \AA}$), and so is responsible for the “competition” between the A^{III} cations (Ba^{2+} and K^+) and the $\{M^{2+}(\text{H}_2\text{O})\}$ complexes and results in the alternative occupancy of these two positions according to the following scheme [5]: $2(\text{Ba}, \text{K}) + \square \rightleftharpoons 2\text{H}_2\text{O} + M^{2+}$. The labuntsovite-like mineral kuzmenkoite $\text{K}_2\text{Mn}(\text{Ti}, \text{Nb})_4(\text{Si}_4\text{O}_{12})_2(\text{OH}, \text{O})_4 \cdot 5\text{H}_2\text{O}$ ($a = 14.369 \text{ \AA}$, $b = 13.906 \text{ \AA}$, $c = 7.812 \text{ \AA}$, $\beta = 117.09^\circ$) [6, 7] differs from the mineral labuntsovite primarily by the extremely low sodium content and, correspondingly, by the absence of the A^I position. The M^{II} position in kuzmenkoite is occupied almost completely, and, consequently, the cationic occupancy of the A^{III} position is insignificant. Wide variations in the character and degree of filling of the cationic and anionic positions lead to a diversity of the mineral types in the labuntsovite group and give impetus to X-ray diffraction studies. In this paper, we report, for the first time, the results

of refining the structure of a labuntsovite-type mineral by the Rietveld method. The mineral under study was discovered by one of the authors in a hydrothermally modified pegmatite among naujaite in the neighborhood of the Kangerdluarssuk fjord (in the Southern region of the Ilimaussaq alkaline complex, South-West Greenland). The pegmatite is composed of common potash feldspar, albite, aegirine, and arfvedsonite with tapersuatsiaite, carbonate-apatite, and zeolites crystallizing in its cavities. The labuntsovite-like mineral forms fine-grained massive pseudomorphs, off-white with a pink tint, after tabular crystals of vuonnemite (up to 2 cm). The mineral attracted our attention because of the peculiarities of its chemical composition. Thus, Nb dominates over Ti, and Ca substantially dominates over alkali and other alkaline-earth cations.

The X-ray diffraction pattern of a powdered sample was measured on a focusing Stoe STADI-P diffractometer equipped with a bent Ge(111) primary-beam monochromator, which provided strictly monochromatic $\lambda\text{MoK}\alpha_1$ radiation. The powdered sample placed in a quartz capillary was continuously rotated to avoid the effects of preferential orientation. The X-ray data were collected in the step-scan mode using a position-sensitive linear detector [8]. The principal details of the X-ray diffraction experiment and the unit cell parameters are given in Table 1. All calculations were carried out using the WYRIET program (version 3.3) [9]. Since the composition and the unit cell metrics of the mineral under study are similar to the corresponding parameters of other representatives of the labuntsovite group, we used the atomic coordinates of the structure of Ba-labuntsovite $\text{Na}_2\text{K}_2\text{Ba}_{1.1}\{\text{Ti}_4(\text{O}, \text{OH})_4[\text{Si}_4\text{O}_{12}]_2\}[\text{Mn}_{0.45}(\text{H}_2\text{O})_{0.9}] \cdot 3.6\text{H}_2\text{O}$ ($a = 14.216 \text{ \AA}$, $b = 13.755 \text{ \AA}$, $c = 7.767 \text{ \AA}$,

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$\beta = 116.7^\circ$, $Z = 2$) [4] as the starting model. The structure of the mineral was refined in space group $C2/m$. The peak shapes were described by the Pearson function with 6FWHM^2 . Asymmetry was refined at $2\theta < 40^\circ$. Ionic scattering curves were used. Refinement was carried out by gradually adding the parameters to be refined with the continued graphical modeling of the background. The structural parameters (the coordinates x , y , and z and the isotropic thermal parameters) were



($Z = 1$). The anionic portion of the structure was separated into O atoms, OH groups, and H_2O molecules based on calculations of the formal and local valence balance taking into account the cation–anion distances according to Pyatenko [10]. The final R factors corresponding to the above composition are given in Table 1. The experimental (solid line) and theoretical (marked with asterisks) X-ray diffraction spectra of the mineral are shown in Fig. 1. The final atomic coordinates, the refined occupancies (per formula unit), and the isotropic thermal parameters are given in Table 2.

In the crystal structure of the title mineral, as in other representatives of the labuntsovite group, the (Nb, Ti) atoms are located in octahedra, which are linked in corrugated chains along the a axis. The chains, in turn, are linked in a framework through the Si–O rings and

refined for 7 cationic and 11 anionic positions. The refinement of the occupancies of the Nb, Ti, and Fe atoms in the Nb(1) = 4(f) and Nb(2) = 4(h) positions, of the Ca and Mn atoms in the $\text{M}^{\text{II}} = 2(\text{c})$ position, of the Ca, Na, and Ba atoms in the $\text{A}^{\text{III}} = 4(\text{i})$ position, of the Na and K atoms in the $\text{A}^{\text{II}} = 4(\text{m})$ position, and of the O atoms in the $\text{H}_2\text{O}(3) = 4(\text{m})$ position resulted in the following detailed formula of the mineral:

additional M^{II} octahedra, which are randomly (by ~70%) filled with Ca atoms. The cation–oxygen distances in the Nb octahedra and Si tetrahedra have standard values. The Si–O–Si angles in the Si–O rings are as follows: $\text{Si}_1\text{–O}_4\text{–Si}_1 = 139.2(9)^\circ$, $\text{Si}_2\text{–O}_5\text{–Si}_2 = 155(1)^\circ$, and $\text{Si}_1\text{–O}_7\text{–Si}_2 = 159(1)^\circ$. Although the geometric parameters of the frameworks of the title mineral and kuzmenkoite are similar, these minerals differ fundamentally in the filling of the octahedral positions (the Ti atoms in the chains are replaced by Nb, and the Ca atoms are located in the “linking” isolated M^{II} octahedra). The cation–anion distances in the octahedra of the mineral under study (2.48–2.56 Å; the average value is 2.53 Å) are larger than the average distances in Ba-labuntsovite and kuzmenkoite (2.16 and 2.17 Å, respectively). The large K and Na cations and water molecules occupy cavities of the framework. As in the case of kuzmenkoite, the A^{I} position in the title mineral remains vacant, and the A^{II} position is statistically occupied by the K and Na cations with the former slightly predominating (the cation–anion distances lie in the range of 2.81(6)–3.58(4) Å; the average distance is 3.20 Å; the coordination environment is a nine-vertex polyhedron).

The mineral under study also differs from all other members of the labuntsovite group in the filling of the A^{III} position. Thus, this position in the title mineral is filled with Ca and Na rather than with Ba and K, as in the case of other minerals. The A^{II} position is shifted (removed) from the M^{II} position and the $\text{H}_2\text{O}(3)$ molecule (the $\text{M}^{\text{II}}\text{–A}^{\text{III}}$ and $\text{A}^{\text{III}}\text{–H}_2\text{O}(3)$ distances are 2.41 and 0.82 Å, respectively), whereas the corresponding distances in Ba-labuntsovite are 2.11 and 0.29 Å, respectively. The Ca and Na cations (partially, the Ba cations) randomly (by ~23%) occupy the A^{III} position (the coordination environment is a nine-vertex polyhedron; the cation–oxygen distances are in the range of 2.48(5)–3.61(6) Å; the average distance is 3.15 Å) alternating with the M^{II} octahedra, and the M^{II} complex dominates over A^{III} (~70 and 23%, respectively). In Ba-labuntsovite, the small Mn, Mg, and Fe cations and the large Ba cations are more uniformly distributed over two “alternative” M^{II} and A^{III} positions (46 and 53%, respectively).

Table 1. Principal crystallographic characteristics, selected details of X-ray data collection, and results of structure refinement of the mineral

Characteristic	Parameter
a , Å	14.641(1)
b , Å	14.214(1)
c , Å	7.9148(2)
β , deg	117.36(1)
V , Å ³	1463(2)
Space group	$C2/m$
2θ range	3–49.8
Scan step (h), deg	0.02
Number of reflections	1407
Number of parameters in the refinement	68
R_p	2.83
R_{wp}	3.91
R_{exp}	1.70
R_B	2.28
R_F	1.66
s^*	2.29

* $s = R_{wp}/R_{exp}$.

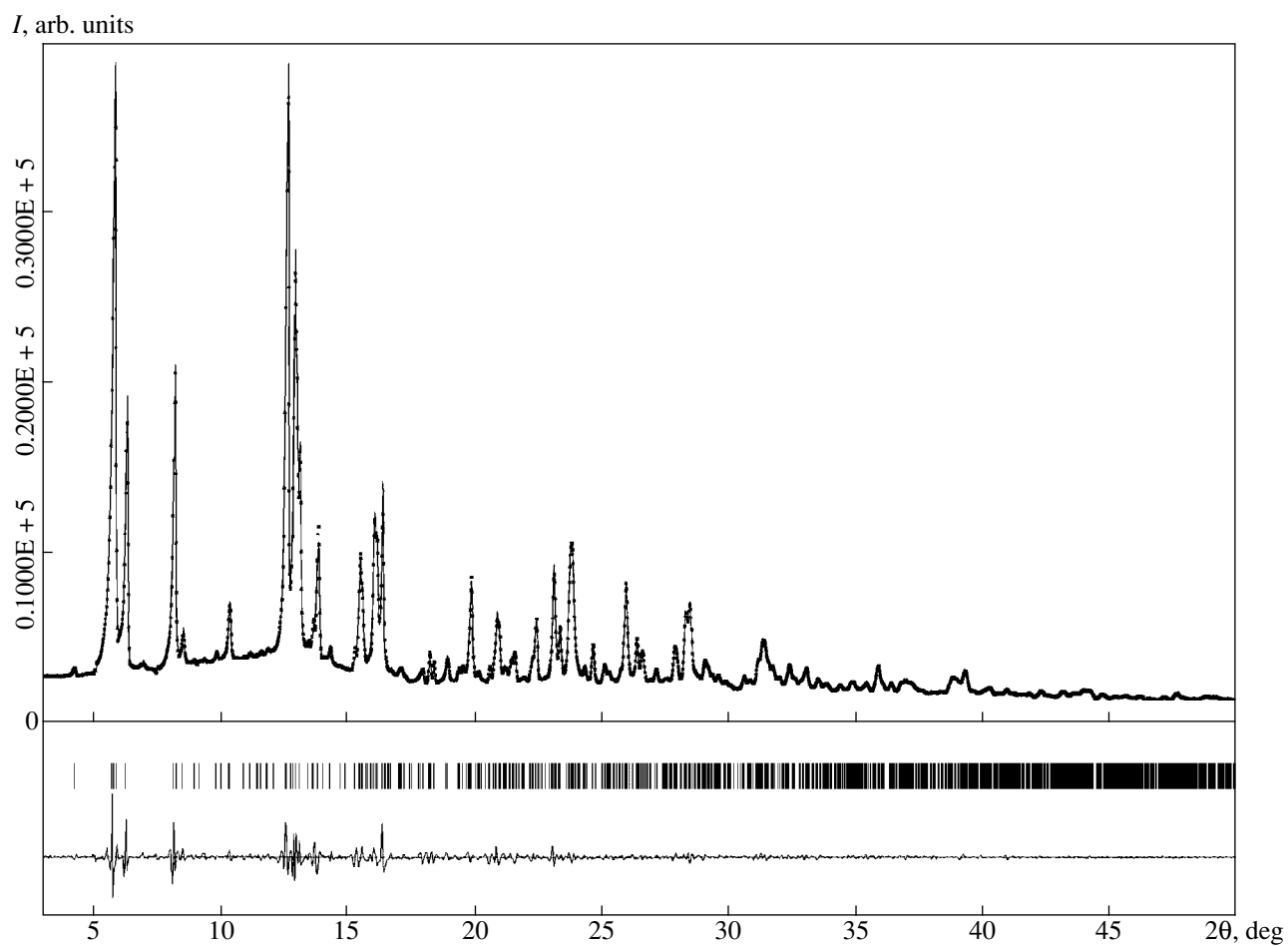


Fig. 1. Experimental (solid line) and theoretical (marked with asterisks) X-ray spectra of the mineral.

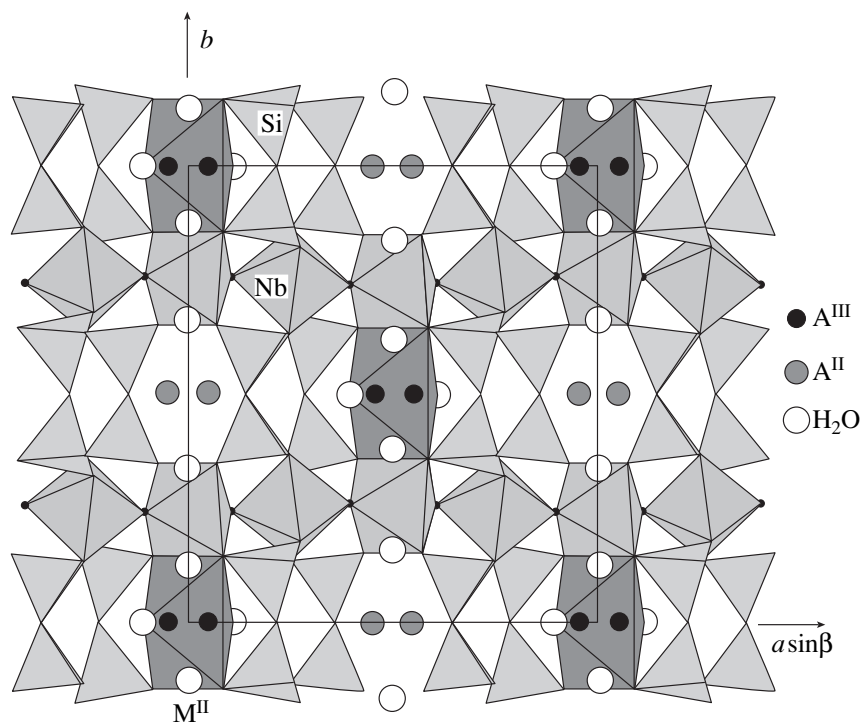


Fig. 2. The structure of the mineral projected onto the (001) plane.

Table 2. Atomic coordinates and thermal parameters for the mineral

Position	Multiplicity	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{iso} , Å ²
Nb ₁	4	0.25	0.25	0.5	1.1(3)
Nb ₂	4	0	0.245(1)	0.5	1.9(3)
M ^{II}	2	0	0	0.5	1.3(8)
A ^{III}	4	0.05(1)	0	0.25(2)	4(3)
A ^{II}	4	0.452(6)	0	0.73(2)	4(2)
Si ₁	8	0.313(2)	0.113(1)	0.235(2)	0.2(4)
Si ₂	8	0.210(1)	0.115(1)	0.795(2)	0.2(4)
O ₁	8	0.086(3)	0.145(6)	0.701(6)	2(1)
O ₂	8	0.273(3)	0.176(3)	0.732(5)	2(1)
O ₃	8	0.252(3)	0.134(3)	0.353(6)	3(1)
O ₄	4	0.359(4)	0	0.277(6)	1(1)
O ₅	4	0.215(5)	0	0.755(8)	4(2)
O ₆	8	0.428(3)	0.150(2)	0.350(6)	1(1)
O ₇	8	0.257(4)	0.134(2)	0.010(8)	3.2(7)
O, OH	8	0.104(3)	0.242(3)	0.388(2)	1.7(6)
H ₂ O(1)	4	0.5	0.163(3)	0	5(2)
H ₂ O(2)	4	0	0.123(4)	0	3(1)
H ₂ O(3)	4	0.109(6)	0	0.334(9)	5(3)

Note: (1) Nb₁ = 2.70(2)Nb + 1.20(4)Ti + 0.05(3)Fe; (2) Nb₂ = 2.65(2)Nb + 1.30(4)Ti + 0.05(3)Fe; (3) M^{II} = 1.4(1)Ca; (4) A^{III} = 0.6(1)Ca + 0.3(1)Na; (5) A^{II} = 1.0(1)K + 0.9(1)Na; and (6) H₂O(3) = 3H₂O.

Therefore, the total deficiency of the extraframework cations is observed in the structure of the mineral under study (2.8 of 12 theoretically possible cations are present) with the simultaneous high H₂O content. The replacement of Ti by the larger Nb cation, the replacement of Mn by Ca, and the high H₂O content cause a noticeable increase in the unit cell parameters.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 99–05–65524) and by the National Science Foundation of China (NSFC) (the joint project of RFBS and NSFC no. 99–05–39019).

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