

Crystal Structures of Gjerdingenite-Ca and Gjerdingenite-Na, New Minerals of the Labuntsovite Group

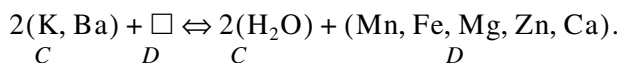
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The labuntsovite group comprises more than 20 mineral species [1] whose structures are based on a heteropolyhedral framework formed by columns of vertex-sharing (Ti,Nb) octahedra extended along the *a* axis and quaternary rings of Si tetrahedra. The cavities of this zeolite-like framework accommodate large low-charge cations and water molecules. Most of the representatives of the labuntsovite group have a monoclinic symmetry and only two of them—nenadkevichite [2] and its Ti analogue, korobitsynite [3]—are orthorhombic. In monoclinic minerals, additional octahedra centered by *D* cations (Mn²⁺, Fe²⁺, Mg, Zn, Ca, □) and bound rigidly to the (Ti,Nb) octahedra by sharing edges can also participate in the network formation. The crystal chemical formula of monoclinic minerals has the form $A_4B_4C_{4-2x}[D_x(H_2O)_{2x}][M_8(O,OH)_8][Si_4O_{12}]_4 \cdot nH_2O$ ($Z = 1$, $n = 8-12$, $x = 0-2$), where *A* and *B* (Na, K, Ca, Sr, Ba, □) are the extraframework cation sites; *C* (K, Ba, □) is the site alternative to the $[D_x(H_2O)_{2x}]$ complex; and *M* = Ti, Nb. The impossibility of the simultaneous presence of cations at the *C* and *D* sites due to the Coulomb repulsion (the distance between these sites is ~2.1 Å) results in alternative isomorphism according to the scheme



Monoclinic labuntsovite-like minerals with a deficiency or absence of extraframework cations at the *A* sites and an occupied *D* octahedron constitute, according to the accepted nomenclature [4], the kuzmenkoite and organovaite subgroups. They correspond to the

general formula $B_4D_2M_8(Si_4O_{12})_4(OH, O)_8 \cdot nH_2O$ ($B = K, Ba, Na$; $D = Mn, Zn, Fe, Ca$; $M = Ti, Nb$; $n = 10-14$). This study presents the results of the Rietveld refinement of the structures of two new minerals of the kuzmenkoite group, namely, gjerdingenite-Ca and gjerdingenite-Na [5].

Gjerdingenite-Ca and gjerdingenite-Na were established in the late parageneses in large highly alkaline pegmatites that had been subjected to intense hydrothermal treatment. Both types of minerals form pseudomorphoses at vuonnemite $Na_{11}TiNb_2Si_4O_{17}(PO_4)F$, which served as the source of Nb and Ti. Gjerdingenite-Ca came from pegmatite no. 61 on Karnasurt Mountain in the Lovozersky alkaline massif (the Kola Peninsula, Russia). The pinkish brown fine-grained dense aggregate of this mineral completely replaced vuonnemite crystals with sizes of up to $0.5 \times 6 \times 10$ mm. These pseudomorphoses occur among potash feldspar and natrolite, being associated with aegerine, modified steenstrupine, organovaite-Mn, organovaite-Zn, berylite, and so on. Gjerdingenite-Na was found in Mont Saint Hilaire alkaline rock (Quebec, Canada). Together with epistolite, it forms cavernous pseudomorphoses at large (up to 15 cm) vuonnemite tabular crystals; they are associated with albite, microcline, analcime, aegirine, eudialyte, natrolite, polyolithionite, steacyite, and so on. Gjerdingenite-Na forms aggregates of colorless, pinkish, and pale cream short prismatic crystals up to 0.5 mm in size. They are coarse and always twisted or split to some extent.

The cationic composition of both minerals was studied by the electron probe method and the water content was determined by thermogravimetry. Chemical composition of gjerdingenite-Ca (wt %): Na₂O, 1.14; K₂O, 3.61; CaO, 3.56; SrO, 3.47; BaO, 1.04; MnO, 0.84; ZnO, 0.05; Fe₂O₃, 0.19; Al₂O₃, 0.13; SiO₂, 39.29; TiO₂, 9.96; Nb₂O₅, 27.34; H₂O, 9.23; sum, 99.85. Chemical composition of gjerdingenite-Na (wt %): Na₂O, 4.04; K₂O, 3.97; CaO, 1.95; BaO, 0.92; MnO, 0.27; ZnO, 0.17; Fe₂O₃, 0.61; Al₂O₃, 0.20; SiO₂, 41.02; TiO₂, 10.20; Nb₂O₅, 27.78; H₂O, 9.85; sum, 100.98.

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Table 1. Selected crystal characteristics, X-ray experiment details, and structure refinement parameters of the minerals

Characteristics	Gjerdingenite-Ca	Gjerdingenite-Na
<i>a</i> , Å	14.6365(6)	14.6119(5)
<i>b</i> , Å	14.2059(5)	14.1426(6)
<i>c</i> , Å	7.8919(4)	7.9022(6)
β, deg	117.467(5)	117.432(6)
<i>V</i> , Å ³	1456(5)	1449(7)
Space group	<i>C2/m</i>	<i>C2/m</i>
2θ range	3–45.99	11–99.98
Scanning step <i>h</i> , deg	0.01	0.02
Number of reflections	1114	1631
Number of refined parameters	112	102
<i>R_p</i>	2.74	3.41
<i>R_{wp}</i>	3.72	4.39
<i>R_{exp}</i>	2.20	3.14
<i>R_B</i>	3.88	1.38
<i>R_F</i>	2.29	0.96
<i>s</i> *	1.69	1.40
σ _{<i>x</i>} **	2.510	1.886

* *s* = *R_{wp}*/*R_{exp}*, where *R_{exp}* is the expected *R_{wp}* value.

** σ_{*x*} is the factor for calculated standard deviations.

The empirical formulas of the new minerals were calculated for (Si,Al)₈O₂₄(OH,O)₄ (*Z* = 2). Gjerdingenite-Ca: (K_{0.93}Na_{0.45}Sr_{0.41}Ca_{0.15}Ba_{0.08})_{Σ2.02}(Ca_{0.62}Mn_{0.14}Fe_{0.03}Zn_{0.01})_{Σ0.80}(Nb_{2.51}Ti_{1.52})_{Σ4.03}(Si_{7.97}Al_{0.03})_{Σ8} · O₂₄[O_{2.86}(OH)_{1.14}]_{Σ4} · 5.67H₂O. Gjerdingenite-Na: (K_{0.98}Na_{0.62}Ca_{0.37}Ba_{0.07})_{Σ2.04}(Na_{0.90}Ca_{0.04}Mn_{0.04}Zn_{0.02})_{Σ1.00} · (Nb_{2.43}Ti_{1.49}Fe³⁺)_{Σ4.01}(Si_{7.95}Al_{0.05})_{Σ8}O₂₄[(OH)_{2.09}O_{1.91}]_{Σ4} · 5.32H₂O.

EXPERIMENTAL

The powder X-ray diffraction spectrum of gjerdingenite-Ca was recorded on an STOE-STADIP focusing diffractometer with a bent Ge(111) primary monochromator ensuring strictly monochromatic λMoK_{α1} radiation. The spectrum of gjerdingenite-Na was measured on an ADP-2 powder diffractometer using λCuK_{α1+α2} radiation. The main X-ray experiment parameters and crystal data are presented in Table 1. All calculations were performed with the WYRIET program, version 3.3 [6]. Owing to the similarity of the composition and unit cell parameters of gjerdingenite-Ca and gjerdingenite-Na to other representatives of the kuzmenkoite series, the atomic coordinates of the karupmoellerite-Ca structure, (Na,Ca,K)₂Ca[(Nb,Ti)₄(Si₄O₁₂)₂(O,OH)₄] · 7H₂O [7, 8], were used as the initial model for the

former mineral and those of gjerdingenite-Mn (K,Na)₂(Mn,Fe)[(Nb,Ti)₄(Si₄O₁₂)₂(O,OH)₄] · 6H₂O [9] served as the initial model for the latter mineral.

The structures of both minerals were refined within space group *C2/m* by gradual addition of the refined parameters with continuous graphical background modeling. The peak profiles were described using the Pearson function at 6FWHM². The asymmetry was refined at 2θ < 40°. The coordinates *x*, *y*, *z* and isotropic thermal corrections were refined for both cationic and anionic sites and anisotropic corrections, only for the cationic sites. The refinement of the site occupancy by Nb, Ti, Ca, Mn, Na, Sr, K, Ca, Na, and Ba gave the following formulas: gjerdingenite-Ca, (□)₄(K_{0.45}Na_{0.2}□_{0.35})₄(□_{0.65}Sr_{0.2}Ca_{0.1}Ba_{0.05})₄(Ca_{0.5}Mn_{0.15}□_{0.35})₂(Nb_{0.7}Ti_{0.3})₄(Nb_{0.6}Ti_{0.4})₄ · [Si₄O₁₂]₄O_{5.20}(OH)_{2.80} · 11.34H₂O (*Z* = 1, *D_x* = 2.68 g/cm³); in the simplified form, K₂Ca(Nb,Ti)₄(Si₄O₁₂)₂(O,OH)₄ · 6H₂O (*Z* = 2); gjerdingenite-Na, (□)₄(K_{0.5}Na_{0.4}Ca_{0.1})₄(□)₄(Na_{0.85}Ca_{0.15})₂ · (Nb_{0.65}Ti_{0.35})₄(Nb_{0.55}Ti_{0.45})₄[Si₄O₁₂]₄(OH)_{4.48}O_{3.52} · 10.64H₂O (*Z* = 1, *D_x* = 2.64 g/cm³); in the simplified form, (K,Na)₂Na[(Nb,Ti)₄(Si₄O₁₂)₂(OH,O)₄] · 5H₂O (*Z* = 2). In the expanded formulas, the contents of cations at sites *A*, *B*, *C*, *D*, *M*(1), and *M*(2) are shown successively in parentheses. The anionic part was separated into O atoms, OH groups, and H₂O molecules based on calculation of the local and formal balance of the valences taking into account the cation–anion distance as described previously [11]. The corresponding final *R* values are summarized in Table 1. Figure 1 shows the experimental and simulated X-ray diffraction spectra of the minerals. The final atom coordinates, refined site occupancies, and isotropic thermal parameters are summarized in Table 2.

In the structures of gjerdingenite-Ca and gjerdingenite-Na, as in the other representatives of the labuntsovite group, the (Nb,Ti) atoms are located in the *M* octahedra connected into zigzag chains by sharing of the (O,OH) vertices. The *M* chains stretched along the *a* axis and located at two levels along the *b* axis are combined along the [010] and [001] directions with the silicon–oxygen quaternary rings and with the “cross-linking” *D* octahedra to give a heteropolyhedral framework (Fig. 2) whose zeolite cavities accommodate large cations, mainly K, and H₂O molecules.

Both minerals studied supplement the list of the kuzmenkoite group (Table 3), which is characterized by predominance of Nb at the *M* octahedral sites, the Nb/Ti ratio being higher at the *M*(1) site. The neighboring *M* octahedra are rotated with respect to each other around the chain axis; the inclination (rotation) angles of the *M*(1)–O(8)–*M*(2) octahedron for all niobium members of the kuzmenkoite subgroup, as well as for other monoclinic minerals of the labuntsovite group, occur in a narrow range (133°–136°). The cation–anion distances in the *M* octahedra in the gjerdingenite-Ca structure lie in the standard ranges for (Nb,Ti) octahe-

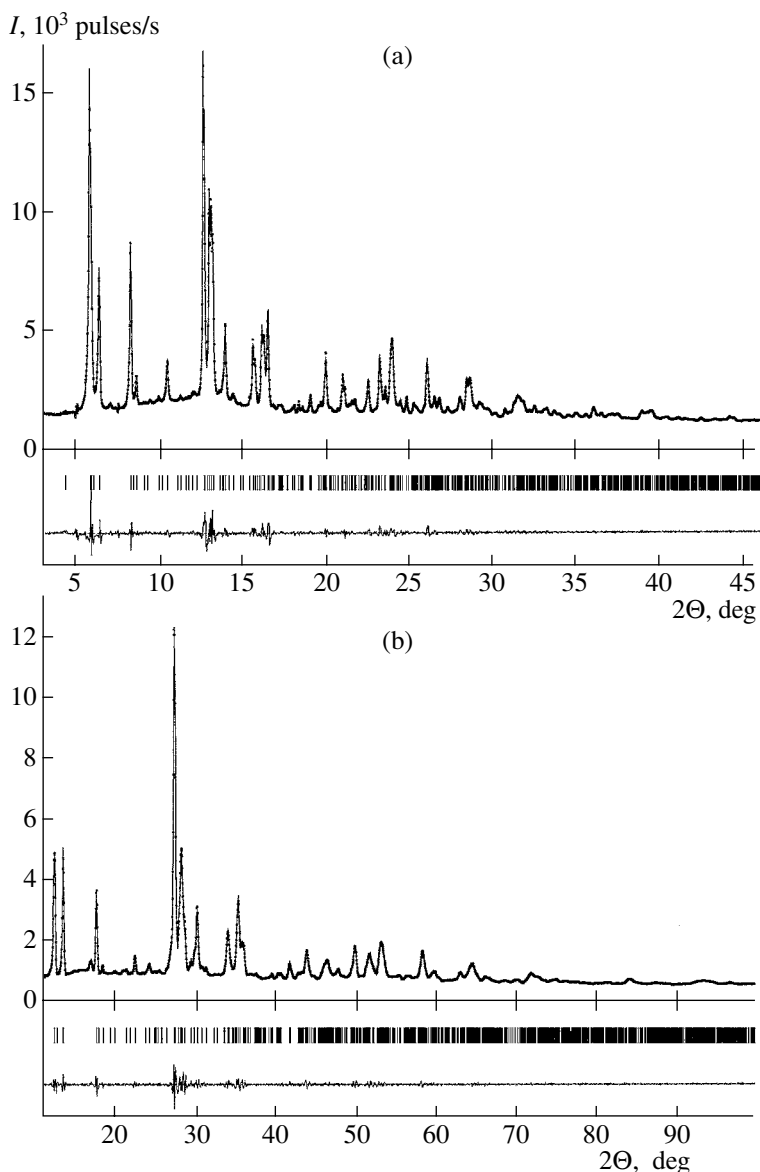


Fig. 1. Experimental (solid line) and theoretical (asterisks) X-ray diffraction spectra of gjerdingenite-Ca and gjerdingenite-Na.

dra, being equal to 1.89(4)–1.94(4) Å (average 1.92 Å) for the $M(1)$ octahedra and 1.88(4)–2.09(4) Å (average 2.02 Å) for the $M(2)$ octahedra. For the gjerdingenite-Na structure, the difference between the shortest and the longest cation–anion distances (Δl) in the M octahedra is greater: the limiting values for the $M(1)$ and $M(2)$ octahedra are 1.82(5)–2.02(3) (average 1.94, $\Delta l = 0.20$ Å) and 1.84(5)–2.21(3) (average 1.99, $\Delta l = 0.37$ Å), which is not typical of other monoclinic labuntsovite-like minerals, for which Δl does not usually exceed 0.15 Å [1]. The niobium representatives of the kuzmenkoite group differ from one another in the D -site composition: in gjerdingenite-Fe [10] and gjerdingenite-Mn [9], the D octahedra cross-linking the (Nb,Ti) octahedral chains are ~85% occupied by the Fe and Mn cations, respectively; in gjerdingenite-Ca, this

site is statistically occupied by Ca (~50%) and Mn (~15%) cations and is partially vacant (~35%). In karupmoellerite-Ca, these sites are occupied only by Ca cations (70%). In gjerdingenite-Na, this site is fully occupied by Na (~80%) and Ca (~20%) cations. Note that, in the gjerdingenite-Ca, karupmoellerite-Ca, and gjerdingenite-Na structures, the coordination sphere of the D site containing Na^+ and Ca^{2+} cations with greater ionic radii than the Fe^{2+} and Mn^{2+} cations can incorporate two bridging $\text{Si}(2)\text{--O}(5)\text{--Si}(2)$ vertices related by a twofold rotation axis (Fig. 2), which are separated from the D cation by ~2.8 Å (in the gjerdingenite-Fe and gjerdingenite-Mn structures, these distances are ~3.2 Å). This induces deformation of the silicon–oxygen ring manifested as both a distortion of Si tetrahedra

Table 2. Atomic coordinates, isotropic thermal factors (B_{iso}), and site occupancies in the gjerdingenite-Ca (upper row) and gjerdingenite-Na (lower row) structures

Site	Multiplicity	x/a	y/b	z/c	$B_{\text{iso}}, \text{\AA}^2$	Occupancy
Si(1)	8	0.307(2)	0.115(2)	0.229(3)	0.2(3)	Si _{1.00}
		0.308(1)	0.110(2)	0.240(3)	1.1(4)	The same
Si(2)	8	0.210(2)	0.116(2)	0.785(4)	0.4(3)	Si _{1.00}
		0.208(1)	0.106(2)	0.780(3)	0.6(5)	The same
<i>M</i> (1)	4	0.25	0.25	0.5	1.6(2)	Nb _{0.68(3)} Ti _{0.32(3)}
		0.25	0.25	0.5	0.4(2)	Nb _{0.66(2)} Ti _{0.34(2)}
<i>M</i> (2)	4	0	0.247(1)	0.5	2.1(2)	Nb _{0.57(3)} Ti _{0.43(3)}
		0	0.247(1)	0.5	1.1(3)	Nb _{0.52(2)} Ti _{0.48(2)}
<i>D</i>	2	0	0	0.5	1.6(6)	Ca _{0.48(1)} Mn _{0.15(1)} □ _{0.37}
		0	0	0.5	0.2(7)	Na _{0.84(2)} Ca _{0.16(2)}
<i>B</i>	4	0.467(3)	0	0.745(5)	3.5(8)	K _{0.46(1)} Na _{0.21(1)} □ _{0.33}
		0.458(2)	0	0.760(3)	4.5(9)	K _{0.50(2)} Na _{0.38(2)} Ca _{0.12(2)}
<i>C</i>	4	0.048(4)	0	0.25(1)	3.3(9)	□ _{0.66} Sr _{0.19(1)} Ca _{0.12(1)} Ba _{0.03(1)}
		–	–	–	–	□ _{1.00}
O(1)	8	0.085(3)	0.145(2)	0.704(6)	2.5(8)	O _{1.00}
		0.088(3)	0.133(3)	0.699(7)	3.2(12)	The same
O(2)	8	0.275(3)	0.187(2)	0.733(5)	0.7(6)	O _{1.00}
		0.275(2)	0.183(3)	0.739(6)	1.3(10)	The same
O(3)	8	0.241(3)	0.150(3)	0.326(5)	0.8(10)	O _{1.00}
		0.244(2)	0.152(3)	0.346(7)	0.2(10)	The same
O(4)	4	0.344(4)	0	0.276(5)	0.8(10)	O _{1.00}
		0.339(3)	0	0.264(8)	0.7(14)	The same
O(5)	4	0.214(4)	0	0.754(7)	4.4(13)	O _{1.00}
		0.215(4)	0	0.758(9)	4.4(19)	The same
O(6)	8	0.425(3)	0.151(2)	0.345(5)	1.1(8)	O _{1.00}
		0.428(2)	0.156(3)	0.339(7)	1.1(8)	The same
O(7)	8	0.255(4)	0.135(2)	0.002(8)	3.5(4)	O _{1.00}
		0.253(4)	0.136(2)	0.014(8)	3.9(8)	The same
O(8)	8	0.105(3)	0.243(3)	0.391(2)	1.9(4)	O _{0.65} (OH) _{0.35}
		0.095(2)	0.252(4)	0.395(3)	1.4(5)	(OH) _{0.56} O _{0.44}
H ₂ O(1)	4	0.5	0.173(3)	0	4.7(10)	H ₂ O
		0.5	0.165(3)	0	2.4(15)	The same
H ₂ O(2)	4	0	0.128(3)	0	2.0(8)	H ₂ O
			0.130(4)	0	2.5(14)	The same
H ₂ O(3)	4	0.069(9)	0	0.29(3)	2.4(18)	H ₂ O
		0.066(4)	0	0.293(8)	2.6(14)	The same

(deviation of the OSiO angles and the Si–O distances from the standard values) and an increase in the SiOSi angles (to 145°–160°) with respect to those for other monoclinic labuntsovite-like minerals (135°–148°) [1],

in particular, gjerdingenite-Fe and gjerdingenite-Mn (138°–146°). In the orthorhombic nenadkevichite and korobitsynite structures, the SiOSi angles in the silicon–oxygen ring are greater (150°–172°); for mono-

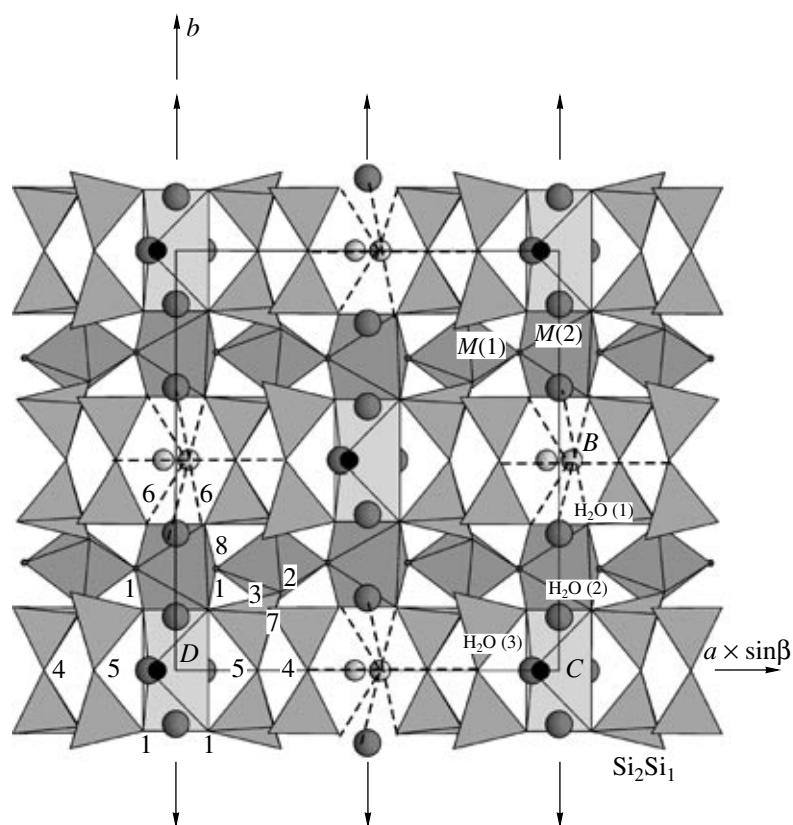


Fig. 2. Projection of the structures of gjerdingenite-Ca and gjerdingenite-Na onto the (001) plane. The dashed lines show the cation–oxygen bonds in the coordination sphere of one of the *B* sites related by twofold rotation axes (bold arrows). The small black circles show the oxygen atoms partially replaced by (OH) groups. Site *C* in the gjerdingenite-Na structure is vacant. The digits denote the oxygen sites.

clinic minerals, their increase has been noted for the *D*-vacancy vuoriyavite-K structure (137° – 154°) [12].

The SiOSi angles influence the SiOSi stretching frequency, manifested in the IR spectra of the labuntsovite group minerals in the range from 1000 to 1150 cm^{-1} [1]. In particular, for the niobium members of the labuntsovite group, the maximum of the highest frequency band

in this range regularly decreases with a decrease in the greatest angles in the $[\text{Si}_4\text{O}_{12}]$ ring: 1138 cm^{-1} for nenadkevichite; 1136 cm^{-1} for vuoriyavite-K; 1135 cm^{-1} for gjerdingenite-Ca; 1110 cm^{-1} (shoulder) for gjerdingenite-Na (underestimated due to the overlap with the neighboring band); and 1104 cm^{-1} for gjerdingenite-Mn and gjerdingenite-Fe. Infrared spectra confirm the

Table 3. Comparative crystal characteristics of the niobium members of the kuzmenkoite subgroup

Mineral, formula	Space group	Unit cell parameters, Å			$V, \text{Å}^3$	Z	$D_{\text{exp}}, \text{g/cm}^3$	Source
		a	b β, deg	c				
Gjerdingenite-Fe $\text{K}_2\text{Fe}(\text{Nb}, \text{Ti})_4(\text{Si}_4\text{O}_{12})_2(\text{O}, \text{OH})_4 \cdot 6\text{H}_2\text{O}$	<i>C2/m</i>	14.53	13.94 117.6	7.84	1407	2	2.82	[10]
Gjerdingenite-Mn $\text{K}_2\text{Mn}(\text{Nb}, \text{Ti})_4(\text{Si}_4\text{O}_{12})_2(\text{O}, \text{OH})_4 \cdot 6\text{H}_2\text{O}$	<i>C2/m</i>	14.56	13.96 117.6	7.85	1414	2	2.93	[9]
Gjerdingenite-Na $(\text{K}, \text{Na})_2\text{Na}(\text{Nb}, \text{Ti})_4(\text{Si}_4\text{O}_{12})_2(\text{OH}, \text{O})_4 \cdot 5\text{H}_2\text{O}$	<i>C2/m</i>	14.61	14.14 117.4	7.90	1449	2	2.71	[5], this work
Gjerdingenite-Ca $\text{K}_2\text{Ca}(\text{Nb}, \text{Ti})_4(\text{Si}_4\text{O}_{12})_2(\text{O}, \text{OH})_4 \cdot 6\text{H}_2\text{O}$	<i>C2/m</i>	14.64	14.21 117.5	7.89	1456	2	2.79	[5], this work
Karupmoellerite-Ca $(\text{Na}, \text{Ca}, \text{K})_2\text{Ca}(\text{Nb}, \text{Ti})_4(\text{Si}_4\text{O}_{12})_2(\text{O}, \text{OH})_4 \cdot 7\text{H}_2\text{O}$	<i>C2/m</i>	14.64	14.21 117.6	7.91	1463	2	2.71	[7, 8]

high degree of occupancy of the *D* sites in the gjerdingenite-Ca and gjerdingenite-Na structures. For the *D*-vacancy members of the group, the IR-active (Nb,Ti)-O stretching frequency is equal to 665 cm⁻¹. As shown in terms of the first-order perturbation theory [1], the frequency of this band linearly correlates with the occupancy of the *D* site and, at a 50% occupancy for the *D* cations with relatively high force characteristics (Fe, Mn, Mg, Zn), this value equals 679 cm⁻¹. In the case of *D* cations with low force characteristics (Ca, Na), the expected linear correlation coefficients are lower, which affects the (Nb,Ti)-O stretching frequencies: 675 cm⁻¹ for gjerdingenite-Na for 100% occupancy of the *D* octahedron and 679 cm⁻¹ for gjerdingenite-Ca for 65% occupancy of the *D* octahedron.

In terms of the composition and occupancy of the extraframework sites, gjerdingenite-Ca resembles most closely karupmoellerite-Ca and is the second (apart from the latter) member of the labuntsovite group with predominance of Ca in the *D* octahedron. Gjerdingenite-Na is not only the first member of the labuntsovite group with predominance of Na in the *D* octahedron but also is the only known representative of the kuzmenkoite group with a fully occupied *D* site (Table 3). The presence of Ca²⁺ and Na⁺ cations, which are larger than Fe²⁺ and Mn²⁺, in the cross-linking *D* octahedra of the mixed Si, *M*, *D* framework not only increases the unit cell dimensions for gjerdingenite-Ca, gjerdingenite-Na, and karupmoellerite-Ca with respect to those in gjerdingenite-Mn and gjerdingenite-Fe but also induces deformation of the whole framework.

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