

## GJERDINGENITE-Na AND GJERDINGENITE-Ca, TWO NEW MINERAL SPECIES OF THE LABUNTISOVITE GROUP

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### ABSTRACT

Gjerdingenite-Na,  $(K,Na)_2Na(Nb,Ti)_4(Si_4O_{12})_2(OH,O)_4 \cdot 5H_2O$ , and gjerdingenite-Ca,  $K_2Ca(Nb,Ti)_4(Si_4O_{12})_2(O,OH)_4 \cdot 6H_2O$ , are two new mineral species of the labuntsovite group, kuzmenkoite subgroup, and analogs of gjerdingenite-Fe and gjerdingenite-Mn with dominant Na and Ca at the *D* site, respectively. They are alteration products of vuonnemite formed in hydrothermal assemblages of peralkaline pegmatites. Gjerdingenite-Na occurs at Mont Saint-Hilaire, Quebec, Canada, with microcline, albite, aegirine, analcime, a eudialyte-group mineral, natrolite, epistolite and polyolithionite as a pseudomorph (up to 12 cm) after vuonnemite crystals, and as equant, prismatic or tabular crystals up to  $0.2 \times 0.3 \times 0.5$  mm. Gjerdingenite-Ca occurs at Mount Karnasurt, Lovozero massif, Kola Peninsula, Russia, as a fine-grained pseudomorph (up to  $0.5 \times 6 \times 10$  mm) after lamellar crystals of vuonnemite and as divergent crystals, elongate along [010], up to  $0.2 \times 0.3 \times 2$  mm, with microcline, natrolite, albite, aegirine, organovaite-Mn, organovaite-Zn, beryllite, epididymite and yofortierite. Both new minerals are transparent in tiny grains and translucent to opaque in aggregates, with a vitreous luster and a white streak. Gjerdingenite-Na is colorless to pale pink, whitish pink or cream colored. Gjerdingenite-Ca is white or pale brown to pinkish brown. Both minerals are brittle, with no observed cleavage and an uneven fracture. The Mohs hardness is 5. For gjerdingenite-Na,  $D_{meas} = 2.71(1)$ ,  $D_{calc} = 2.69$ ; for gjerdingenite-Ca,  $D_{meas} = 2.79(1)$ ,  $D_{calc} = 2.775$  g/cm<sup>3</sup>. The IR spectra are similar to those of other members of the kuzmenkoite subgroup. Both minerals are optically biaxial positive. For gjerdingenite-Na:  $\alpha$  1.647(2),  $\beta$  1.653(2),  $\gamma$  1.755(3),  $2V_{meas} = 25(10)^\circ$ ,  $2V_{calc} = 28.5^\circ$ ; for gjerdingenite-Ca:  $\alpha$  1.680(1),  $\beta$  1.682(2),  $\gamma$  1.762(3),  $2V_{meas} = 25(10)^\circ$ ,  $2V_{calc} = 19^\circ$ . For both minerals, the optical orientation is  $Y = b$ . The chemical composition (electron microprobe, H<sub>2</sub>O by TGA) of gjerdingenite-Na is Na<sub>2</sub>O 4.04, K<sub>2</sub>O 3.97, CaO 1.95, BaO 0.92, MnO 0.27, ZnO 0.17, Fe<sub>2</sub>O<sub>3</sub> 0.61, Al<sub>2</sub>O<sub>3</sub> 0.20, SiO<sub>2</sub> 41.02, TiO<sub>2</sub> 10.20, Nb<sub>2</sub>O<sub>5</sub> 27.78, H<sub>2</sub>O 9.85, sum 100.98 wt.%; that of gjerdingenite-Ca is Na<sub>2</sub>O 1.14, K<sub>2</sub>O 3.61, CaO 3.56, SrO 3.47, BaO 1.04, MnO 0.84, ZnO 0.05, Fe<sub>2</sub>O<sub>3</sub> 0.19, Al<sub>2</sub>O<sub>3</sub> 0.13, SiO<sub>2</sub> 39.29, TiO<sub>2</sub> 9.96, Nb<sub>2</sub>O<sub>5</sub> 27.34, H<sub>2</sub>O 9.23, sum 99.85 wt.%. The empirical formulae, based on [(Si,Al)<sub>8</sub>O<sub>24</sub>](O,OH)<sub>4</sub>, are: for gjerdingenite-Na:  $(K_{0.98}Na_{0.62}Ca_{0.37}Ba_{0.07})_{\Sigma 2.04}(Na_{0.90}Ca_{0.04}Mn_{0.04}Zn_{0.02})_{\Sigma 1.00}(Nb_{2.43}Ti_{1.49}Fe^{3+}_{0.09})_{\Sigma 4.01}(Si_{7.95}Al_{0.05})_{\Sigma 8}O_{24}[(OH)_{2.09}O_{1.91}]_{\Sigma 4} \cdot 5.32H_2O$ ; for gjerdingenite-Ca:  $(K_{0.93}Na_{0.45}Sr_{0.41}Ca_{0.15}Ba_{0.08})_{\Sigma 2.02}(Ca_{0.62}Mn_{0.14}Fe_{0.03}Zn_{0.01})_{\Sigma 0.80}(Nb_{2.51}Ti_{1.52})_{\Sigma 4.03}(Si_{7.97}Al_{0.03})_{\Sigma 8}O_{24}[O_{2.86}(OH)_{1.14}]_{\Sigma 4} \cdot 5.67H_2O$ . Both minerals are monoclinic, *C2/m*, *Z* = 2. Unit-cell dimensions for gjerdingenite-Na are *a* 14.626(2), *b* 14.160(1), *c* 7.910(1) Å,  $\beta$  117.43(2)°, *V* 1454(1) Å<sup>3</sup>, and for gjerdingenite-Ca: *a* 14.6365(6), *b* 14.2049(5), *c* 7.8919(4) Å,  $\beta$  117.467(5)°, *V* 1455.9(2) Å<sup>3</sup>. The strongest reflections in the X-ray powder-diffraction pattern for gjerdingenite-Na [*d*(in Å)(*hkl*)] are: 7.102(29)(020), 7.044(54)(001), 6.510(42)(200), 4.995(44)(02 $\bar{1}$ ,021), 3.252(51)(42 $\bar{1}$ ), 3.249(100)(400), 3.148(28)(02 $\bar{2}$ ,022), and for gjerdingenite-Ca: 7.100(100)(020),

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6.999(88)(001), 6.476(38)(20 $\bar{1}$ ), 4.985(78)(02 $\bar{1}$ ,021), 3.252(42)(42 $\bar{1}$ ), 3.246(43)(400), 3.167(46)(04 $\bar{1}$ ,041), 3.140(36)(02 $\bar{2}$ ,022). The crystal structures of both minerals were refined by the Rietveld method using X-ray powder-diffraction data, yielding  $R_p = 3.41$ ,  $R_B = 1.38$ ,  $R_F = 0.96$  for gjerdingenite-Na, and  $R_p = 2.74$ ,  $R_B = 3.88$ ,  $R_F = 2.29$  for gjerdingenite-Ca. Both minerals are isotopic with other members of the kuzmenkoite subgroup.

**Keywords:** gjerdingenite-Na, gjerdingenite-Ca, new mineral species, labuntsovite group, kuzmenkoite subgroup, infrared spectroscopy, peralkaline pegmatites, Mont Saint-Hilaire, Quebec, Canada, Lovozero massif, Kola Peninsula, Russia.

### SOMMAIRE

La gjerdingenite-Na,  $(K,Na)_2Na(Nb,Ti)_4(Si_4O_{12})_2(OH,O)_4 \cdot 5H_2O$ , et la gjerdingenite-Ca,  $K_2Ca(Nb,Ti)_4(Si_4O_{12})_2(O,OH)_4 \cdot 6H_2O$ , sont deux espèces minérales découvertes récemment; elles appartiennent au groupe de la labuntsovite, sous-groupe de la kuzmenkoïte, et sont les analogues de la gjerdingenite-Fe et la gjerdingenite-Mn ayant Na et Ca dominants au site *D*, respectivement. Ces minéraux sont des produits de l'altération de la vuonnemite formée dans des assemblages hydrothermaux de pegmatites hyperalkalines. La gjerdingenite-Na se trouve au mont Saint-Hilaire, Québec, Canada, avec microcline, albite, aegyrine, analcime, un minéral du groupe de l'eudialyte, natrolite, épistolite et polyolithionite en pseudomorphose de la vuonnemite (en cristaux atteignant 12 cm), et en cristaux équidimensionnels, prismatiques ou tabulaires atteignant  $0.2 \times 0.3 \times 0.5$  mm. La gjerdingenite-Ca a été découverte au mont Karnasurt, massif de Lovozero, péninsule de Kola, en Russie, sous forme d'amas à grains fins (jusqu'à  $0.5 \times 6 \times 10$  mm) en pseudomorphose de cristaux lamellaires de vuonnemite, et de cristaux divergents allongés selon [010], atteignant  $0.2 \times 0.3 \times 2$  mm, avec microcline, natrolite, albite, aegyrine, organovaïte-Mn, organovaïte-Zn, beryllite, épidadymite et yofortierite. Les deux nouveaux minéraux sont transparents en grains infimes et translucides ou opaques en agrégats, avec un éclat vitreux et une rayure blanche. La gjerdingenite-Na est incolore ou rose pâle, rose blanchâtre ou crèmeux. La gjerdingenite-Ca est blanche ou brun pâle à brun rosâtre. Les deux minéraux sont cassants, sans clivage évident, et une fracture inégale. La dureté de Mohs est 5. La densité mesurée de la gjerdingenite-Na est 2.71(1), et la densité calculée, 2.69; la densité mesurée de la gjerdingenite-Ca est 2.79(1), et la densité calculée, 2.775 g/cm<sup>3</sup>. Les spectres infra-rouges sont semblables à ceux d'autres membres du sous-groupe de la kuzmenkoïte. Les deux minéraux sont biaxes positifs. Pour la gjerdingenite-Na:  $\alpha$  1.647(2),  $\beta$  1.653(2),  $\gamma$  1.755(3),  $2V_{mes} = 25(10)^\circ$ ,  $2V_{calc} = 28.5^\circ$ ; pour la gjerdingenite-Ca:  $\alpha$  1.680(1),  $\beta$  1.682(2),  $\gamma$  1.762(3),  $2V_{mes} = 25(10)^\circ$ ,  $2V_{calc} = 19^\circ$ . L'orientation optique des deux minéraux est  $Y = b$ . La composition chimique de la gjerdingenite-Na (données de microsonde électronique, H<sub>2</sub>O par thermogravimétrie) est: Na<sub>2</sub>O 4.04, K<sub>2</sub>O 3.97, CaO 1.95, BaO 0.92, MnO 0.27, ZnO 0.17, Fe<sub>2</sub>O<sub>3</sub> 0.61, Al<sub>2</sub>O<sub>3</sub> 0.20, SiO<sub>2</sub> 41.02, TiO<sub>2</sub> 10.20, Nb<sub>2</sub>O<sub>5</sub> 27.78, H<sub>2</sub>O 9.85, total 100.98% (poids); celle de la gjerdingenite-Ca est Na<sub>2</sub>O 1.14, K<sub>2</sub>O 3.61, CaO 3.56, SrO 3.47, BaO 1.04, MnO 0.84, ZnO 0.05, Fe<sub>2</sub>O<sub>3</sub> 0.19, Al<sub>2</sub>O<sub>3</sub> 0.13, SiO<sub>2</sub> 39.29, TiO<sub>2</sub> 9.96, Nb<sub>2</sub>O<sub>5</sub> 27.34, H<sub>2</sub>O 9.23, total 99.85%. Les formules empiriques, sur une base de  $[(Si,Al)_8O_{24}](O,OH)_4$ , sont: pour la gjerdingenite-Na:  $(K_{0.98}Na_{0.62}Ca_{0.37}Ba_{0.07})_{\Sigma 2.04} (Na_{0.90}Ca_{0.04}Mn_{0.04}Zn_{0.02})_{\Sigma 1.00} (Nb_{2.43}Ti_{1.49}Fe^{3+}_{0.09})_{\Sigma 4.01} (Si_{7.95}Al_{0.05})_{\Sigma 8}O_{24}[(OH)_{2.09}O_{1.91}]_{\Sigma 4} \cdot 5.32H_2O$ ; pour la gjerdingenite-Ca:  $(K_{0.93}Na_{0.45}Sr_{0.41}Ca_{0.15}Ba_{0.08})_{\Sigma 2.02} (Ca_{0.62}Mn_{0.14}Fe_{0.03}Zn_{0.01})_{\Sigma 0.80} (Nb_{2.51}Ti_{1.52})_{\Sigma 4.03} (Si_{7.97}Al_{0.03})_{\Sigma 8}O_{24}[(O_{2.86}OH)_{1.14}]_{\Sigma 4} \cdot 5.67H_2O$ . Les deux minéraux sont monocliniques, *C2/m*, *Z* = 2. Les paramètres réticulaires de la gjerdingenite-Na sont *a* 14.626(2), *b* 14.160(1), *c* 7.910(1) Å,  $\beta$  117.43(2)°, *V* 1454(1) Å<sup>3</sup>, tandis que ceux de la gjerdingenite-Ca sont: *a* 14.6365(6), *b* 14.2049(5), *c* 7.8919(4) Å,  $\beta$  117.467(5)°, *V* 1455.9(2) Å<sup>3</sup>. Les raies les plus intenses du spectre de diffraction X (méthode des poudres) de la gjerdingenite-Na [*d*(en Å)/(*hkl*)] sont: 7.102(29)(020), 7.044(54)(001), 6.510(42)(200), 4.995(44)(02 $\bar{1}$ ,021), 3.252(51)(42 $\bar{1}$ ), 3.249(100)(400), 3.148(28)(02 $\bar{2}$ ,022), et pour la gjerdingenite-Ca: 7.100(100)(020), 6.999(88)(001), 6.476(38)(20 $\bar{1}$ ), 4.985(78)(02 $\bar{1}$ ,021), 3.252(42)(42 $\bar{1}$ ), 3.246(43)(400), 3.167(46)(04 $\bar{1}$ ,041), 3.140(36)(02 $\bar{2}$ ,022). La structure cristalline des deux minéraux a été affinée avec la méthode de Rietveld pour donner  $R_p = 3.41$ ,  $R_B = 1.38$ ,  $R_F = 0.96$  pour la gjerdingenite-Na, et  $R_p = 2.74$ ,  $R_B = 3.88$ ,  $R_F = 2.29$  pour la gjerdingenite-Ca. Les deux minéraux sont isotypiques des autres membres du sous-groupe de la kuzmenkoïte.

(Traduit par la Rédaction)

**Mots-clés:** gjerdingenite-Na, gjerdingenite-Ca, nouvelles espèces minérales, groupe de labuntsovite, sous-groupe de la kuzmenkoïte, spectroscopie infrarouge, pegmatites hyperalkalines, mont Saint-Hilaire, Québec, Canada, massif de Lovozero, péninsule de Kola, Russie.

### INTRODUCTION

We describe here two new species of the kuzmenkoite subgroup within the labuntsovite group. They are niobium minerals and representatives of the gjerdingenite series, having the general formula  $K_2D(Nb,Ti)_4(Si_4O_{12})_2(O,OH)_4 \cdot 5-6H_2O$ . Gjerdingenite-Fe (*D* = Fe) and gjerdingenite-Mn (*D* = Mn) were earlier discovered in miaroles in alkaline granites of the Gjerdingen complex, Lunner, Oppland, Norway (Raade *et al.* 2002, 2004). One of the new members of the series is characterized

by dominant Na, and the other, by dominant Ca at the *D* site. In accordance with the IMA-accepted nomenclature of labuntsovite-group minerals (Chukanov *et al.* 2002), they are named **gjerdingenite-Na** and **gjerdingenite-Ca**, respectively (Cyrillic: гъердингенит-Na and гъердингенит-Ca). Both new minerals and their names have been approved by the IMA CNMMN (IMA nos. 2005-030 and 2005-029, respectively). The type specimens are deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow (catalog nos. 92111 for gjerdingenite-Ca and 92112

for gjerdingenite-Na) and the Canadian Museum of Nature, Ottawa (catalog no. CMNMC 85457, gjerdingenite-Na).

#### BACKGROUND INFORMATION

The labuntsovite group (Chukanov *et al.* 1999, 2002) includes orthorhombic and monoclinic zeolite-like silicates with the general crystallochemical formula  $A_4B_4C_{4-2x}[D_x(H_2O)_{2x}][M_8(O,OH)_8][Si_4O_{12}]_4 \cdot 8-14H_2O$  where  $0 < x < 2$ ; the simplified general formula is:  $A_2B_2C_2DM_4[Si_4O_{12}]_2(O,OH)_4 \cdot 4-7H_2O$ . Their structures are based on a unique mixed three-dimensional framework consisting of infinite chains of  $MO_6$  ( $M = Ti, Nb$ ) octahedra and  $[Si_4O_{12}]$  silicate rings. Some monoclinic members of the group also contain additional  $DO_6$  octahedra occupied by Mn, Fe, Zn, Mg and, rarely, Ca or Na. The  $SiO_4$  tetrahedra and  $MO_6$  octahedra are linked by O vertices, the  $M$  octahedra in chains are linked *via* common (O,OH) vertices, and the  $MO_6$  octahedra link with the  $DO_6$  octahedra *via* O–O edges. Large alkali (Na, K) and alkaline-earth (Ba, Sr, Ca) cations and  $H_2O$  molecules are situated in zeolite-like channels within the framework. These extra-framework sites (*B* and especially *A* and *C*) are typically only partially occupied.

Until 1998, only two minerals with such structures, namely labuntsovite and nenadkevichite, first described in the mid-1950s, were considered to be valid species. However, crystallochemical data from various samples of “labuntsovite” and “nenadkevichite” from several localities in the Kola Peninsula (Lovozero, Khibiny, Kovdor and Turiy Mys alkaline complexes), Quebec (Mont Saint-Hilaire), Wyoming (Trona mine) and Greenland (Ilímaussaq) revealed that significant crystallochemical diversity, which could not be correctly described in the context of these two mineral species, was hidden behind their names (Chukanov *et al.* 2003). In 1996, data on a synthetic compound closely related to nenadkevichite and having technologically important zeolitic properties were first published (Rocha *et al.* 1996). These facts and numerous new finds of labuntsovite–nenadkevichite-like minerals in various alkaline massifs led to a systematic investigation beginning in the second half of the 1990s. As a result, a number of new mineral species were described, and a nomenclature of the labuntsovite group was proposed and approved by the IMA Commission on New Minerals and Mineral Names (CNMMN) (Chukanov *et al.* 2002). A comprehensive compilation of data on labuntsovite-group minerals was also published (Chukanov *et al.* 2003).

The diversity of mineral species in the labuntsovite group is caused by extensive substitutions at all cation sites except the tetrahedrally coordinated ones, with related significant variations in the framework configuration, symmetry and cation ordering. Each of eleven octahedral and extra-framework cations, namely

Ti, Nb, Mg, Zn, Mn, Fe, Na, K, Ca, Sr and Ba, can be absent in a labuntsovite-group mineral as well as play a species-forming role by predominantly occupying a specific site in the structure. The strong cation-exchange properties of labuntsovite-group minerals were first discovered and studied by two of the authors (IVP, NVC). Owing to their crystallochemical diversity and strong zeolitic properties, members of the labuntsovite group have been the subject of a great deal of interest and investigation during the last decade, and they are now the best-studied group of natural zeolite-like titanate and niobosilicates. Many features of the crystal chemistry, properties and genesis of natural microporous silicates with mixed frameworks were discovered as a result. Twenty-nine labuntsovite-group mineral species are known at present. They are classified into nine subgroups (Table 1), corresponding to nine structural types with different framework topology, symmetry and unit-cell dimensions (Chukanov & Pekov 2005).

Labuntsovite-group minerals crystallize in peralkaline environments, under hydrothermal conditions. Considered as very rare minerals until recently, they are now known from 16 alkaline complexes. They have been found in large amounts in the Khibiny, Lovozero, and Kovdor massifs in the Kola Peninsula, Russia, in the Vuoriyarvi massif in northern Karelia, Russia, and at Mont Saint-Hilaire, Quebec, Canada. In some cases, they are the principal concentrators of Nb, Ti, Ba and Zn in hydrothermally altered alkaline rocks, which emphasizes their geochemical significance (Pekov & Chukanov 2005).

#### OCCURRENCE AND GENERAL APPEARANCE

Both new minerals occur in hydrothermal assemblages of peralkaline pegmatites related to agpaite feldspathoidal syenites. Like the majority Nb-dominant members of the labuntsovite group, they are principally products of the alteration of vuonemite,  $Na_{11}TiNb_2(Si_2O_7)_2(PO_4)_2O_3(F,OH)$ , an important concentrator of Nb in such pegmatites.

Specimens of gjerdingenite-Na were collected in the De-Mix quarry (now incorporated in the Poudrette quarry), Mont Saint-Hilaire, Quebec, Canada, by one of the authors (PT) in 1969. The mineral was briefly described by Perrault *et al.* (1969) as “UK-19-1”, but nothing further was published. The mineral was found in a large hydrothermally altered pegmatite dike that cuts nepheline syenite of the peralkaline East Hill suite (this dike is also the type locality for three other minerals: steacyite, yofortierite and thornasite). It is associated with microcline, albite, aegirine (early coarse prismatic, and late acicular), analcime, a eudialyte-group mineral, natrolite, epistolite, polyolithionite, steacyite, thorite, ekanite, brockite, fluorapatite, yofortierite, calcite, hemimorphite, sauconite (?) and earthy Mn oxides. Gjerdingenite-Na is a relatively abundant mineral in vuggy parts of the pegmatite. Together with

TABLE 1. LABUNTSOVITE-GROUP MINERALS,  $A_2B_2C_2DM_4[Si_4O_{12}]_2(O,OH)_4 \cdot 4-7H_2O$ 

Mineral species	A	B	C	D	M	Z	Space group	Subgroup
Nenadkevichite	Na	( $\Sigma A+B+C$ )	-	-	Nb	1	<i>Pbam</i>	Nenadkevichite*
Korobitsynite	Na	( $\Sigma A+B+C$ )	-	-	Ti	1	<i>Pbam</i>	
Vuorijarvite-K	K	( $\Sigma A+B+C$ )	□	□	Nb	2	<i>Cm</i>	Vuorijarvite*
Tsepinite-Na	Na	( $\Sigma A+B+C$ )	□	□	Ti	2	<i>Cm</i>	
Tsepinite-K	K	( $\Sigma A+B+C$ )	□	□	Ti	2	<i>Cm</i>	
Tsepinite-Ca	Ca	( $\Sigma A+B+C$ )	□	□	Ti	2	<i>C2/m</i>	
Tsepinite-Sr	Sr	( $\Sigma A+B+C$ )	□	□	Ti	2	<i>Cm</i>	
Paratsepinite-Ba	Ba	( $\Sigma A+B+C$ )	□	□	Ti	4	<i>C2/m</i>	Paratsepinite*
Paratsepinite-Na	Na	( $\Sigma A+B+C$ )	□	□	Ti	4	<i>C2/m</i>	
Lemleinite-K	Na	K	K	□	Ti	2	<i>C2/m</i>	Lemleinite
Lemleinite-Ba	Na	K	Ba	□	Ti	2	<i>C2/m</i>	
Labuntsovite-Mn	Na	K	□	Mn	Ti	2	<i>C2/m</i>	Labuntsovite
Labuntsovite-Mg	Na	K	□	Mg	Ti	2	<i>C2/m</i>	
Labuntsovite-Fe	Na	K	□	Fe	Ti	2	<i>C2/m</i>	
Paralabuntsovite-Mg	Na	K	□	Mg	Ti	4	<i>I2/m</i>	Paralabuntsovite
Kuzmenkoite-Mn	□	K	□	Mn	Ti	2	<i>C2/m, Cm</i>	Kuzmenkoite
Kuzmenkoite-Zn	□	K	□	Zn	Ti	2	<i>Cm</i>	
Lepkhenelmitite-Zn	□	Ba	□	Zn	Ti	2	<i>Cm</i>	
Gjerdingenite-Fe	□	K	□	Fe	Nb	2	<i>C2/m</i>	
Gjerdingenite-Mn	□	K	□	Mn	Nb	2	<i>C2/m</i>	
Gjerdingenite-Na	□	K	□	Na	Nb	2	<i>C2/m</i>	
Gjerdingenite-Ca	□	K	□	Ca	Nb	2	<i>C2/m</i>	
Karupmøllerite-Ca	□	Na	□	Ca	Nb	2	<i>C2/m</i>	
Organovaite-Mn	□	K	□	Mn	Nb	4	<i>C2/m</i>	Organovaite
Organovaite-Zn	□	K	□	Zn	Nb	4	<i>C2/m</i>	
Parakuzmenkoite-Fe	□	K	□	Fe	Ti	4	<i>C2/m</i>	
Gutkovaite-Mn	Ca + □	K	□	Mn	Ti	2	<i>Cm</i>	Gutkovaite**
Alsakharovite-Zn	Na + Sr	K	□	Zn	Ti	2	<i>Cm</i>	
Neskevaaraite-Fe	Na + K	K	□	Fe	Ti	2	<i>Cm</i>	

Data for previously described minerals are taken from: Chukanov *et al.* (2002), Chukanov & Pekov (2005). \* In the nomenclature of minerals of the nenadkevichite, vuorijarvite and paratsepinite subgroups, extra-framework cations *A*, *B* and *C* are formally combined. \*\* In gutkovaite-subgroup minerals, the *A* site is split into two independent sites, *A'* and *A''* with different occupancies. □: Vacant site.

epistolite, it forms pseudomorphs up to 12 cm in length after coarse platy crystals with crystal faces whose morphology, together with the presence of what appears to be epistolite, indicates that the precursor mineral was undoubtedly vuonnemite. These pseudomorphs (Fig. 1) are cavernous, or massive and granular. Crystals of gjerdingenite-Na up to  $0.2 \times 0.3 \times 0.5$  mm (usually combined in clusters, Fig. 2) line tiny cavities in the platy masses of the same mineral or are observed on aegirine and microcline crystals proximal to the pseudomorphs after vuonnemite. The crystals are equant, prismatic or tabular, and poorly formed. They are typically slightly curved or divergent (Fig. 2). Some crystals

are hollow. Crystals of the new mineral are monoclinic, in some cases pseudo-hexagonal. The crystals were not appropriate for goniometric measurements, but the major forms are probably pinacoids {100}, {001} and {010}. The inferred sequence of crystallization of the niobium silicates in the assemblage is: vuonnemite  $\rightarrow$  epistolite  $\rightarrow$  gjerdingenite-Na.

Gjerdingenite-Ca was found in 2001 by one of the authors (IVP) in Pegmatite #61 at Mount Karnasurt, Lovozero massif, Kola Peninsula, Russia. This huge (50  $\times$  100 m) lensoid pegmatite body situated in aegirine lujavrite is well known and has been described in detail by Pekov (2000). It is strongly altered hydrothermally

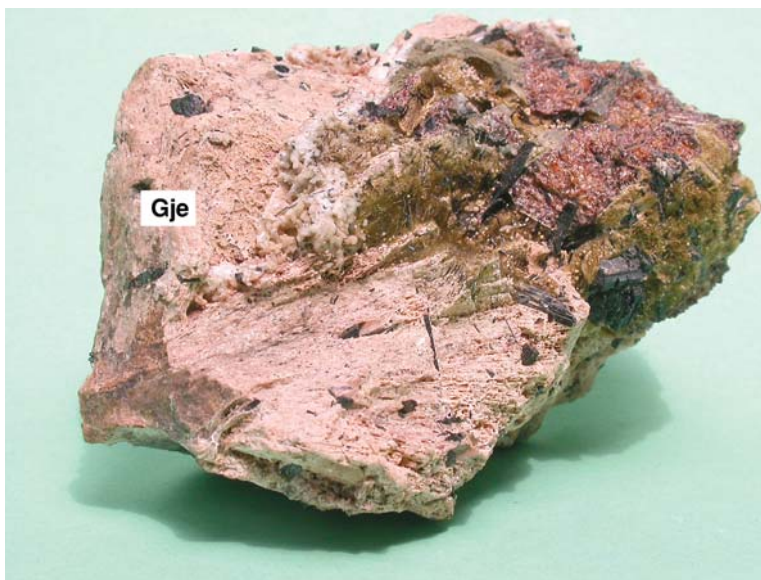


FIG. 1. Pseudomorphs of gjerdingenite-Na (Gje) after vuonnemite with eudialyte and two generations of aegirine (right part of the specimen). Specimen 8 cm across. P. Tarassoff photo.

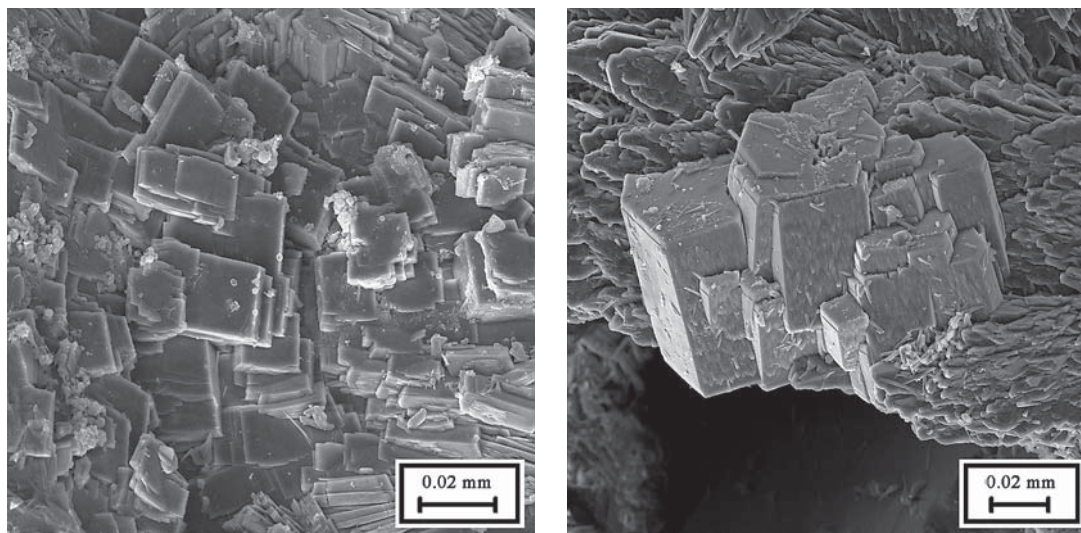


FIG. 2. SEM photomicrographs of gjerdingenite-Na: (a) aggregates of crystals incrusting a cavity in a massive pseudomorph after vuonnemite; (b) cluster of pseudo hexagonal prismatic crystals on microcline.

and contains diverse late-stage minerals. In particular, it is the type locality for beryllite, nenadkevichite, komarovite, organovaite-Mn, organovaite-Zn and the cotype locality for kuzmenkoite-Zn. Gjerdingenite-Ca occurs in two assemblages within this pegmatite. The holotype specimen was found in the marginal part of the pegmatite, with microcline, natrolite, aegirine, organovaite-Mn, organovaite-Zn, beryllite, epididymite, altered steenstrupine-(Ce), ranciéite (pseudomorph after sérandite) and yakhontovite. The new mineral forms fine-grained pseudomorphs up to  $0.5 \times 6 \times 10$  mm after lamellar well-shaped crystals of vuonnemite. In the core of the pegmatite, gjerdingenite-Ca occurs as crystals up to  $0.2 \times 0.3 \times 2$  mm in cavities proximal to pseudomorphs after vuonnemite consisting of komarovite, organovaite-Mn and strontiopyrochlore. Other minerals in the assemblage are microcline, albite, natrolite, aegirine, arfvedsonite, elpidite, kuzmenkoite-Mn, kuzmenkoite-Zn, mangan-neptunite, yofortierite, epididymite, eudidymite, leifite, nontronite, montmorillonite, saucconite and cristobalite. The gjerdingenite-Ca crystals are poorly formed and divergent, with indistinct terminations. They are elongate along [010], and their major forms are probably pinacoids {100} and {001}.

#### PHYSICAL AND OPTICAL PROPERTIES

Both new minerals are transparent in tiny grains, translucent in larger grains and opaque in aggregates, and have a vitreous luster and white streak. They are non-fluorescent in ultraviolet light. Gjerdingenite-Na is colorless to pale pink, whitish pink and cream-colored. Crystals of gjerdingenite-Ca are white, and the pseudomorphs after vuonnemite are pale brown to pinkish

brown. Both minerals are brittle, with an uneven fracture and no observed cleavage and parting. Their Mohs hardness is 5. The measured density of gjerdingenite-Na is 2.71(1), and the calculated density is 2.69 g/cm<sup>3</sup>. The measured density of gjerdingenite-Ca is 2.79(1), and the calculated density is 2.775 g/cm<sup>3</sup>.

Both minerals are optically biaxial positive. For gjerdingenite-Na:  $\alpha$  1.647(2),  $\beta$  1.653(2),  $\gamma$  1.755(3),  $2V_{\text{meas}} = 25(10)^\circ$ ,  $2V_{\text{calc}} = 28.5^\circ$ . For gjerdingenite-Ca:  $\alpha$  1.680(1),  $\beta$  1.682(2),  $\gamma$  1.762(3),  $2V_{\text{meas}} = 25(10)^\circ$ ,  $2V_{\text{calc}} = 19^\circ$ . For both minerals, dispersion was not observed, and the optical orientations are  $Y = b$ . Gjerdingenite-Na and the white variety of gjerdingenite-Ca are colorless and non-pleochroic. The pinkish brown variety of gjerdingenite-Ca shows very weak pleochroism:  $X$  and  $Z$ : colorless,  $Y$ : pale yellowish.

#### INFRARED SPECTROSCOPY

The infrared-absorption spectra of both new minerals were obtained using a Specord 75 IR spectrophotometer (powder samples prepared in KBr tablets; polystyrene and gaseous NH<sub>3</sub> were used as frequency standards). The spectra (Fig. 3) of the new species are similar to the spectra of other members of the kuzmenkoite subgroup (see Chukanov *et al.* 2003, Raade *et al.* 2004). The IR spectrum of gjerdingenite-Ca is especially similar to the spectrum of karupmøllerite-Ca (Pekov *et al.* 2002), another niobium-dominant member of this subgroup having Ca dominant at the  $D$  site. Absorption bands (in cm<sup>-1</sup>, frequencies of the most intense bands are underlined; sh: shoulder, br: broad) are as follows: gjerdingenite-Na: 3540sh, 3345br, 1640, 1115sh, 1098, 945sh, 925, 750sh, 677, 580, 449; gjerdingenite-Ca:

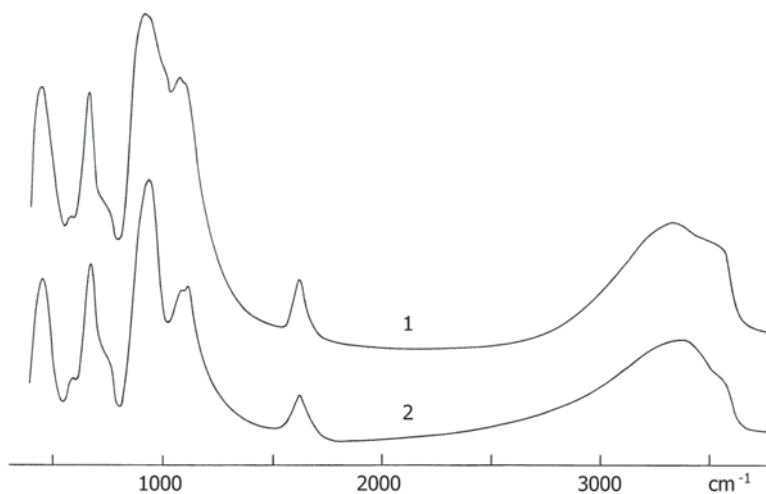


FIG. 3. Infrared spectra of gjerdingenite-Na (1) and gjerdingenite-Ca (2).

3360br, 1637, 1129, 1100, 945, 930sh, 750sh, 680, 600, 459 (see Discussion).

#### CHEMICAL COMPOSITION

The composition of both new minerals was determined by electron-microprobe analysis, and the H<sub>2</sub>O content was determined by thermogravimetric analysis (heating to 900°C in vacuum using an ATV-13 thermobalance). The electron-microprobe data were obtained with a Camebax SX 50 instrument in wavelength-dispersion (WDS) mode using an operating voltage of 20 kV and an estimated beam-current of 20 nA. The electron beam was rastered over an area of 10 × 10 μm<sup>2</sup> to minimize damage to the sample. We used the following standards: albite (Na), orthoclase (K, Al), amphibole (Ca, Fe, Si), SrSO<sub>4</sub> (Sr), BaSO<sub>4</sub> (Ba), MnTiO<sub>3</sub> (Mn, Ti), ZnO (Zn), and LiNbO<sub>3</sub> (Nb). The average results of nine analyses for gjerdingenite-Na and eight analyses for gjerdingenite-Ca (with ranges) are given in Table 2. Contents of Mg, REE, Zr, Ta, F, Cl are below detection limits.

The empirical formulae, based on [(Si,Al)<sub>8</sub>O<sub>24</sub>](O,OH)<sub>4</sub>, are: for gjerdingenite-Na: (K<sub>0.98</sub>Na<sub>0.62</sub>Ca<sub>0.37</sub>Ba<sub>0.07</sub>)<sub>Σ2.04</sub>(Na<sub>0.90</sub>Ca<sub>0.04</sub>Mn<sub>0.04</sub>Zn<sub>0.02</sub>)<sub>Σ1.00</sub>(Nb<sub>2.43</sub>Ti<sub>1.49</sub>Fe<sup>3+</sup><sub>0.09</sub>)<sub>Σ4.01</sub>(Si<sub>7.95</sub>Al<sub>0.05</sub>)<sub>Σ8</sub>O<sub>24</sub>[(OH)<sub>2.09</sub>O<sub>1.91</sub>]<sub>Σ4</sub>•5.32H<sub>2</sub>O, and for gjerdingenite-Ca: (K<sub>0.93</sub>Na<sub>0.45</sub>Sr<sub>0.41</sub>Ca<sub>0.15</sub>Ba<sub>0.08</sub>)<sub>Σ2.02</sub>(Ca<sub>0.62</sub>Mn<sub>0.14</sub>Fe<sub>0.03</sub>Zn<sub>0.01</sub>)<sub>Σ0.80</sub>(Nb<sub>2.51</sub>Ti<sub>1.52</sub>)<sub>Σ4.03</sub>(Si<sub>7.97</sub>Al<sub>0.03</sub>)<sub>Σ8</sub>O<sub>24</sub>[O<sub>2.86</sub>(OH)<sub>1.14</sub>]<sub>Σ4</sub>•5.67H<sub>2</sub>O. Both Na and Ca are distributed between the *D* site (with Mn, Zn, Fe) and extra-framework (*B*) sites (with K, Ba, Sr) according to the structural data (see below). The OH:O ratio is calculated from charge-balance considerations.

The simplified formula of gjerdingenite-Na is: (K,Na)<sub>2</sub>Na(Nb,Ti)<sub>4</sub>(Si<sub>4</sub>O<sub>12</sub>)<sub>2</sub>(OH,O)<sub>4</sub>•5H<sub>2</sub>O. The ideal

formula K<sub>2</sub>Na(Nb<sub>3</sub>Ti)Si<sub>8</sub>O<sub>24</sub>(OH)<sub>2</sub>O<sub>2</sub>•5H<sub>2</sub>O requires: Na<sub>2</sub>O 2.60, K<sub>2</sub>O 7.90, SiO<sub>2</sub> 40.30, TiO<sub>2</sub> 6.70, Nb<sub>2</sub>O<sub>5</sub> 33.43, H<sub>2</sub>O 9.07, total 100 wt.%.

The simplified formula of gjerdingenite-Ca is: K<sub>2</sub>Ca(Nb,Ti)<sub>4</sub>(Si<sub>4</sub>O<sub>12</sub>)<sub>2</sub>(O,OH)<sub>4</sub>•6H<sub>2</sub>O. The ideal formula K<sub>2</sub>Ca(Nb<sub>3</sub>Ti)Si<sub>8</sub>O<sub>24</sub>O<sub>3</sub>(OH)•6H<sub>2</sub>O requires: K<sub>2</sub>O 7.68, CaO 4.57, SiO<sub>2</sub> 39.19, TiO<sub>2</sub> 6.51, Nb<sub>2</sub>O<sub>5</sub> 32.50, H<sub>2</sub>O 9.55, total 100 wt.%.

The Gladstone–Dale compatibility indices (Mandarino 1981) for gjerdingenite-Na is 0.008 or superior if *D*<sub>meas</sub> is used, and –0.001 or superior if *D*<sub>calc</sub> is used; for gjerdingenite-Ca is –0.010 or superior if *D*<sub>meas</sub> is used, and –0.015 or superior if *D*<sub>calc</sub> is used.

#### X-RAY CRYSTALLOGRAPHY AND FEATURES OF THE CRYSTAL STRUCTURE

Attempts to examine single crystals of both gjerdingenite-Na and gjerdingenite-Ca were unsuccessful because of the poor quality of the crystals, which are curved or split (or both). Unit-cell dimensions of the new minerals were obtained from the X-ray powder-diffraction data, and their crystal structures were refined by the Rietveld method: *R*<sub>p</sub> = 3.41, *R*<sub>B</sub> = 1.38, *R*<sub>F</sub> = 0.96 for gjerdingenite-Na, and *R*<sub>p</sub> = 2.74, *R*<sub>B</sub> = 3.88, *R*<sub>F</sub> = 2.29 for gjerdingenite-Ca (Yamnova *et al.*, in press). The structure model of gjerdingenite-Mn (Raade *et al.* 2004) was used for the structure refinement of gjerdingenite-Na; for gjerdingenite-Ca, we used the model of karupmøllerite-Ca (Yamnova *et al.* 2000), another kuzmenkoite-subgroup member with Ca dominant at the *D* site. The X-ray powder-diffraction pattern of gjerdingenite-Na (Table 3) was obtained using an ADP-2 diffractometer with CuKα<sub>1+2</sub> radiation. The powder pattern of gjerdingenite-Ca given in Table 4 was obtained using a STOE STADIP focusing diffractometer with MoKα<sub>1</sub> radiation and a Ge (111) monochromator.

Both minerals are monoclinic, space group *C2/m*. The unit-cell dimensions of gjerdingenite-Na are: *a* 14.626(2), *b* 14.160(1), *c* 7.910(1) Å, β 117.43(2)°, *V* 1454(1) Å<sup>3</sup>, *a* : *b* : *c* 1.0329 : 1 : 0.5586, *Z* = 2. The unit-cell dimensions of gjerdingenite-Ca are: *a* 14.6365(6), *b* 14.2049(5), *c* 7.8919(4) Å, β 117.467(5)°, *V* 1455.9(2) Å<sup>3</sup>, *a* : *b* : *c* = 1.0303 : 1 : 0.5555, *Z* = 2.

“UK-19-1”, which now becomes gjerdingenite-Na, was originally described as orthorhombic (space group *Cmm2*) with unit-cell dimensions: *a* 7.34, *b* 14.0, *c* 7.15 Å (Perrault *et al.* 1969). We checked this hypothesis and found that the X-ray powder-diffraction pattern cannot be indexed with an orthorhombic unit-cell with such dimensions (nenadkevichite-type cell). Our attempts to refine the structure using orthorhombic models were unsuccessful because of major differences between the observed and calculated X-ray powder-diffraction patterns. We also note that no labuntsovite-group minerals with space group *Cmm2* are known. We surmise that Perrault *et al.* (1969) probably studied a

TABLE 2. CHEMICAL COMPOSITION OF GJERDINGENITE-Na AND GJERDINGENITE-Ca

	Gjerdingenite-Na		Gjerdingenite-Ca	
	mean	range	mean	range
Na <sub>2</sub> O wt.%	4.04	3.7–4.2	1.14	0.9–1.3
K <sub>2</sub> O	3.97	3.8–4.2	3.61	3.1–4.2
CaO	1.95	1.6–2.1	3.56	2.3–4.5
SrO	b.d.l.*	–	3.47	3.1–3.8
BaO	0.92	0.5–1.2	1.04	0.8–1.3
MnO	0.27	0.2–0.3	0.84	0.4–1.1
ZnO	0.17	0.1–0.3	0.05	0.00–0.2
Fe <sub>2</sub> O <sub>3</sub>	0.61	0.5–0.7	0.19	0.1–0.2
Al <sub>2</sub> O <sub>3</sub>	0.20	0.05–0.3	0.13	0.1–0.2
SiO <sub>2</sub>	41.02	40.2–41.6	39.29	38.0–40.7
TiO <sub>2</sub>	10.20	9.2–10.5	9.96	8.7–11.1
Nb <sub>2</sub> O <sub>5</sub>	27.78	27.1–28.4	27.34	25.8–28.4
H <sub>2</sub> O	9.85	–	9.23	–
Total	100.98	–	99.85	–

\* b.d.l.: below detection limit.





Karupmøllerite-Ca is the mineral closest to gjerdingenite-Ca with regards to unit-cell dimensions and IR spectrum. The presence of the large cations Na or Ca instead of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in the octahedral part of the mixed Si,*M*,*D* framework results in increased unit-cell dimensions in gjerdingenite-Na, gjerdingenite-Ca and karupmøllerite-Ca in comparison with gjerdingenite-Fe and gjerdingenite-Mn (Table 5).

The discovery of labuntsovite-group minerals with large cations, Ca and (especially!) monovalent Na, at the *D* site, which is the center of an isolated octahedron linking  $\text{MO}_6$  (*M* = Nb,Ti) chains of octahedra, is important in the crystal chemistry of microporous (zeolite-like) silicates with mixed octahedron-tetrahedron frameworks. It shows, on one hand, that cations with relatively low force-characteristics (*i.e.* low-force constants of cation-anion bonds; for details, see Chukanov & Pekov 2005) can build units of mixed frameworks and, on the other hand, it demonstrates the double role of Ca and Na in such structures, unlike “true” large cations such as K and Ba (and Sr?), which always occupy only extra-framework sites.

In terms of cluster approximation and first-order perturbation theory, as shown previously by Chukanov *et al.* (2003) and Chukanov & Pekov (2005), the linking of chains of (Ti,Nb) $\text{O}_6$  octahedra (*M*-octahedra) by

additional  $\text{DO}_6$  octahedra (*D* = Fe, Mg, Mn or Zn) in the labuntsovite group results in a linear correlation between the frequency  $\nu$  of the band due to (Ti,Nb)-O stretching vibrations in the range 660–700  $\text{cm}^{-1}$  and the number of *D* atoms per formula unit. This band is single and does not depend on the Ti:Nb ratio. Indeed, experimental data for 34 samples of labuntsovite-group minerals (most of which have been structurally investigated) show that the position of the Ti(Nb)-O stretching band correlates linearly with the occupancy *x* of the *D* site in accordance with the equation:  $\nu$  ( $\text{cm}^{-1}$ ) = 667 + 27.02*x*. This means that the *D* cations Fe, Mg, Mn and Zn give rise to substantial (and approximately similar) local perturbations of the force field; in the case of complete occupancy of the *D* site by these cations, the observed shifts of the (Ti,Nb)-O stretching bands under the influence of the *D* cations reach 27  $\text{cm}^{-1}$ .

Using available spectral and structural data for karupmøllerite-Ca, the following correlation was obtained for the *D*-site composition  $(\text{Fe,Mg,Mn,Zn})_x\text{Ca}_y\Box_{1-x-y}$ :

$$\nu$$
 ( $\text{cm}^{-1}$ ) = 667 + 27.02*x* + 18.32*y*.

On the basis of the new data for gjerdingenite-Na and gjerdingenite-Ca, the latter correlation can be generalized for the case  $D = (\text{Fe,Mg,Mn,Zn})_x\text{Ca}_y\text{Na}_z\Box_{1-x-y-z}$ :

TABLE 5. COMPARATIVE DATA FOR NIOBIUM MEMBERS OF THE KUZMENKOITE SUBGROUP OF THE LABUNTSOVITE GROUP

Mineral	Gjerdingenite-Fe	Gjerdingenite-Mn	Gjerdingenite-Na	Gjerdingenite-Ca	Karupmøllerite-Ca
Formula	$\text{K}_2\text{Fe}(\text{Nb,Ti})_4$ [ $\text{Si}_4\text{O}_{12}$ ] $_2(\text{O,OH})_4$ •6 $\text{H}_2\text{O}$	$\text{K}_2\text{Mn}(\text{Nb,Ti})_4$ [ $\text{Si}_4\text{O}_{12}$ ] $_2(\text{O,OH})_4$ •6 $\text{H}_2\text{O}$	$(\text{K,Na})_2\text{Na}(\text{Nb,Ti})_4$ [ $\text{Si}_4\text{O}_{12}$ ] $_2(\text{OH,O})_4$ •5 $\text{H}_2\text{O}$	$\text{K}_2\text{Ca}(\text{Nb,Ti})_4$ [ $\text{Si}_4\text{O}_{12}$ ] $_2(\text{O,OH})_4$ •6 $\text{H}_2\text{O}$	$(\text{Na,Ca,K})_2\text{Ca}(\text{Nb,Ti})_4$ [ $\text{Si}_4\text{O}_{12}$ ] $_2(\text{O,OH})_4$ •7 $\text{H}_2\text{O}$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/m</i>	<i>C2/m</i>	<i>C2/m</i>	<i>C2/m</i>	<i>C2/m</i>
Unit-cell data					
<i>a</i> , Å	14.53	14.56	14.63	14.64	14.64
<i>b</i> , Å	13.94	13.96	14.16	14.21	14.21
<i>c</i> , Å	7.84	7.85	7.91	7.89	7.91
$\beta$ , °	117.6	117.6	117.4	117.5	117.4
<i>V</i> , Å <sup>3</sup>	1407	1414	1454	1456	1463
<i>Z</i>	2	2	2	2	2
<i>D</i> , g/cm <sup>3</sup>	2.82	2.93 (calc.)	2.71	2.79	2.71
Optical data					
$\alpha$	1.668	1.670	1.647	1.680	1.656
$\beta$	1.700	1.685	1.653	1.682	1.662
$\gamma$	1.794	1.775	1.755	1.762	1.755
Optical sign, 2 <i>V</i>	+59°	+52°	+25°	+25°	+30°
References	Raade <i>et al.</i> (2002)	Raade <i>et al.</i> (2004)	This work	This work	Yamnova <i>et al.</i> (2000); Pekov <i>et al.</i> (2002)

$$\nu \text{ (cm}^{-1}\text{)} = 667 + 27.02x + 18.32y + 8.60z.$$

The coefficients 27.02, 18.32 and 8.60 (cm<sup>-1</sup>) in the linear correlation reflect the force characteristics of the (Ti,Nb)-O-(Fe,Mg,Mn,Zn), (Ti,Nb)-O-Ca and (Ti,Nb)-O-Na bonds respectively. The IR spectral and structural data for other labuntsovite-group minerals (vuoriyarvite-K, tsepinite-Sr, tsepinite-Na, paratsepinite-Na) show that not only *D*-cations, but also other cations with different coordination-numbers situated near the *D* site influence the  $\nu$  value. The corresponding correlation-coefficients are about 28 cm<sup>-1</sup> for <sup>IV</sup>Na ("flat square" in type vuoriyarvite-K from Vuoriyarvi) and about 7 cm<sup>-1</sup> for <sup>VII</sup>Sr and <sup>VIII</sup>Sr. Thus, the force characteristics decrease with an increase in the cation radius and coordination number in the order: <sup>IV</sup>Na  $\geq$  <sup>VI</sup>Fe, <sup>VI</sup>Mg, <sup>VI</sup>Mn, <sup>VI</sup>Zn > <sup>VI</sup>Ca > <sup>VI</sup>Na > <sup>VII</sup>Sr, <sup>VIII</sup>Sr.

The presence of large cations (Ca, Na) at the *D* site results in deformation of the heteropolyhedral frameworks. In particular, in the [Si<sub>4</sub>O<sub>12</sub>] rings of gjerdingenite-Na, gjerdingenite-Ca and karupmøllerite-Ca, the Si-Si distances and Si-O-Si angles vary within wider limits than in other *D*-occupied monoclinic labuntsovite-group minerals. The values of Si-O-Si angles correlate with the band frequencies of Si-O-Si stretching vibrations in IR spectra in the range from 1000 to 1150 cm<sup>-1</sup> (Yamnova *et al.*, in press). For Nb-dominant members of the group, the highest frequency of the bands in this range decreases with a decrease in the largest Si-O-Si angle in the [Si<sub>4</sub>O<sub>12</sub>] ring: from 1138 cm<sup>-1</sup> for nenadkevichite, to 1136 cm<sup>-1</sup> for vuoriyarvite-K, 1135 cm<sup>-1</sup> for gjerdingenite-Ca, 1110 cm<sup>-1</sup> (shoulder) for gjerdingenite-Na, and 1104 cm<sup>-1</sup> for gjerdingenite-Mn and gjerdingenite-Fe. These values can be used as diagnostic characteristics for labuntsovite-group minerals.

The rarity of labuntsovite-group minerals with Ca and Na at the *D* site relative to those in which Mn, Fe, Mg or Zn dominate (and in comparison with the minerals containing Ca and especially Na at extra-framework sites) probably can be explained by crystallochemical restrictions. The substitution of Mn<sup>2+</sup> (Fe<sup>2+</sup>, Mg, Zn) by Ca<sup>2+</sup> or Na<sup>+</sup>, which are larger cations with lower force-characteristics determined by the charge: radius ratio, leads to: 1) significant distortion of the Si<sub>4</sub>*M* part of the framework (Yamnova *et al.* 2000, in press), and 2) a general weakening of bonds in the Si<sub>4</sub>*M,D* framework. Thus there is an affinity of the *D* octahedral site for divalent cations with higher force-characteristics. A specific geochemical environment therefore seems to be necessary for the crystallization of labuntsovite-group minerals with Ca and especially Na at this site, such as a strong enrichment of hydrothermal solutions in one of the following pairs of cations: Na + Ca, Ca + K or Na + K (in the last case, the Na activity probably must be higher than that of K, as otherwise

the formation of lemmleinite-K, Na<sub>2</sub>K<sub>2</sub>K<sub>2</sub>(Ti,Nb)<sub>4</sub>(Si<sub>4</sub>O<sub>12</sub>)<sub>2</sub>(O,OH)<sub>4</sub>•4H<sub>2</sub>O, a common mineral in K-enriched hydrothermally altered peralkaline pegmatites, would seem more probable) and a depletion of Mn, Fe, Mg and Zn. This would explain the occurrence and abundance of gjerdingenite-Na in the hydrothermally altered pegmatite at Mont Saint-Hilaire. The low-temperature hydrothermal solutions at Mont Saint-Hilaire were more highly enriched in Na in comparison with their analogs in peralkaline complexes of the Kola Peninsula such as Lovozero, Khibiny and Kovdor (Pekov *et al.* 2004), which leads to the observed difference in the crystal chemistry of labuntsovite-group minerals found there.

The existence of karupmøllerite-Ca with Ca prevailing at the *D* site and Na prevailing at extra-framework sites clearly shows that the *D* site has a stronger affinity for Ca than Na. In general, the relative distribution of labuntsovite-group minerals in nature (taking into account also their parageneses) suggests the affinity of the *D* sites in labuntsovite-type structures for cations decreases in the order: Mn > (Fe, Zn) > Mg > Ca > Na.

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