

Gjerdingenite-Mn from Norway – a new mineral species in the labuntsovite group: descriptive data and crystal structure

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Abstract: Gjerdingenite-Mn occurs as orange-yellow to brownish prisms up to 1 mm long in miarolitic cavities of a sodic granite ('ekerite') at Gjerdingselva, Lunner, Oppland, Oslo Region, Norway. The simplified formula is $(K,Na)_2(Mn,Fe)[(Nb,Ti)_4(Si_4O_{12})_2(O,OH)_4] \cdot 6H_2O$. It is the Mn-dominant analogue of gjerdingenite-Fe, the Ti analogue of kuzmenkoite-Mn and a dimorph of organovaite-Mn. The mineral is monoclinic, $C2/m$, with $a = 14.563(3)$, $b = 13.961(3)$, $c = 7.851(2)$ Å, $\beta = 117.62(3)^\circ$, $V = 1414.3(6)$ Å³, $Z = 2$. The crystal structure was refined to $R(F) = 0.079$ on the basis of 1207 observed reflections and is compared to the structure of gjerdingenite-Fe. The strongest five reflections of the X-ray powder-diffraction pattern [d_{obs} in Å (hkl)] are: 6.96 (100) (020, 001), 4.94 (80) (021), 3.22 (90) (42-1, 400, 40-2), 3.10 (80) (041, 022) and 2.510 (40) (44-1, 401, 40-3, 042). The mineral is optically biaxial (+) with $\alpha = 1.670(2)$, $\beta = 1.685(2)$, $\gamma = 1.775(5)$; $2V_{meas} = 52(8)^\circ$, $2V_{calc} = 46(5)^\circ$. The axial dispersion is weak, $r < v$; the orientation is $Z = a$, $Y = b$. Mohs hardness is about 5; $D_{calc} = 2.93$ g/cm³. The pseudo-orthorhombic crystals are twinned on {001}, elongate along [010] and show the forms {001}, {100}, {201} and {021}. Some general aspects on the formation of labuntsovite-group minerals are discussed.

Key-words: gjerdingenite-Mn, new mineral, labuntsovite group, chemical analysis, crystal structure, Norway.

Introduction

Gjerdingenite-Fe, a member of the labuntsovite group of microporous Nb–Ti silicates, was recently described as a new mineral species from Gjerdingselva, Lunner, Oppland, Norway (Raade *et al.*, 2002). One of the published analyses has Mn > Fe (Crystal 1 in Table 1, *loc. cit.*), which shows that a second mineral species can be distinguished. The purpose of the present paper is to describe the Mn-dominant analogue, gjerdingenite-Mn, from this locality and to discuss some substitutional features in minerals of the gjerdingenite series and some related series within the labuntsovite group. The two gjerdingenite species occur in miarolitic cavities of a sodic granite (local name: ekerite) from the "Oslo Region", a Permian paleorift area in southern Norway. The mineral and name were approved by the Commission on New Minerals and Mineral Names, IMA (No. 2003-015). Type material is deposited in the Mineralogical Collection of the Freiberg University of

Mining and Technology (Bergakademie Freiberg), Germany, with inventory number 80250.

The root name is derived from the nearby Lake Gjerdingen, from which the river Gjerdingselva flows. The suffix -Mn indicates the dominant cation in the D site of the structure, in accordance with the accepted rules of nomenclature for labuntsovite-group minerals (Chukanov *et al.*, 2002).

Elpidite and kupletskite are in part rock-forming minerals of the Gjerdingselva ekerite. A compilation of the cavity minerals in this pluton was published by Raade & Haug (1982). Interestingly, the cavities contain a suite of late-stage Na–Al fluorides (Raade & Haug, 1980 and 1981). Janhaugite, an Na–Mn–Ti silicate of the cuspidine group, was described as a new mineral species from this ekerite (Raade & Mladeck, 1983; Annehed *et al.*, 1985). Gjerdingenite-Mn is associated with gjerdingenite-Fe, janhaugite, elpidite, kupletskite, aegirine, orthoclase, albite, quartz, pyrochlore, monazite-(Ce) and ralstonite.

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Table 1. Electron-microprobe data on gjerdingenite-Mn.

Constituent	Wt. % [†]	Range [†]	Wt. % [‡]		Probe standard
Na ₂ O	1.45	1.21-1.99	2.09	2.06	albite
K ₂ O	5.83	5.13-7.22	4.43	4.72	orthoclase
CaO			0.10	0.04	wollastonite
BaO	0.69	0-1.36	0.84	1.00	BaSO ₄
MgO	0.05	0-0.21	0.16	0.36	diopside
MnO	2.59	2.03-2.88	2.99	2.46	MnTiO ₃
FeO	2.03	1.38-2.79	2.75	2.14	Fe
ZnO	0.54	0.05-1.24	0.77	1.20	Zn
Al ₂ O ₃	0.18	0-0.47			Al ₂ O ₃
SiO ₂	38.55	36.94-39.25	40.39	38.42	albite
TiO ₂	7.07	5.07-8.17	10.95	8.17	MnTiO ₃
Nb ₂ O ₅	31.74	29.69-35.35	26.99	27.49	LiNbO ₃
H ₂ O*	9.9(4)				
Total	100.62		92.46	88.06	

[†] Means and ranges of four point analyses on several crystals.

[‡] Two analyses performed on the fragment used for single-crystal study.

* Water by weight loss on heating in vacuum up to 900°C.

Note: The composition with the highest FeO content of 2.79 wt.% also corresponds to the Mn-dominant phase with an MnO content of 2.88 wt.%.

Physical properties and morphology

Gjerdingenite-Mn is biaxial (+) with $\alpha = 1.670(2)$, $\beta = 1.685(2)$, $\gamma = 1.775(5)$ (measured in yellow light); $2V_{\text{meas}} = 52(8)^\circ$, $2V_{\text{calc}} = 46(5)^\circ$. The axial dispersion is weak, $r < v$; the orientation is $Z = a$, $Y = b$. The pleochroism is from yellowish brown for β to colourless for α and γ . The macroscopic colour varies from orange-yellow to brownish, and the streak is white. It appears that gjerdingenite-Mn generally has a darker colour than the Fe-dominant analogue. The crystals are translucent to transparent, with a vitreous lustre. They show no fluorescence in either long- or short-wave ultraviolet light. No cleavage or parting was observed; the fracture is uneven. The mineral is brittle and has a Mohs hardness of approximately 5. No crystal with known Mn content was available for density determination; $D_{\text{calc}} = 2.93 \text{ g/cm}^3$ (from the empirical formula and cell parameters refined from structural data).

The mineral occurs as prismatic crystals up to 1 mm in length and elongate along [010]. The forms {001}, {100}, { $\bar{2}01$ } and {021} could be visually determined by analogy with gjerdingenite-Fe (Fig. 1 and 2 in Raade *et al.*, 2002). The a:b:c ratio calculated from the single-crystal cell parameters is 1.0431:1:0.5624. Analogous to gjerdingenite-Fe, microtwinning on {001} is present, and epitaxial overgrowth of gjerdingenite-Mn on elpidite is often observed.

Chemical data

Four quantitative EDS (energy-dispersive X-ray spectroscopy) analyses of the holotype specimen were obtained by means of a CAMEBAX-MBX electron microprobe equipped with a LINK AN 10000 spectrometer, using an operating voltage of 15.7 kV and an estimated beam current of 1.0-1.5 nA. Areas of 8 x 8 and 16 x 16 μm^2 were

scanned to minimise loss of Na. The average result and the standards used are given in Table 1. Several crystals from the same association were analysed. Each of the four point analyses corresponds to gjerdingenite-Mn. Special attention was paid to the problem of analysing Ba and Ti in EDS mode by testing with a series of appropriate standards (*inter alia* BaTiO₃ and a series of labuntsovite-group minerals whose compositions were investigated using wet-chemical analysis or WDS). The contents of Ca, Sr, REE, Zr, Ta and F are below the detection limits. Water was determined by weight loss on heating in vacuum up to 900°C. The absence of hydrogen-containing groups in the sample after heating was proved by infrared spectroscopy.

The empirical formula, based on 16(Si+Al) p.f.u. and for $Z = 1$, is:

$$(\text{K}_{3.07}\text{Na}_{1.16}\text{Ba}_{0.11})_{\Sigma 4.34}(\text{Mn}_{0.91}\text{Fe}_{0.70}\text{Zn}_{0.16}\text{Mg}_{0.03})_{\Sigma 1.80}(\text{Nb}_{5.92}\text{Ti}_{2.19})_{\Sigma 8.11}(\text{Si}_{15.91}\text{Al}_{0.09}\text{O}_{48})[\text{O}_{6.32}(\text{OH})_{1.68}]_{\Sigma 8} \cdot 12.8\text{H}_2\text{O}$$

(the O/OH ratio is calculated from charge-balance requirements). The simplified formula (for $Z = 2$) is: $(\text{K},\text{Na})_2(\text{Mn},\text{Fe})[(\text{Nb},\text{Ti})_4(\text{Si}_4\text{O}_{12})_2(\text{O},\text{OH})_4] \cdot 6\text{H}_2\text{O}$. The idealized end-member formula is: $\text{K}_2\text{Mn}[\text{Nb}_4(\text{Si}_4\text{O}_{12})\text{O}_4] \cdot 6\text{H}_2\text{O}$.

The Gladstone-Dale relationship gives with D_{calc} a compatibility index $1 - (K_p/K_C) = 0.039$, which is rated as 'good' (Mandarino, 1981).

Two analyses made on the fragment used for X-ray single-crystal study are also listed in Table 1. The corresponding empirical formulae are:

$$(\text{K}_{2.23}\text{Na}_{1.62}\text{Ba}_{0.14}\text{Ca}_{0.05})_{\Sigma 4.04}(\text{Mn}_{1.00}\text{Fe}_{0.90}\text{Zn}_{0.23}\text{Mg}_{0.09})_{\Sigma 2.22}[(\text{Nb}_{4.83}\text{Ti}_{3.26})_{\Sigma 8.09}(\text{Si}_4\text{O}_{12})_4(\text{O},\text{OH})_8] \cdot n\text{H}_2\text{O}$$

$$(\text{K}_{2.50}\text{Na}_{1.66}\text{Ba}_{0.16}\text{Ca}_{0.02})_{\Sigma 4.34}(\text{Mn}_{0.88}\text{Fe}_{0.75}\text{Zn}_{0.36}\text{Mg}_{0.23})_{\Sigma 2.22}[(\text{Nb}_{5.18}\text{Ti}_{2.55})_{\Sigma 7.73}(\text{Si}_4\text{O}_{12})_4(\text{O},\text{OH})_8] \cdot n\text{H}_2\text{O}$$

Infrared-absorption data

The infrared spectrum of gjerdingenite-Mn, obtained with a Specord 75 IR spectrophotometer and using a KBr

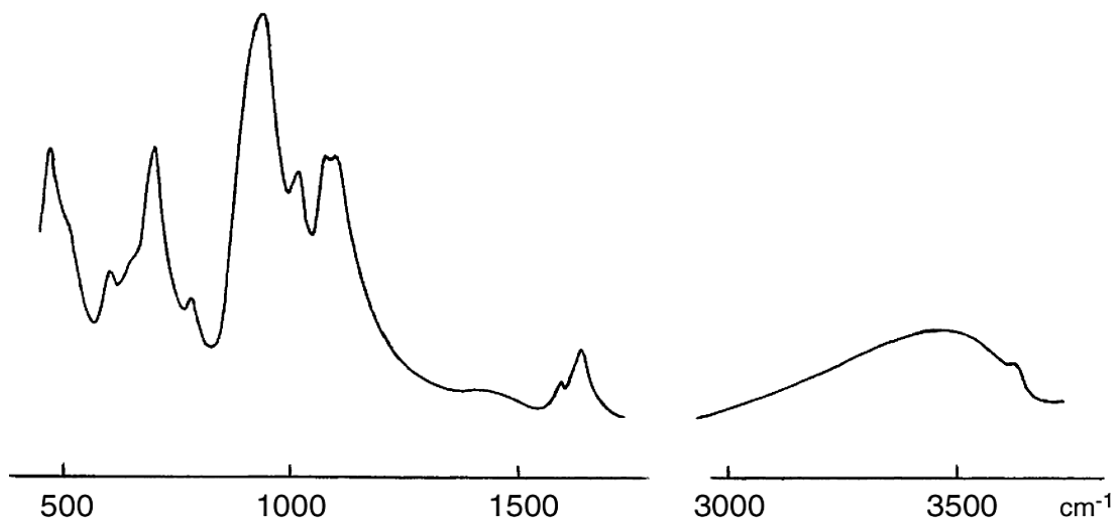


Fig. 1. Infrared spectrum of gjerdingenite-Mn in KBr pellet.

pellet, is shown in Fig. 1. Wavenumbers (in cm^{-1}) of the absorption bands are (sh – shoulder, b – broad, strong bands are underlined): 3625, ~ 3470 b, 1640, 1600, 1104, 1089, 1022, 945, 920 sh, 779, 693, 650 sh, 597, 490 sh, 467. The presence of both water and hydroxyl is confirmed by these data. A comparison with the infrared spectra of related minerals in the labuntsovite group is made in the Discussion section.

X-ray powder-diffraction data

The X-ray powder-diffraction pattern of gjerdingenite-Mn is given in Table 2. It was obtained by the Debye-Scherrer method: camera diameter 57 mm, Mn-filtered $\text{FeK}\alpha$ radiation. Correct hkl indices were assigned by taking into account the calculated intensities obtained from the structural data. The unit-cell parameters refined from the powder data are: $a = 14.55(3)$, $b = 13.894(8)$, $c = 7.91(1)$ Å, $\beta = 117.7(1)^\circ$, $V = 1416(4)$ Å³.

Crystal structure

Almost all the crystal fragments studied were twinned on {001} to simulate an F -centred orthorhombic cell, as was reported for gjerdingenite-Fe (Raade *et al.*, 2002), and additionally formed subparallel intergrowths. However, a very small untwinned fragment of reasonably sufficient quality and with the approximate dimensions 0.03 x 0.05 x 0.08 mm was finally found and used for the crystal-structure determination. Cell parameters obtained from the single-crystal study are: $a = 14.563(3)$, $b = 13.961(3)$, $c = 7.851(2)$ Å, $\beta = 117.62(3)^\circ$, $V = 1414.3(6)$ Å³, $Z = 2$.

A full sphere of single-crystal X-ray diffractometer data was collected at room temperature with a Nonius KappaCCD diffractometer equipped with a 300 μm diameter capillary-optics collimator to provide increased resolu-

Table 2. X-ray powder-diffraction data for gjerdingenite-Mn.

I_{obs}	d_{obs}	I_{calc}	d_{calc}^*	hkl^{**}
100	6.96	75	6.981	020
		100	6.956	001
20	6.40	26	6.452	200
		37	6.451	20-1
80	4.94	73	4.927	021
5	4.48	1	4.524	31-1
10	3.90	5	3.912	201
		9	3.911	20-2
5	3.62	1	3.641	40-1
90	3.22	39	3.228	42-1
		38	3.226	400
		37	3.226	40-2
80	3.10	66	3.120	041
		39	3.113	022
10	2.931	20	2.928	420
		13	2.928	42-2
10	2.832	3	2.836	51-1
10	2.608	8	2.604	241
		7	2.604	24-2
		5	2.599	202
		8	2.599	20-3
40	2.510	25	2.519	44-1
		8	2.515	401
		13	2.515	40-3
		16	2.464	042
5	2.309	2	2.275	33-3
		2	2.262	62-1
5	2.202	6	2.207	061
		2	2.201	023
5	1.909	3	1.906	35-3
10	1.710	5	1.708	461
		6	1.708	46-3
		7	1.706	442
		8	1.706	44-4
5	1.685	4	1.687	153
		1	1.685	28-1
20	1.431	9	1.434	48-3
		7	1.431	443
		8	1.431	44-5

* Calculated with unit-cell parameters refined from single-crystal data.

** hkl indices are assigned taking into account I_{calc} obtained from the structural data.

Table 3. Crystal data, data collection information and refinement details for gjerdingenite-Mn.

<i>Crystal data</i>	
Formula (simplified)	(K,Na) ₂ (Mn,Fe)[(Nb,Ti) ₄ (Si ₄ O ₁₂) ₂ (O,OH) ₄]·6H ₂ O
Space group, <i>Z</i>	<i>C2/m</i> , 2
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.563(3), 13.961(3), 7.851(2)
β(°), <i>V</i> (Å ³)	117.62(3), 1414.3(6)
<i>F</i> (000), ρ _{calc} (g·cm ⁻³)	1154, 2.806
μ (mm ⁻¹)	2.52
Absorption correction	multi-scan*
Crystal dimensions (mm)	0.03 x 0.05 x 0.08
<i>Data Collection and Refinement</i>	
Diffractometer	Nonius KappaCCD system
λ (Mo-Kα) (Å), <i>T</i> (K)	0.71073, 293
Crystal-detector dist. (mm)	30
Rotation axis, width (°)	φ, ω, 2.0
Total no. of frames	260
Collect. time per degree (s)	320
Collection mode, 2θ _{max} (°)	sphere, 60 (used: 52.68)
<i>h</i> , <i>k</i> , <i>l</i> ranges	-18 → 18, -17 → 17, -9 → 9
Total reflections measured	2873
Unique reflections	1510 (<i>R</i> _{int} = 2.92 %)
Refinement on	<i>F</i> ²
<i>R</i> 1(<i>F</i>), <i>wR</i> 2 _{all} (<i>F</i> ²)**	0.079, 0.183
'Observed' refls.	1207 [<i>F</i> _o > 4σ(<i>F</i> _o)]
Extinct. coefficient	0.0014(3)
No. of refined parameters	134
Goof	1.205
(Δ/σ) _{max}	0.071
Δρ _{min} , Δρ _{max} (e/Å ³)	-1.05, 1.58

Note: Unit-cell parameters were refined from 2063 recorded reflections. Scattering factors for neutral atoms were employed in the refinement.

* Otwinowski & Minor (1997)

** $w = 1/[\sigma^2(F_o^2) + (0.0P)^2 + 88P]$; $P = ((\max \text{ of } (0 \text{ or } F_o^2)) + 2F_c^2)/3$

tion (for details, see Table 3). The structure was solved (SHELXS-97; Sheldrick, 1997a) and refined (SHELXL-97; Sheldrick, 1997b) in space group *C2/m* to *R*(*F*) = 0.079 for 1207 observed reflections. Hydrogen positions could not be located. The model and atomic coordinates for gjerdingenite-Fe (Raade *et al.*, 2002) were adopted to facilitate comparisons. The relatively high *R* value is attributed to the very small size of the crystal fragment, its imperfect quality, and the presence of substitutional disorder and partially occupied sites in the mineral. A refinement in *Cm* gave *R*(*F*) ~ 0.072, but clearly worse s.u.s., and a search for higher symmetry with the program PLATON (Spek, 2003) demonstrated that *C2/m* is the correct space group. No weak reflections (which would double the *c* axis) or streaks were noted on either normally exposed or overexposed CCD frames. Table 4 gives fractional atomic coordinates and displacement parameters, with values for gjerdingenite-Fe included; Table 5 shows selected interatomic distances.

The crystal structure of gjerdingenite-Mn (Fig. 2) is very close to that of its Fe-dominant analogue gjerdingenite-Fe, as described by Raade *et al.* (2002). The *A* alkali site is vacant in both species. The octahedrally coordinated *D* site (with mainly Mn,Fe) contains a similarly small number of vacancies (15 % in gjerdingenite-Fe and 17 % in

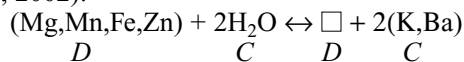
the Mn analogue). Occupancies of the extra-framework sites *B*, *B'* and *C* are also similar. The compositions of the two octahedrally coordinated *M* sites in gjerdingenite-Mn are Nb_{0.71}Ti_{0.29} and Nb_{0.55}Ti_{0.45} (Table 4, Fig. 2); occupancy refinements of the *M1* and *M2* sites in gjerdingenite-Fe show a higher scattering power of the *M2* site (Raade *et al.*, 2002).

There are, however, also some slight differences between the two structures. Specifically, in gjerdingenite-Mn there is a five-coordinated cation site with a very low occupancy (*ca.* 10 %), which does not seem to be present in gjerdingenite-Fe. This new site, labelled *D'*, might be occupied by any cation that can show such a coordination, *i.e.* Mn, Fe and/or Zn. The *B* site is located on a mirror plane (*y* = 0), whereas in gjerdingenite-Fe it is slightly shifted off this plane; nonetheless, the atoms on the *B* site in gjerdingenite-Mn show a strongly anisotropic behaviour perpendicular to the mirror plane (Table 4). It was checked if the *B* site could be refined using a split model, but this was impossible; SHELXL-97 did also not suggest any splitting of the *B* site (or other sites). The average *B*-O and *B'*-O distances, 3.24 and 3.02 Å, are distinctly larger than those in gjerdingenite-Fe (3.05 and 2.96 Å). This structural feature is probably caused in part by the larger unit cell of the Mn analogue, and is in part also due to somewhat different occupancies of the involved sites. The two SiO₄ tetrahedra are less distorted than their equivalents in gjerdingenite-Fe. Average Si-O distances are, however, comparable. The average *M1*-O, *M2*-O, *C*-O and *D*-O distances in both minerals are again similar.

Discussion

The labuntsovite group and gjerdingenite-Mn

Minerals of the labuntsovite group are represented by the general formula $A_4B_4[C_{4-2x}(H_2O)_{2x}]D_x[M_8(Si_4O_{12})_4(O,OH)_8] \cdot nH_2O$ (*Z* = 1), where *x* = 0-2 and *n* ~ 8. Here, *A* and *B* mainly represent alkali atoms. Position *C* can be occupied by both cations (usually K or Ba) and water. Position *D* is populated by small bivalent cations (Mg, Mn, Fe or Zn) and usually contains vacancies. Since the distance between the *C* and *D* sites is short (~ 2.1 Å), cations cannot occur in both sites at the same time. If the *D* site is occupied by cations, H₂O molecules occur in *C* and complete the octahedral coordination of the *D* cations; if *D* is vacant, *C* can contain cations. The following mechanism governs the occupancy of the *C* and *D* sites (Chukanov *et al.*, 2002):



Chains of corner-sharing *MO*₆ (*M* = Ti, Nb) octahedra are linked by four-membered rings of SiO₄ tetrahedra to form a complex framework anion $[M_8(Si_4O_{12})_4(O,OH)_8]^{n-}$. The additional octahedrally coordinated site *D* is regarded as part of the framework; the *A*, *B* and *C* cations and water molecules occupy zeolite-like channels and cages. Orthorhombic members (*a* ~ 7.5, *b* ~ 14.2, *c* ~ 7 Å) have straight octahedral chains and only two extra-framework

Table 4. Fractional atomic coordinates and displacement parameters (in Å²) for gjerdingenite-Mn, compared to the values for gjerdingenite-Fe (given on every second line).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} / <i>U</i> _{iso}	<i>e</i> _{ref} [*]	Occupancy
Si1	0.2055(2)	0.1088(2)	0.7984(4)	0.0185(7)	–	
	0.2079(2)	0.1091(1)	0.7998(3)	0.0143(7)		
Si2	0.6854(2)	0.8904(2)	0.7573(4)	0.0183(7)	–	
	0.6852(2)	0.8897(1)	0.7542(3)	0.0147(7)		
<i>M1</i>	0	0.76495(14)	1/2	0.0321(6)	16.2	Nb _{0.547(4)} Ti _{0.453(4)} <i>M1</i> + <i>M2</i> =
	0	0.7676(1)	1/2	0.0191(9)		Nb _{0.54} Ti _{0.43} Fe _{0.025} Zr _{0.005}
<i>M2</i>	3/4	3/4	1/2	0.0357(6)	17.7	Nb _{0.707(4)} Ti _{0.293(4)} see <i>M1</i>
	3/4	3/4	1/2	0.0204(9)		
<i>B</i>	0.4336(11)	0.0000	0.731(2)	0.100(8)	10.4	O _{1.30(6)} (i.e., H ₂ O + some K)
	0.4307(7)	0.0323(5)	0.731(1)	0.078(3)		K _{0.30} Na _{0.18} (H ₂ O) _{0.52}
<i>B'</i>	1/2	0.8285(9)	0	0.090(4)	6.8	K _{0.72(2)} (+ H ₂ O)
	1/2	0.8312(5)	0	0.084(3)		K _{0.52} (H ₂ O) _{0.48}
<i>C</i>	0.0870(10)	0	0.3353(18)	0.035(3)	–	H ₂ O (+ minor K, Ba?)
	0.0899(6)	0	0.335(1)	0.079(3)		(H ₂ O) _{0.85} K _{0.14} Ca _{0.01}
<i>D</i>	0	0	1/2	0.0197(14)	5.2	(Mn,Fe) _{0.831(16)} □ _{0.169}
	0	0	1/2	0.016(1)		Fe _{0.475} Mn _{0.375} □ _{0.15}
<i>D'</i>	0.2510(19)	0	0.501(4)	0.017(9)	1.1	Mn _{0.091(11)} (or similar cation)
	–	–	–	–		
O1	0.9018(5)	0.7669(6)	0.6081(10)	0.0231(16)	–	OH**
	0.9032(5)	0.7704(3)	0.6113(8)	0.017(1)		OH
O2	0.9181(6)	0.8810(6)	0.3351(11)	0.0285(18)	–	
	0.9161(4)	0.8822(3)	0.3308(7)	0.017(1)		
O3	0.2585(6)	0.8716(6)	0.3740(11)	0.0290(18)	–	
	0.2598(3)	0.8705(3)	0.3787(7)	0.018(1)		
O4	0.2707(6)	0.8205(6)	0.7307(11)	0.0259(17)	–	
	0.2721(3)	0.8198(3)	0.7334(7)	0.018(1)		
O5	0.4153(6)	0.8215(6)	0.3032(11)	0.0286(18)	–	
	0.4152(4)	0.82098(4)	0.3032(7)	0.022(1)		
O6	0.3563(9)	0	0.2678(19)	0.033(3)	–	
	0.3557(5)	0	0.2710(9)	0.012(2)		
O7	0.2326(6)	0.8718(6)	0.0195(11)	0.0310(19)	–	
	0.2331(3)	0.8721(4)	0.0260(7)	0.020(1)		
O8	0.2411(9)	0	0.7822(18)	0.031(3)	–	
	0.2422(5)	0	0.7844(9)	0.020(2)		
<i>W</i>	0	0.134(2)	0	0.117(9)	–	H ₂ O
	0	0.140(1)	0	0.102(4)		H ₂ O

* Refined number of electrons per site (taking into account site multiplicities). Scattering factors used are: *M1* and *M2* - Nb+Ti; *B* - O; *B'* - K; *C* - O (occupancy not refined); *D* - Mn; *D'* - Mn.

** Note, however, that the bond-valence sum of O1 is 1.52 v.u. if the refined Nb:Ti ratios on the *M1* and *M2* sites are taken into account (bond-valence parameters from Brese & O'Keefe, 1991). Thus, O1 does not seem to be a "pure" OH.

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Si1	0.0235(15)	0.0107(13)	0.0204(14)	0.0017(11)	0.0093(12)	0.0007(11)
Si2	0.0222(14)	0.0103(13)	0.0217(14)	-0.0003(11)	0.0095(12)	-0.0007(11)
<i>M1</i>	0.0266(11)	0.0205(10)	0.0284(11)	0	-0.0051(8)	0
<i>M2</i>	0.0639(14)	0.0275(10)	0.0313(10)	0.0035(8)	0.0355(10)	0.0062(9)
<i>B</i>	0.058(10)	0.156(19)	0.095(14)	0	0.043(9)	0
<i>B'</i>	0.060(6)	0.134(10)	0.073(7)	0	0.027(5)	0
<i>C</i>	0.044(7)	0.027(6)	0.037(7)	0	0.022(6)	0
<i>D</i>	0.021(2)	0.019(2)	0.016(2)	0	0.0060(17)	0
O1	0.019(4)	0.031(4)	0.013(3)	0.002(3)	0.002(3)	0.001(3)
O2	0.024(4)	0.028(4)	0.031(4)	-0.001(4)	0.011(3)	-0.003(3)
O3	0.029(4)	0.028(4)	0.034(4)	0.001(4)	0.017(4)	0.000(3)
O4	0.026(4)	0.027(4)	0.028(4)	0.000(3)	0.015(3)	0.001(3)
O5	0.027(4)	0.029(4)	0.033(4)	0.014(4)	0.017(4)	0.010(3)
O6	0.037(7)	0.017(5)	0.051(8)	0	0.027(6)	0
O7	0.042(5)	0.027(4)	0.021(4)	0.001(3)	0.011(3)	0.002(4)
O8	0.034(7)	0.019(5)	0.042(7)	0	0.018(6)	0
<i>W</i>	0.14(2)	0.18(3)	0.038(10)	0	0.039(12)	0

Table 5. Selected interatomic distances (Å) in gjerdingenite-Mn.

Si1-O2	1.615(8)	Si2-O7	1.620(8)
O4	1.622(8)	O3	1.607(8)
O8	1.629(5)	O6	1.623(5)
O7	1.614(8)	O5	1.630(8)
<Si1-O>	1.62	<Si2-O>	1.62
M1-O5 x2	1.897(8)	M2-O3 x2	1.997(8)
O1 x2	1.973(7)	O4 x2	1.958(8)
O2 x2	2.071(8)	O1 x2	1.980(7)
<M1-O>	1.98	<M2-O>	1.98
D-O2 x4	2.104(8)	B-B'	3.039(15), 3.039(14)*
C x2	2.190(12)	O8	3.011(18)
<D-O/C>	2.13	O3 x2	3.309(16)
		O4 x2	3.450(12)
C-O3 x2	2.973(13)	O5 x2	3.416(13)
O2 x2	2.968(13)	O6	3.056(18)
W x2	2.99(2)	O6	3.27(2)
O2 x2	3.105(13)	<B-O>	3.24
O8	3.169(18)		
O1	3.279(8)	B'-B	3.039(15), 3.039(14)*
<C-O>	3.05	W	2.71(3)
		O4 x2	3.014(8)
D'-O3 x2	2.077(15)	O1 x2	3.034(9)
C	2.12(3)	O5 x2	3.149(8)
O8	2.28(3)		
B	2.43(3)	<B'-O>	3.02
<D'-O/C>	2.15		

* In gjerdingenite-Fe, the B'-B distance is only 2.667(9) Å (Raade *et al.*, 2002).

sites. Monoclinic members ($a \sim 14.2$, $b \sim 13.8$, $c \sim 7.8$ Å), which are the most common, show a doubled a parameter and in some cases also a doubled c parameter (subgroups

of paralabuntsovite, paratsepinite and organovaite). They have zigzag octahedral chains. Structural modifications of the basic structure, including splitting of the extra-framework sites, combined with variations in chemical composition, have resulted in the description of more than 20 mineral species in the labuntsovite group (Chukanov *et al.*, 2002, 2003b).

In the case of gjerdingenite, the A site is empty and the B , B' and C sites have mainly K and H_2O (Table 4). The suffix -Mn or -Fe denotes the prevailing cation in the D site. Gjerdingenite-Mn is the Mn-dominant analogue of gjerdingenite-Fe (Raade *et al.*, 2002), the Nb analogue of kuzmenkoite-Mn, which has $Ti > Nb$ (Chukanov *et al.*, 1999), and is a dimorph of organovaite-Mn (Chukanov *et al.*, 2001). Comparative characteristics of these four species are given in Table 6. A complete list of the approved species within the labuntsovite group is given in Table 7, from which the position of gjerdingenite within the kuzmenkoite subgroup can be seen.

Diagnostics

The optical properties of a representative collection of labuntsovite-group minerals, including all known species of this group and a number of minerals belonging to the gjerdingenite series, have been investigated. Minerals of the gjerdingenite series differ from the other minerals of the labuntsovite group (with $2V = 25 \pm 10^\circ$) by a distinctly larger $2V$ value ($> 50^\circ$). In addition, gjerdingenite samples are characterized by lower α values than organovaite and kuzmenkoite.

The infrared spectrum of gjerdingenite-Mn is close to the spectra of gjerdingenite-Fe (Raade *et al.*, 2002), its Ti

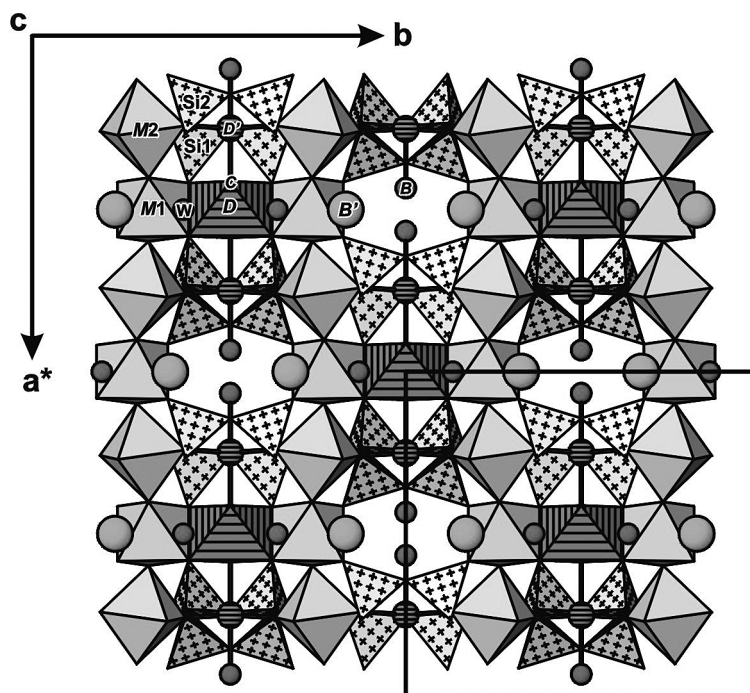


Fig. 2. The crystal structure of gjerdingenite-Mn seen along [001].

Table 6. Comparative characteristics of gjerdingenite-Mn and related minerals of the labuntsovite group.

Mineral	Gjerdingenite-Mn*	Gjerdingenite-Fe*	Kuzmenkoite-Mn	Organovaite-Mn
Idealised formula	$K_2Mn[Nb_4(Si_4O_{12})_2O_4] \cdot 6H_2O$	$K_2Fe[Nb_4(Si_4O_{12})_2O_4] \cdot 6H_2O$	$K_2Mn[Ti_4(Si_4O_{12})_2(OH)_4] \cdot 5H_2O$	$K_2Mn[Nb_4(Si_4O_{12})_2O_4] \cdot 6H_2O$
Symmetry, S.G.	Monoclinic, $C2/m$	Monoclinic, $C2/m$	Monoclinic, Cm or $C2/m$	Monoclinic, $C2/m$
Unit-cell parameters				
a (Å)	14.56	14.53	14.37*	14.55*
b (Å)	13.96	13.94	13.91*	14.00*
c (Å)	7.85	7.84	7.81*	15.70*
β (°)	117.6	117.6	117.1*	117.6*
Z	2	2	2*	4*
Density (g/cm ³)	2.93 (calc.)	2.82	2.67*	2.88*
Optical properties				
α	1.670	1.668	1.680-1.683	1.672-1.683
β	1.685	1.700	1.687-1.691	1.682-1.692
γ	1.775	1.794	1.775-1.795	1.770-1.785
Optical sign, 2V	(+) 52	(+) 58.5	(+) 20 to (+) 35	(+) 20 to (+) 35
References	This work	Raade <i>et al.</i> (2002)	Chukanov <i>et al.</i> (1999) Rastsvetaeva <i>et al.</i> (2000) Chukanov <i>et al.</i> (2003b)	Chukanov <i>et al.</i> (2001) Chukanov <i>et al.</i> (2003b)

*The data are given for holotype samples.

Table 7. Approved species in the labuntsovite group, $A_2B_2C_2D[M_4(Si_4O_{12})_2(O,OH)_4] \cdot nH_2O$.

Name	A	B	C	D	M	Z	Symmetry	Space group	Subgroup
Nenadkevichite	Na (for $A+B+C$)			-	Nb	1	Orth	$Pbam$	Nenadkevichite
Korobitsynite	Na (for $A+B+C$)			-	Ti	1	Orth	$Pbam$	subgroup
Vuoriyarvite-K	K (for $A+B+C$)			□	Nb	2	Mon	Cm	Vuoriyarvite subgroup
Tsepinite-Na	Na (for $A+B+C$)			□	Ti	2	Mon	Cm	
Tsepinite-K¹	K (for $A+B+C$)			□	Ti	2	Mon	Cm	
Tsepinite-Ca²	Ca (for $A+B+C$)			□	Ti	2	Mon	Cm	
Paratsepinite-Ba¹	Ba (for $A+B+C$)			□	Ti	4	Mon	$C2/m$	Paratsepinite subgroup
Paratsepinite-Na	Na (for $A+B+C$)			□	Ti	4	Mon	$C2/m$	
Lemleinite-K	Na	K	K	□	Ti	2	Mon	$C2/m$	Lemleinite subgroup
Lemleinite-Ba	Na	K	Ba	□	Ti	2	Mon	$C2/m$	
Labuntsovite-Mn	Na	K	□	Mn	Ti	2	Mon	$C2/m$	Labuntsovite subgroup
Labuntsovite-Mg	Na	K	□	Mg	Ti	2	Mon	$C2/m$	
Labuntsovite-Fe	Na	K	□	Fe	Ti	2	Mon	$C2/m$	
Paralabuntsovite-Mg	Na	K	□	Mg	Ti	4	Mon	$I2/m$	Paralabuntsovite subgroup
Karupmøllerite-Ca	□	Na	□	Ca	Nb	2	Mon	$C2/m$	Kuzmenkoite subgroup
Gjerdingenite-Fe	□	K	□	Fe	Nb	2	Mon	$C2/m$	
Gjerdingenite-Mn	□	K	□	Mn	Nb	2	Mon	$C2/m$	
Kuzmenkoite-Mn	□	K	□	Mn	Ti	2	Mon	$C2/m$ or Cm	
Kuzmenkoite-Zn	□	K	□	Zn	Ti	2	Mon	$C2/m$	
Lepkhenelmitite-Zn³	□	Ba	□	Zn	Ti	2	Mon	$C2/m$	
Organovaite-Mn	□	K	□	Mn	Nb	4	Mon	$C2/m$	Organovaite subgroup
Organovaite-Zn	□	K	□	Zn	Nb	4	Mon	$C2/m$	
Parakuzmenkoite-Fe	□	K	□	Fe	Ti	4	Mon	$C2/m$	
Gutkovaite-Mn	Ca+□	K	□	Mn	Ti	2	Mon	Cm	Gutkovaite subgroup
Alsakharovite-Zn⁴	Na+Sr	K	□	Zn	Ti	2	Mon	Cm	
Neskevaaraite-Fe⁵	Na+K	K	□	Fe	Ti	2	Mon	Cm	

Note: All these species are described by Chukanov *et al.* (2003b), although without name for the most recently approved minerals. References to these are: ¹Chukanov *et al.* (2003a); ²Pekov *et al.* (2003a); ³Pekov *et al.* (2004); ⁴Pekov *et al.* (2003b); ⁵Chukanov *et al.* (2003c).

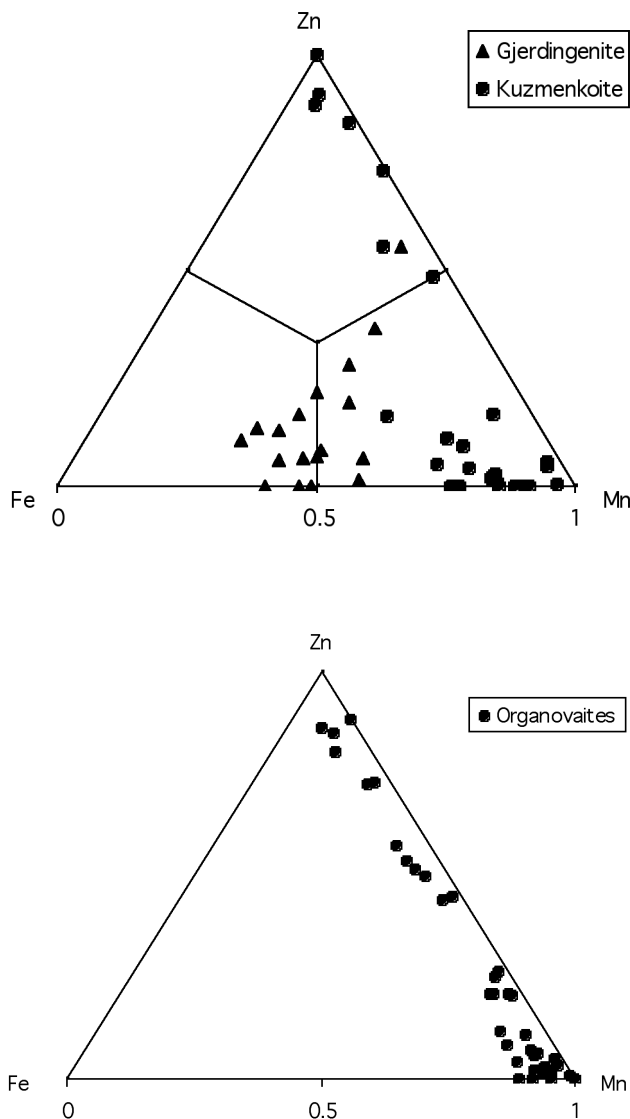


Fig. 3. Triangular plots of the Fe–Mn–Zn contents in the *D* site of gjerdingenite from the type locality and in kuzmenkoite and organovaites from Lovozero (point analyses). This site may also have vacancies.

analogue kuzmenkoite–Mn (Chukanov *et al.*, 1999) and its dimorph organovaites–Mn (Chukanov *et al.*, 2001). The following differences can be noted: infrared spectra of kuzmenkoite–Mn and organovaites–Mn show, in comparison with gjerdingenite–Mn, lower frequencies for most bands (*e.g.* 3200–3300 and 3300–3370, 772 and 775, 580 and 587, 452 and 460 cm^{-1} for kuzmenkoite–Mn and organovaites–Mn, respectively). In the infrared spectrum of gjerdingenite–Fe, as compared with gjerdingenite–Mn, higher frequencies of some bands are observed, *e.g.* 3560, 1110 and 950 cm^{-1} (Raade *et al.*, 2002). In general, infrared spectroscopy is not a very reliable method for the identification of gjerdingenite.

A reliable identification of gjerdingenite–Mn is only achievable by using a combination of chemical-analytical, optical and/or single-crystal X-ray investigations.

Formation of labuntsovite minerals

Minerals of the labuntsovite group are always of late-hydrothermal origin. The formation of these minerals from alkaline hydrothermal solutions is stimulated by a high activity of silica (Chukanov *et al.*, 2003b). The combination of high activities of Si and F in alkaline pegmatites prevents the formation of common aluminosilicate zeolites and promotes the formation of microporous zeolite-like (Ti,Nb) or Zr silicates with mixed frameworks (*e.g.* elpidite, labuntsovite-group minerals). In the Russian occurrences, labuntsovite minerals are often the result of late-stage, hydrothermal alteration of previously formed minerals (like rinkite, lamprophyllite, vuonnemite). Zn-dominated species are found close to dissolution cavities after sphalerite (Chukanov *et al.*, 2003b).

For gjerdingenite from the Gjerdingsselve ekerite pluton, conditions of formation inside the miarolitic cavities are different. In particular, there is little or no late-stage alteration of earlier-formed minerals. Only rarely are remnants of dissolved microcrystals of sphalerite encountered. Crystallization inside the cavities has occurred in complex chemical systems during decreasing temperature, from the common rock-forming minerals (feldspars, quartz, aegirine) lining the cavities to sodium-fluoride minerals in the very last stage. Rock samples of ekerite have been collected from all accessible parts of the pluton (which measures about 2 x 4 km^2), and the mineral content of the miarolitic cavities has been studied in detail. Large local variations are evident. For instance, neighborite [NaMgF_3] is only found in a small area where the rock shows signs of assimilation of more mafic bedrock, and a very close to end-member genthelvite [$\text{Zn}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$] is restricted to a small outcrop poor in other minerals. Gjerdingenite, on the other hand, is quite wide-spread in the cavities but invariably in small amounts.

Plots of the Fe–Mn–Zn contents in the *D* sites of gjerdingenites from the type locality and of kuzmenkoites and organovaites from Lovozero are shown in Fig. 3. Evidently there is a series between gjerdingenite–Fe and –Mn, with an increased Zn content with increasing Mn content; there is even one analysis with a dominance of Zn, from a zone in Zn-rich gjerdingenite–Mn. Zoning seems to be irregular, as is typical for labuntsovite-group minerals. Kuzmenkoites and organovaites are mainly Fe-poor and are dominated by Mn or Zn in the *D* site. Thus, according to these plots, the observed compositional field of gjerdingenite differs from those of kuzmenkoite and organovaites. At least in the case of kuzmenkoite, which is isostructural with gjerdingenite, this difference is probably of a geochemical rather than a crystallochemical nature.

Gjerdingenite is one of the few K-rich minerals (apart from orthoclase and kupletskite) in parageneses dominated by Na-rich silicates and fluorides. Based on this fact, it is conceivable that K could be partially incorporated in the structure of gjerdingenite at a very late stage of mineral formation as the result of cation-exchange processes. Our experiments show that its Ti analogue kuzmenkoite is an ion-exchanger towards large monovalent cations (Na, K, Cs) at low temperatures (Pekov *et al.*, 2002). However, it

should be noted that Na-rich silicates formed prior to and contemporaneously with gjerdingenite, and that Na-rich fluorides (especially ralstonite) were the last minerals to crystallize.

It would seem strange that gjerdingenite-Fe can occur in association with Mn-dominant minerals like kupletskite and janhaugite, especially as gjerdingenite-Fe is the youngest of these minerals. This is in contrast to the situation in the alkaline pegmatites of the Kola Peninsula where Fe-dominant members of the labuntsovite group are rather rare. Even in the Khibiny massif, where the role of Fe at earlier stages is predominant (e.g. astrophyllite strongly predominates over kupletskite), labuntsovite-Mn is a much more common mineral than labuntsovite-Fe. In conclusion, the Fe–Mn–Zn variations in gjerdingenite from the Gjerdingselva ekerite pluton are the result of local geochemical differences in complex multicomponent chemical systems inside individual miarolitic cavities.

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