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GEOCHEMISTRY

High Degree of Cationic Ordering in the Structure of a New Mineral of the Labuntsovite Group

A. A. Zolotarev, Jr.[a], S. V. Krivovichev[a], V. N. Yakovenchuk[b],
Ya. A. Pakhomovsky[b], N. I. Organova[c], and T. Armbruster[c]

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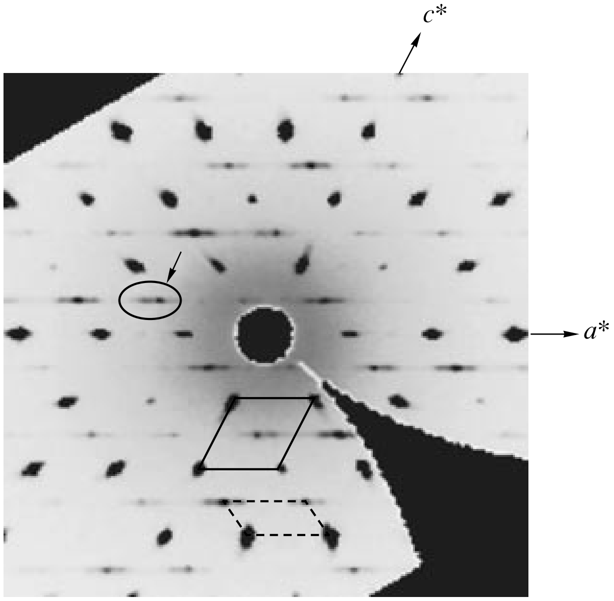
In recent years, minerals of the labuntsovite group (hereafter, LG) have become objects of many detailed mineralogical and crystallochemical studies stimulated by numerous findings of these minerals and the diversity of their chemical compositions and physicochemical properties [1]. The LG minerals also attract interest owing to the possibility of their application in catalytic processes, adsorption, and ion exchange.

The structurally characterized monoclinic LG minerals have either a simple unit cell with $c \sim 7$ Å(sp. gr. *C*2/*m* or *Cm*) or a double unit cell with $c \sim 14$ Å (sp. gr. *C*2/*m*). In 1958, Milton et al. [2] described an LG mineral with a double unit cell with space group *I*2/*m* named paralabuntsovite-Mg in the modern classification. However, the structure of a mineral with such characteristics has not yet been studied despite the repeated detections of diffuse features of diffraction patterns that generally fit group *I*2/*m* [3, 4].

In this communication, we present new data on the identification and specification of the crystalline structure of a new LG mineral with a high degree of cationic ordering that provides the doubling of the unit cell and a change of symmetry up to *I*2/*m*.

The mineral sample for study was taken from a hydrothermal vein in the Khibiny alkaline pluton, Kola Peninsula, Russia. The averaged chemical composition of the mineral determined by electron microprobe is as follows (wt %): K_2O 6.96, Na_2O 2.64, BaO 10.42, FeO 0.48, MgO 0.34, MnO 1.24, TiO_2 22.26, Nb_2O_5 3.59, SiO_2 39.68, and H_2O 12.39 (calculated as difference from 100 wt %). The empirical formula recalculated for 16 atoms of Si appears as $Na_{2.06}K_{3.58}Ba_{1.65}(H_2O)_{1.58}(Mn_{0.42}Mg_{0.20}Fe_{0.16})[Ti_{6.75}Nb_{0.65}((OH_{0.9}O_{0.1})_8)(Si_4O_{12})_4] \cdot 11.5H_2O$.

The chosen monocrystal was placed on a STOE IPDS II diffractometer equipped with an Image Plate plane detector. The reconstruction of *h*0*l* sections of the reciprocal diffraction space (figure) revealed distinct Bragg reflections that double parameter *c* in comparison with those of the common monoclinic labuntsovite and rules of extinction that unequivocally indicate the presence of space group *I*2/*m*. Parameters of the unit



The reconstructed *h*0*l* section of reciprocal diffraction space for a highly ordered LG mineral. The arrow indicates the reflection that doubles parameter *c* of the minor labuntsovite unit cell (shown with the dashed line) and corresponds to the double body-centered lattice (solid line).

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[a] *St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 119034 Russia*
e-mail: skrivovi@mail.ru

[b] *Geological Institute, Kola Scientific Center, Russian Academy of Sciences, ul. Fersmana 14, Apatity, Murmansk oblast, 184200 Russia*

[c] *Laboratory of Chemical and Mineralogical Crystallography, University of Bern, Switzerland*

Table 1. Coordinates, occupancy of sites, and equivalent thermal parameters of atoms in the structure of a highly ordered LG mineral

Atom	x	y	z	q*	$U_{\rm eq} \cdot 100$, Å^2
Si1	0.81929(7)	0.61116(7)	0.37408(7)	1	1.14(2)
Si2	0.70831(7)	0.61030(6)	0.15122(6)	1	1.12(2)
Si3	−0.20787(7)	0.11018(7)	−0.15218(6)	1	1.13(2)
Si4	−0.17930(7)	0.38841(7)	−0.12450(6)	1	1.19(2)
Ti1	0	0.22606(7)	0	1	1.86(3)
Ti2	−0.25146(6)	0.25118(4)	−0.50064(4)	1	1.91(3)
Ti3	1/2	0.27199(7)	0	1	2.10(4)
Ba1**	0.08700(3)	0	−0.07874(3)	0.70	1.75(2)
Ba2***	−0.0892(1)	0	−0.42214(9)	0.23	1.63(6)
Mg1	0	0	0	0.08	2.1(1)
Mg2	1/2	1/2	0	0.12	1.91(4)
Mn1	0	0	0	0.16	2.1(1)
Mn2	1/2	1/2	0	0.48	1.91(4)
Na1	0.9109(4)	0.7628(4)	0.2548(4)	0.40	4.0(1)
Na2	−0.127(2)	−0.028(1)	−0.434(1)	0.18	7.0(0)
K1	0.0802(2)	1/2	−0.1009(2)	0.60	2.4(1)
K2	−0.0795(2)	1/2	−0.3991(2)	0.60	2.6(1)
K3	−0.0758(5)	0.4661(9)	−0.3961(5)	0.19	3.2(3)
O1	0.9192(2)	0.6806(2)	0.4012(2)	1	1.78(5)
O2	0.7639(2)	0.6230(2)	0.4432(2)	1	1.53(5)
O3	0.5824(2)	0.6160(2)	0.0865(2)	1	1.52(5)
O4	0.7327(2)	0.6285(2)	0.2630(2)	1	1.80(5)
O5	0.7485(3)	1/2	0.1443(3)	1	1.60(7)
O6	−0.0819(2)	0.1151(2)	−0.0873(2)	1	1.64(5)
O7	−0.2329(2)	0.1276(2)	−0.2641(2)	1	1.85(5)
O8	−0.2467(3)	0	−0.1424(3)	1	1.56(7)
O9	−0.2734(2)	0.1826(2)	−0.1194(2)	1	1.62(5)
O10	−0.0795(2)	0.3192(2)	−0.0987(2)	1	1.81(5)
O11	−0.2336(2)	0.3742(2)	−0.0547(2)	1	1.58(5)
O12	0.1003(2)	0.2209(2)	−0.0520(2)	1	1.57(5)
O13	0.8644(3)	1/2	0.3840(3)	1	1.65(7)
O14	−0.1347(3)	1/2	−0.1137(3)	1	1.64(7)
O15	0.7737(2)	0.6835(2)	0.1189(2)	1	1.58(5)
O16	−0.1007(2)	0.2261(2)	−0.4480(2)	1	1.68(5)
Ow1	−0.08700(3)	0	−0.07874(3)	0.24	1.75(6)
Ow2	−0.0892(1)	0	−0.42214(9)	0.60	1.63(6)
Ow3	−0.0877(3)	0.2365(3)	−0.2449(3)	0.78	2.7(1)
Ow4	0.0241(8)	0.1142(5)	−0.2478(5)	0.67	4.9(3)
Ow5	0.0264(7)	0.3510(5)	−0.2550(5)	0.60	4.6(3)
Ow6	−0.0242(9)	0.3496(7)	−0.2448(7)	0.54	5.8(4)
Ow7	−0.023(1)	0.1113(7)	−0.2527(7)	0.37	3.4(4)
Ow8	0.0768(6)	0.467(1)	−0.1031(5)	0.42	1.3(3)

* Occupancy of site; ** Ba1 = $Ba_{0.68}K_{0.08}$; *** Ba2 = $Ba_{0.21}K_{0.19}$.

Table 2. Interatomic spacings (Å) in the structure of a highly ordered LG mineral

Si1–O2	1.607(2)	(Mn, Mg)1–O6	2.075(3) 4×	K1–O5	2.817(4)
Si1–O1	1.608(3)	(Mn, Mg)1–Ow1	2.1032(4) 2×	K1–Ow6	2.92(1) 2×
Si1–O4	1.630(3)	⟨(Mn, Mg)1–O⟩	2.089	K1–O11	2.983(3) 2×
Si1–O13	1.641(2)			K1–O14	2.984(4)
⟨Si1–O⟩	1.622	(Mn, Mg)2–O3	2.081(1) 4×	K1–Ow5	2.986(7) 2×
		(Mn, Mg)2–Ow2	2.119(2) 2×	K1–O14	3.075(4)
Si2–O15	1.602(3)	⟨(Mn, Mg)2–O⟩	2.100	K1–O15	3.369(3) 2×
Si2–O3	1.620(3)			⟨K1–O⟩	3.036
Si2–O4	1.636(3)	Ba1–O6	2.839(3) 2×		
Si2–O5	1.645(2)	Ba1–Ow4	2.846(7) 2×	K2–O8	2.833(4)
⟨Si2–O⟩	1.626	Ba1–Ow7	2.88(1) 2×	K2–Ow5	2.913(8) 2×
		Ba1–O2	2.930(2) 2×	K2–O13	2.973(4)
Si3–O9	1.601(3)	Ba1–O6	3.065(3) 2×	K2–O2	2.995(3) 2×
Si3–O6	1.620(3)	Ba1–O12	3.065(3) 2×	K2–Ow6	3.00(1) 2×
Si3–O7	1.634(3)	⟨Ba1–O⟩	2.938	K2–O13	3.106(5)
Si3–O8	1.646(2)			K2–O9	3.372(3) 2×
⟨Si3–O⟩	1.625	Ba2–Ow7	2.82(1) 2×	⟨K2–O⟩	3.040
		Ba2–O3	2.877(3) 2×		
Si4–O11	1.606(2)	Ba2–Ow4	2.920(7) 2×	K3–Ow5	2.57(1)
Si4–O10	1.608(3)	Ba2–O11	2.952(3) 2×	K3–Ow6	2.67(1)
Si4–O7	1.636(3)	Ba2–O3	3.060(3) 2×	K3–O2	2.804(9)
Si4–O4	1.643(2)	Ba2–O16	3.136(3) 2×	K3–O8	2.894(8)
⟨Si4–O⟩	1.623	⟨Ba2–O⟩	2.962	K3–O13	2.975(8)
				K3–O1	3.04(1)
Ti1–O10	1.931(3) 2×	Na1–Ow6	2.29(1)	K3–O9	3.06(1)
Ti1–O12	1.938(2) 2×	Na1–Ow7	2.37(1)	K3–O13	3.173(8)
Ti1–O6	2.031(3) 2×	Na1–O15	2.405(6)	K3–Ow5	3.23(1)
⟨Ti1–O⟩	1.967	Na1–O4	2.452(6)	K3–Ow6	3.32(1)
		Na1–O1	2.503(6)	K3–O2	3.32(1)
Ti2–O12	1.935(3)	Na1–Ow3	2.596(8)	⟨K3–O⟩	3.000
Ti2–O16	1.959(3)	Na1–O3	2.951(6)		
Ti2–O15	1.960(2)	Na1–O16	3.015(6)		
Ti2–O9	1.965(2)	⟨Na1–O>	2.580		
Ti2–O11	1.986(2)				
Ti2–O2	1.998(2)	Na2–O11	2.34(3)		
⟨Ti2–O⟩	1.967	Na2–O16	2.77(2)		
		Na2–Ow7	2.78(2)		
Ti3–O1	1.921(3) 2×	Na2–O11	2.86(2)		
Ti3–O16	1.943(2) 2×	Na2–Ow4	2.98(2)		
Ti3–O3	2.038(3) 2×	Na2–O3	2.98(2)		
⟨Ti3–O⟩	1.967	Na2–O3	3.10(2)		
		⟨Na2–O⟩	2.83		

cell specified with the least-squares method are as follows: a = 14.278(1), b = 13.778(1), and c = 15.592(2) Å, β = 116.76(1)°, and V = 2738.96 Å^3. Correction for absorption was introduced analytically with allowance for crystal shape. The structure was deciphered with the SHELX software package [5]. The structure was solved by direct methods and refined to R_1 = 0.049 (wR_2 = 0.143) for 3349 reflections with

$|F_{hkl}| \geq 4\sigma|F_{hkl}|$. The final model included coordinates and anisotropic thermal parameters for all atoms (Table 1). We failed to localize the site of hydrogen atoms. Interatomic spacings are shown in Table 2.

The crystal structure of the mineral contains three symmetrically independent Ti atoms with octahedral coordination of six oxygen atoms. The Ti–O bond length in octahedrons varies within a range of 1.91–2.04 Å. Four symmetrically independent Si atoms make up O–Si tetrahedrons with a bond length of 1.60–1.65 Å.

The competing isomorphism at *C* and *D* sites with a spacing of 2.1–2.2 Å is a key specific feature of the structure of LG minerals. Site *C* may be occupied by water molecules or a large cation (K^+, Ba^{2+}, and others), whereas site *D* with octahedral coordination is occupied by cations, such as Mg^{2+}, Mn^{2+}, Fe^{2+}, and others. All LG minerals studied previously are distinguished by disordered location of cations at sites *C* and *D*, whereas the structure of the studied mineral is the first example of cationic *C*–*D* ordering, which is accompanied by splitting of *C* and *D* sites into different (in occupancy) sites *C*1–*C*2 and *D*1–*D*2. Pairs *C*1–*D*1 and *C*2–*D*2 are antagonistic, and only one site may be occupied by cations. Occupancy of the sites calculated from chemical composition and structural data may be represented as follows:

*C*1: $Ba_{0.68}(H_2O)_{0.24}K_{0.08}$; *C*2: $(H_2O)_{0.60}Ba_{0.21}K_{0.19}$; *D*1: $Mn_{0.16}Mg_{0.08}$; and *D*2: $Mn_{0.48}Mg_{0.12}$. Thus, Ba^{2+} dominates at site *C*1 and induces prevalent vacancy of site *D*1, whereas site *C*2 is largely occupied by water molecules due to the predominance of Mn^{2+} at site *D*2. The high degree of cationic ordering may be schematically represented as a sequential alternation of unit cells of lemmleinite-Ba and labuntsovite-Mn, although the bulk formula of the studied mineral corresponds to lemmleinite-Ba [6].

The structural formula of the mineral is as follows: $Na_{2.32}K_{2.96}(H_2O)_{1.04}Ba_{1.74}(H_2O)_{1.68}K_{0.58} \cdot (Mn_{0.64}Mg_{0.2})[Ti_8((OH_{0.6}O_{0.4})_8)(Si_4O_{12})_4] \cdot 12.9H_2O$, which is consistent with the formula given above on the basis of chemical composition.

Like other LG minerals, the studied mineral has a mixed framework based on $[Si_4O_{12}]$ rings that tie together the chains of apex-connected TiO_6 octahedrons extended along [100]. Additional octahedrons with *D* sites as their centers are located between the octahedral chains. The cavities of the framework are filled with Ba^{2+}, Na^+, and K^+ cations and H_2O molecules.

As was already mentioned, the structure of this mineral is the first example of a highly ordered (at the unit cell level) arrangement of *C* and *D* cations. It should be noted, however, that the ordering remains incomplete. This is suggested by the diffusion "tails" that accompany Bragg reflections, which double parameter *c* [7] (figure). Most likely, the cationic *C*–*D* ordering in the LG minerals is caused by the thermodynamic regime of their formation [3]. The Milton paralabuntsovite-Mg with a doubled *I*-cell was found in low-temperature sodium carbonate deposits of the Green River Formation (Trona Mine, Wyoming, United States). As in pyroxenes [8] and vesuvianites [9–11], the cationic ordering in labuntsovites is a typomorphic feature that may be used for the reconstruction of *PT* conditions of hydrothermal mineral formation. Elucidation of these conditions will be the subject of further investigations.

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