The crystal chemistry of malinkoite, NaBSiO4, and lisitsynite, KBSi2O6, from the Khibina-Lovozero complex, Kola Peninsula, Russia

Article *in* The Canadian Mineralogist · February 2001

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THE CRYSTAL CHEMISTRY OF MALINKOITE, NaBSiO$_4$, AND LISITSYNITE, KBSi$_2$O$_6$, FROM THE KHIBINA–LOVOZERO COMPLEX, KOLA PENINSULA, RUSSIA

ELENA V. SOKOLOVA§ AND FRANK C. HAWTHORNE¶

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

ALEXANDER P. KHOMYAKOV

Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, Moscow 121357, Russia

ABSTRACT

The crystal structure of malinkoite, NaBSiO$_4$, *a* 13.8964(4) Å, *c* 7.7001(2) Å, *P*6$_3$, *Z* = 18, *D*$_x$ = 2.922 g cm^{-3}, from the Khibina–Lovozero complex, Kola peninsula, Russia, has been solved by direct methods and refined to an *R* index of 3.8% using 2094 unique observed ($|F_o| > 4\sigma F$) reflections collected with a single-crystal diffractometer fitted with a CCD detector and Mo*K*α X-radiation. Malinkoite is a framework borosilicate with a structure consisting of six-membered rings of regularly alternating (SiO$_4$) and (BO$_4$) tetrahedra, and Na located in the large channels extending along [001]. There are three unique *Si* sites, each occupied by Si and each coordinated by four O atoms in a tetrahedral arrangement, with <*Si*–O> distances of 1.625, 1.622 and 1.622 Å, respectively. There are three unique *B* sites, each occupied by B and each coordinated by four O atoms in a tetrahedral arrangement, with <*B*–O> distances of 1.476, 1.476 and 1.473 Å, respectively. There are five unique *Na* sites, each completely occupied by Na. Three of the *Na* sites are [9]-coordinated, with <*Na*–O> distances of 2.626, 2.642 and 2.630 Å, respectively; the remaining two *Na* sites are [6]-coordinated, with <*Na*–O> distances of 2.444 and 2.440 Å, respectively. The (SiO$_4$) and (BO$_4$) tetrahedra link to form six-membered rings of two different configurations based on the following sequences of up (*U*) and down (*D*) linkages: *UDUDUD* and *UUDUDD* in the ratio of 1:2. Nine-coordinated Na polyhedra are located in big cages formed by stacking of *UDUDUD* rings. Stacking of *UUDUDD* rings produces smaller cages occupied by [6]-coordinated Na. In accord with the ratio of two types of rings, there are twelve Na octahedra and six [9]-coordinated Na polyhedra per unit cell in malinkoite. The framework topology is related to that of beryllonite NaBePO$_4$.

In the crystal structure of lisitsynite, KBSi$_2$O$_6$, four-membered rings consist of two (SiO$_4$) and two (BO$_4$) tetrahedra, and are linked into zig-zag chains (puckered ladders) along [001]. There are two types of chemically distinct six- and eight-membered rings: (4Si + 2B) and (5Si + B); (5Si + 3B) and (6Si + 2B). Two different pairs of six-membered and eight-membered rings, (4Si + 2B) and (5Si + 3B), and (5Si + B) and (6Si + 2B), respectively, form sheets on (100) and (010). Stacking of sheets and zig-zag chains gives rise to a three-dimensional framework. There are one-dimensional seven-ring channels along the *c* direction. Lisitsynite, KBSi$_2$O$_6$, and synthetic "boroleucite", K(Si$_2$B)O$_6$, may be regarded as polymorphs with different patterns of Si–B order.

Keywords: malinkoite, lisitsynite, new mineral species, borosilicate, crystal structure, Khibina, Lovozero, Russia.

SOMMAIRE

Nous avons résolu la structure cristalline de la malinkoïte, NaBSiO$_4$, *a* 13.8964(4), *c* 7.7001(2) Å, *P*6$_3$, *Z* = 18, *D*$_x$ = 2.922 g cm^{-3}, provenant du complexe de Khibina–Lovozero, péninsule de Kola, en Russie, par méthodes directes, et l'avons affiné jusqu'à un résidu *R* de 3.8% en utilisant 2094 réflexions uniques observées ($|F_o| > 4\sigma F$), prélevées avec un diffractomètre pour cristaux uniques muni d'un détecteur CCD et avec rayonnement Mo*K*α. Il s'agit d'un borosilicate à charpente dont la structure contient des anneaux à six membres, des tétraèdres (SiO$_4$) et (BO$_4$) en alternance régulière, et des atomes Na logés dans des canaux alongés selon [001]. Il y a trois sites *Si* uniques, chacun étant occupé par Si en coordinence avec quatre atomes d'oxygène dans un agencement tétraédrique, avec des distances <*Si*–O> de 1.625, 1.622 et 1.622 Å, respectivement. Il y a trois sites *B* uniques, chacun occupé par B en coordinence avec quatre atomes d'oxygène dans un agencement tétraédrique, avec des distances <*B*–O> de 1.476, 1.476 et 1.473 Å, respectivement. Il y a cinq sites uniques *Na*, chacun complètement occupé par Na. Trois des sites *Na* ont une coordinence [9], avec des distances <*Na*–O> de 2.626, 2.642 et 2.630 Å, respectivement; les deux autres sites *Na* ont une coordinence [6], avec des distances <*Na*–O> de 2.444 et 2.440 Å, respectivement. Les tétraèdres (SiO$_4$)

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§ Permanent address: Department of Crystallography and Crystal Chemistry, Faculty of Geology, Moscow State University, Moscow 119899, Russia.

et (BO_4) sont agencés en anneaux de six membres en deux configurations distinctes, selon que l'orientation soit vers le haut (*U*) ou le bas (*D*): *UDUDUD* et *UUDUDD* dans un rapport de 1:2. Les polyèdres dans lesquels le Na a une coordinance [9] sont situés dans des cages volumineuses formés par l'empilement des anneaux *UDUDUD*. L'empilement des anneaux *UUDUDD* mène à des cages moins volumineuses, qu'occupe le Na à coordinance [6]. Comme le prédit le rapport entre les deux sortes d'anneaux, il y a douze octaèdres de Na et six polyèdres ayant le Na en coordinance [9] dans chaque maille élémentaire de malinkoïte. La topologie de la trame est semblable à celle de la beryllonite, $NaBePO_4$.

Dans la structure de la lisitsynite, $KBSi_2O_6$, des anneaux à quatre membres contiennent deux tétraèdres (SiO_4) et deux tétraèdres (BO_4), qui sont liés en chaînes en zig-zag comme une échelle affaissée le long de [001]. Il y a deux sortes d'anneaux à six et à huit membres, chimiquement distincts: (4Si + 2B) et (5Si + B) d'une part, et (5Si + 3B) et (6Si + 2B) de l'autre. Deux paires différentes d'anneaux à six et huit membres, (4Si + 2B) et (5Si + 3B), et (5Si + B) et (6Si + 2B), respectivement, forment des feuillets parallèles à (100) et à (010). L'empilement de ces feuillets et des chaînes en zig-zag est à l'origine d'une trame tri-dimensionnelle. Il y a des canaux dans une dimension, le long de l'axe *c*, formés par sept anneaux. On peut considérer la lisitsynite, $KBSi_2O_6$, et la "boroleucite", produit de synthèse de composition $K(Si_2B)O_6$, commes formes polymorphiques ayant des schémas d'ordre Si–B distincts.

(Traduit par la Rédaction)

Mots-clés: malinkoïte, lisitsynite, nouvelle espèce minérale, borosilicate, structure cristalline, Khibina, Lovozero, Russie.

INTRODUCTION

The first occurrence of two natural compounds with a chemical composition $NaBSiO_4$ at Mont Saint Hilaire, Quebec (UK53) *a* 8.001, *b* 7.693, *c* 13.885 Å, β 89.80°, $P2_1/n$ and (UK53A) *a* 8.036, *c* 7.709 Å, P6/*m* or P6, was reported by Chao *et al.* (1990). At the same time, natural $NaBSiO_4$ was found at Mount Karnasurt, Lovozero alkaline complex, Kola Peninsula, Russia, in an intensely mineralized lenticular hyperagpaitic pegmatite intruded into foyaite and associated with ussingite, chkalovite, nordite, gerasimovskite and neptunite. The crystal structure of natural $NaBSiO_4$, *a* 8.035(3), *c* 7.703(2) Å, $P6_3$, from the Lovozero complex, was solved and refined to an *R* index of 6.3% (Sokolova & Khomyakov 1991), and sample UK53A from Mont Saint Hilaire was described as a variant of the Lovozero material. However, the crystals from Lovozero used for that work were of inferior quality (only 293 unique reflections with $I > 1.96\sigma I$), and the resulting refinement of the structure was unsatisfactory. The Lovozero material has now been described as the new mineral malinkoite (Khomyakov *et al.* 2000), and here we report the crystal structure of malinkoite.

Lisitsynite, $KBSi_2O_6$, is a new borosilicate mineral occurring in hyperalkaline rocks of the Khibina massif, Kola Peninsula, Russia, and was described by Khomyakov *et al.* (2000). Lisitsynite is the sixth boro-silicate mineral found at the Khibina and Lovozero massifs, the others being kalborsite, $K_6 Al_4 Si_6 O_{20} B (OH)_4 Cl$, leucosphenite, $Ba Na_4 Ti_2 B_2 Si_{10} O_{30}$, reedmergnerite, $NaBSi_3O_8$, searlesite, $NaBSi_2O_5$, and malinkoite, $NaBSiO_4$. In accordance with the recommended nomenclature for zeolite minerals (Coombs *et al.* 1997), lisitsynite can be regarded as a new zeolite. Sokolova *et al.* (2000) briefly reported the crystal structure of lisitsynite; here, we discuss the structure in more detail.

EXPERIMENTAL DETAILS: MALINKOITE

Chemical analysis

The chemical data for malinkoite (Khomyakov *et al.* 2000) are given in Table 1. No other element with atomic number greater than 8 was detected. Electron-microprobe analysis of the mineral for B was based on the *K*α line and was done with an ODPB crystal analyzer (2*d* = 99.98 Å) at 5 kV and 110 nA using differential discrimination. A defocused beam (30 μm) was rastered across the sample during analysis. Owing to the possible influence of chemical bonding on the analytical results, the *K* ratio ($K = S_{sample} / S_{standard}$) was determined from integral intensities. The empirical formula of malinkoite was calculated based on four anions: $Na_{1.00} B_{0.98} Si_{1.01} O_4$, ideally $NaBSiO_4$.

Collection of X-ray data

Single-crystal X-ray data for malinkoite were collected with a Siemens *P*4 diffractometer fitted with a CCD detector, using Mo*K*α radiation and an irregular crystal measuring 0.08 × 0.15 × 0.15 mm. Integrated intensities of 15151 reflections with $\overline{1}9 < h < 20$, $\overline{2}0 < k < 20$, $\overline{1}\overline{1} < l < 11$ were collected up to 2θ = 60° using 30 s per frame. The refined cell-parameters (Table 2)

TABLE 1. CHEMICAL COMPOSITION (wt.%) AND FORMULA UNIT (*apfu*) FOR MALINKOITE

	(1)*	(2)**		
Na_2O	24.36	24.62	Na	1.00
B_2O_3	26.88	27.65	B	0.98
SiO_2	47.83	47.73	Si	1.01
Total	99.07	100		

* Taken from Khomyakov *et al.* (2000)
**(2) calculated based on the ideal formula $NaBSiO_4$

TABLE 2. MISCELLANEOUS REFINEMENT DATA FOR MALINKOITE

a (Å)	13.8964(4)	Radiation	Mo$K\alpha$
c (Å)	7.7001(2)	2θ-range for data collection (°)	60.03
V (Å^3)	1287.8(1)	R(int)	0.0289
Space group	$P6_3$	Reflections collected $F_o > 4\sigma F$	15151 12166
Z	18	Independent reflections $F_o > 4\sigma F$	2506 2094
D_{meas} (g/cm^3)	2.85(2)	Refinement method	Full-matrix least squares on F^2; fixed weights proportional to $1/\sigma(F^2)$
Absorption coefficient (mm^{-1})	0.79	Goodness of fit on F^2	1.022
F(000)	1116	Final R indices $F_o > 4\sigma(F_o)$]	3.8
Crystal size (mm)	0.08 x 0.15 x 0.15	R indices (all data)	R_1 = 4.7 wR_2 = 8.8 Goo$F$ = 1.022

TABLE 3. FINAL ATOMIC PARAMETERS FOR MALINKOITE

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	0.87861(7)	0.78275(7)	0.3325(1)	0.0077(2)	0.0070(4)	0.0065(4)	0.0099(5)	0.0004(4)	0.0009(4)	0.0035(3)
Si(2)	0.78805(6)	0.55086(6)	0.7395(1)	0.0061(2)	0.0062(3)	0.0072(4)	0.0056(3)	0.0005(3)	-0.0006(3)	0.0038(3)
Si(3)	0.43112(6)	0.54549(6)	0.7456(1)	0.0061(2)	0.0060(3)	0.0061(3)	0.0057(3)	0.0009(4)	0.0008(4)	0.0026(3)
B(1)	0.5524(3)	0.7657(3)	0.8665(4)	0.0086(6)	0.0075(14)	0.0087(14)	0.0079(15)	0.0010(11)	-0.0014(11)	0.0029(12)
B(2)	0.5670(3)	0.4537(3)	0.8673(4)	0.0089(6)	0.0090(14)	0.0081(14)	0.0107(17)	-0.0022(11)	-0.0002(11)	0.0049(12)
B(3)	0.1206(3)	0.2191(3)	0.2137(4)	0.0054(7)	0.0055(14)	0.0084(15)	0.0033(20)	0.0012(11)	-0.0010(10)	0.0042(12)
Na(1)	0	0	0.0534(3)	0.0166(6)	0.0183(8)	0.0183(8)	0.0131(13)	0	0	0.0091(4)
Na(2)	0.6542(1)	0.6668(1)	0.5673(2)	0.0135(3)	0.0092(5)	0.0221(6)	0.0056(5)	-0.0003(5)	0.0000(4)	0.0051(5)
Na(3)	1/3	2/3	0.5246(5)	0.0183(5)	0.0180(6)	0.0180(6)	0.0190(13)	0	0	0.0090(3)
Na(4)	2/3	1/3	0.5233(5)	0.0197(5)	0.0188(6)	0.0188(6)	0.0213(14)	0	0	0.0094(3)
Na(5)	0.3115(1)	0.3262(1)	0.5023(2)	0.0168(3)	0.0207(7)	0.0136(6)	0.0165(6)	0.0005(4)	-0.0022(5)	0.0089(5)
O(1)	0.8652(2)	0.6626(2)	0.2871(2)	0.0082(6)	0.0086(13)	0.0067(13)	0.0079(16)	0.0014(6)	0.0036(6)	0.0028(11)
O(2)	0.5389(2)	0.5350(2)	0.7911(2)	0.0086(6)	0.0082(13)	0.0090(14)	0.0105(16)	0.0036(7)	0.0013(6)	0.0057(11)
O(3)	0.8012(2)	0.6714(2)	0.7847(2)	0.0080(6)	0.0093(13)	0.0050(13)	0.0088(16)	0.0008(6)	0.0014(7)	0.0030(11)
O(4)	0.8692(2)	0.5288(2)	0.8639(3)	0.0081(4)	0.0113(9)	0.0095(9)	0.0057(9)	-0.0020(7)	-0.0022(7)	0.0068(8)
O(5)	0.0083(2)	0.8777(2)	0.3118(3)	0.0089(5)	0.0074(12)	0.0086(12)	0.0105(9)	-0.0002(9)	0.0036(9)	0.0038(10)
O(6)	0.3931(2)	0.5113(2)	0.5456(3)	0.0103(4)	0.0120(9)	0.0094(9)	0.0052(9)	-0.0008(8)	-0.0005(7)	0.0020(8)
O(7)	0.3269(2)	0.4647(2)	0.8683(3)	0.0087(4)	0.0071(9)	0.0113(9)	0.0076(9)	0.0034(7)	0.0004(7)	0.0045(8)
O(8)	0.8429(2)	0.7873(2)	0.5327(3)	0.0102(4)	0.0097(9)	0.0143(10)	0.0060(9)	0.0006(8)	0.0002(9)	0.0054(8)
O(9)	0.6589(2)	0.4559(2)	0.7671(3)	0.0089(5)	0.0042(10)	0.0082(10)	0.0128(9)	-0.0014(8)	0.0008(8)	0.0020(9)
O(10)	0.8245(2)	0.5479(1)	0.5418(2)	0.0092(4)	0.0095(9)	0.0143(9)	0.0054(8)	0.0006(7)	0.0015(7)	0.0072(8)
O(11)	0.4648(2)	0.6758(2)	0.7626(3)	0.0097(4)	0.0089(10)	0.0058(10)	0.0137(9)	0.0000(9)	-0.0024(9)	0.0032(8)
O(12)	0.7998(2)	0.8064(2)	0.2049(3)	0.0108(5)	0.0134(11)	0.0097(10)	0.0116(12)	-0.0003(8)	-0.0030(8)	0.0075(9)

were obtained from 9179 reflections ($I > 10\sigma I$). An empirical absorption correction (SADABS, Sheldrick 1996) was applied.

Solution and refinement of the structure of malinkoite

The structure of malinkoite was solved by direct methods. The SHELXTL 5.1 program was used for solution and refinement of the structure. Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography (Ibers & Hamilton

1974). Details of the structure refinement are given in Table 2. The structure was refined to an R index of 3.8% and a GoF of 1.02 for a total of 196 refined parameters. Twinning by merohedry is well known for related compounds, *e.g.*, kalsilite KAlSiO$_4$ (Cellai *et al.* 1997) and RbLiCrO$_4$ (Makarova *et al.* 1993); however, upon careful analysis of the structural data, we found no evidence of twinning in malinkoite. Final atom parameters are given in Table 3, selected interatomic distances are presented in Table 4, and a bond-valence analysis is shown in Table 5. Structure factors for malinkoite and

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR MALINKOITE

Si(1)–O(1)	1.623(3)	Si(2)–O(3)	1.629(3)	Si(3)–O(2)	1.614(3)
Si(1)–O(5)	1.624(3)	Si(2)–O(4)	1.621(2)	Si(3)–O(6)	1.620(2)
Si(1)–O(8)	1.630(3)	Si(2)–O(9)	1.625(2)	Si(3)–O(7)	1.620(2)
Si(1)–O(12)	1.622(2)	Si(2)–O(10)	1.611(2)	Si(3)–O(11)	1.633(3)
<Si(1)–O>	1.625	<Si(2)–O>	1.622	<Si(3)–O>	1.622
O(1)–Si(1)–O(5)	108.9(1)	O(3)–Si(2)–O(4)	109.7(1)	O(2)–Si(3)–O(6)	111.2(1)
O(1)–Si(1)–O(8)	111.3(1)	O(3)–Si(2)–O(9)	108.5(1)	O(2)–Si(3)–O(7)	111.0(1)
O(1)–Si(1)–O(12)	109.6(1)	O(3)–Si(2)–O(10)	110.7(1)	O(2)–Si(3)–O(11)	108.5(1)
O(5)–Si(1)–O(8)	107.3(1)	O(4)–Si(2)–O(9)	111.1(1)	O(6)–Si(3)–O(7)	107.7(1)
O(5)–Si(1)–O(12)	111.3(1)	O(4)–Si(2)–O(10)	107.2(1)	O(6)–Si(3)–O(11)	105.8(1)
O(8)–Si(1)–O(12)	108.4(1)	O(9)–Si(2)–O(10)	109.7(1)	O(7)–Si(3)–O(11)	112.5(1)
<O–Si(1)–O>	109.5	<O–Si(2)–O>	109.5	<O–Si(3)–O>	109.5
B(1)–O(1)	1.496(4)	B(2)–O(2)	1.490(4)	B(3)–O(3)	1.463(4)
B(1)–O(7)	1.475(4)	B(2)–O(4)	1.468(4)	B(3)–O(5)	1.453(4)
B(1)–O(10)	1.462(4)	B(2)–O(6)	1.469(4)	B(3)–O(8)	1.502(4)
B(1)–O(11)	1.471(4)	B(2)–O(9)	1.478(4)	B(3)–O(12)	1.473(4)
<B(1)–O>	1.476	<B(2)–O>	1.476	<B(3)–O>	1.473
O(1)–B(1)–O(7)	110.0(3)	O(2)–B(2)–O(4)	111.4(2)	O(3)–B(3)–O(5)	111.6(2)
O(1)–B(1)–O(10)	109.1(2)	O(2)–B(2)–O(6)	108.3(2)	O(3)–B(3)–O(8)	108.2(2)
O(1)–B(1)–O(11)	108.5(3)	O(2)–B(2)–O(9)	109.2(3)	O(3)–B(3)–O(12)	112.1(3)
O(7)–B(1)–O(10)	111.3(3)	O(4)–B(2)–O(6)	111.3(3)	O(5)–B(3)–O(8)	106.4(2)
O(7)–B(1)–O(11)	109.7(2)	O(4)–B(2)–O(9)	109.0(2)	O(5)–B(3)–O(12)	110.1(3)
O(10)–B(1)–O(11)	108.0(2)	O(6)–B(2)–O(9)	107.6(2)	O(8)–B(3)–O(12)	108.2(2)
<O–B(1)–O>	109.4	<O–B(2)–O>	109.5	<O–B(3)–O>	109.4
Na(1)–O(5) x3	2.561(3)	Na(2)–O(1)	2.441(3)	Na(3)–O(6) x3	2.678(2)
Na(1)–O(5)′ x3	2.657(3)	Na(2)–O(2)	2.441(2)	Na(3)–O(9) x3	2.651(4)
Na(1)–O(8) x3	2.660(2)	Na(2)–O(3)	2.618(3)	Na(3)–O(11) x3	2.546(4)
<Na(1)–O>	2.626	Na(2)–O(4)	2.308(2)	<Na(3)–O>	2.625
		Na(2)–O(7)	2.497(2)		
		Na(2)–O(8)	2.316(2)		
		<Na(2)–O>	2.436		
Na(4)–O(9) x3	2.573(4)	Na(5)–O(1)	2.539(3)		
Na(4)–O(10) x3	2.680(2)	Na(5)–O(2)	2.584(2)		
Na(4)–O(11) x3	2.675(4)	Na(5)–O(3)	2.306(3)		
<Na(4)–O>	2.643	Na(5)–O(6)	2.257(2)		
		Na(5)–O(10)	2.394(2)		
		Na(5)–O(12)	2.317(2)		
		<Na(5)–O>	2.400		
Framework angles					
Si(1)–O(1)–B(1)	128.0(2)	Si(1)–O(5)–B(3)	131.5(2)	Si(2)–O(9)–B(2)	132.6(2)
Si(3)–O(2)–B(2)	139.6(2)	Si(3)–O(6)–B(2)	141.0(2)	Si(2)–O(10)–B(1)	138.4(2)
Si(2)–O(3)–B(3)	129.2(2)	Si(3)–O(7)–B(1)	128.3(2)	Si(3)–O(11)–B(1)	130.0(2)
Si(2)–O(4)–B(2)	128.9(2)	Si(1)–O(8)–B(3)	139.2(2)	Si(1)–O12–B(3)	126.5(2)

THE CRYSTAL STRUCTURE OF MALINKOITE

Coordination of the cations

There are three unique *Si* sites in the structure of malinkoite, each occupied by Si and surrounded by four O atoms in a tetrahedral arrangement. The Si–O dis-tances vary from 1.611 to 1.633 Å, with <Si–O> distances of 1.625, 1.622 and 1.622 Å, respectively. There is only insignificant variation of the O–Si–O angles (Table 4), indicating relatively regular SiO_4 tetrahedra. There is no evidence for any substitution of Si by B. There are three unique *B* sites, each occupied by B and surrounded by four O atoms in a tetrahedral arrangement. The B–O distances vary from 1.453 to 1.502 Å, with <B–O> distances of 1.476, 1.476 and 1.473 Å, respectively. There is no evidence for any substitution of B by Si.

TABLE 5. BOND-VALENCE TABLE FOR MALINKOITE

	Si(1)	Si(2)	Si(3)	B(1)	B(2)	B(3)	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	Σ
O(1)	1.00			0.71				0.18			0.14	2.03
O(2)			1.03		0.73			0.18			0.12	2.06
O(3)		0.96				0.78		0.11			0.26	2.11
O(4)		1.01			0.77			0.26				2.04
O(5)	1.00					0.80	$0.13^{\times 3}\downarrow$ $0.10^{\times 3}\downarrow$					2.03
O(6)			1.01		0.77				$0.09^{\times 3}\downarrow$		0.29	2.16
O(7)			1.01	0.75				0.15				1.91
O(8)	0.98					0.70	$0.10^{\times 3}\downarrow$	0.25				2.03
O(9)		1.00			0.75				$0.10^{\times 3}\downarrow$	$0.12^{\times 3}\downarrow$		1.97
O(10)		1.04		0.78						$0.09^{\times 3}\downarrow$	0.20	2.11
O(11)			0.98	0.76					$0.13^{\times 3}\downarrow$	$0.09^{\times 3}\downarrow$		1.96
O(12)	1.01					0.76					0.27	2.04
Σ	3.99	4.01	4.03	3.00	3.02	3.04	0.99	1.13	0.96	0.90	1.28	

Bond-valences curves (*vu*) from Brown & Altermatt (1985)

There are five unique *Na* sites, each completely occupied by Na but with somewhat diverse coordinations. The *Na*(2) and *Na*(5) sites are each surrounded by six O atoms in an octahedral arrangement, with <Na–O> distances of 2.444 and 2.400 Å, respectively. The *Na*(1), *Na*(3) and *Na*(4) sites are each surrounded by nine O atoms in a tri-augmented trigonal antiprismatic arrangement (point symmetry 3), and the <Na–O> distances are 2.626, 2.630 and 2.643 Å, respectively. All O atoms link to one Si cation and one B cation (Table 5). Most O atoms further link to two Na cations; O(4), O(7) and O(12) link to one Na cation. However, all bond-valence sums incident at the O atoms lie within 0.16 *vu* (valence units) of the ideal value of 2 *vu* (Table 5).

Structure topology

In the crystal structure of malinkoite, six distinct tetrahedra are linked to form a borosilicate framework consisting of six-membered rings of alternating (SiO_4) and (BO_4) tetrahedra (Fig. 1a). It is convenient to describe the configuration of the rings according to the sequences of up (*U*) and down (*D*) linkages of the constituent tetrahedra (Smith 1978). In malinkoite, there are two distinct types of six-membered rings: *UDUDUD* and *UUDUDD* in the ratio 1:2. The *UDUDUD* rings are characteristic for the high-tridymite-like topology of kalsilite, $KAlSiO_4$ (Perrota & Smith 1965). The *UUDUDD* rings occur in beryllonite, $NaBePO_4$ (Golovastikov 1961, Giuseppetti & Tadini 1973). These rings are stacked along the *c* axis and link *via* the O(6), O(8) and O(10) atoms (Fig. 1b). The Si–O–B framework angles, corresponding to linkage of rings along the *c* axis, vary from 138.4 to 141.0º (Table 4). There is different tilting of tetrahedra within the two types of rings. The *UDUDUD* rings are more regular and more open than the *UUDUDD* rings. The *Si*(1)–O(8)–*B*(3)

angle involves linkage between *UDUDUD* rings, and the *Si*(1)–O(8)–*B*(3) angle of 139.2° is close to the angle of 139° characteristic for unstrained bonds in framework silicates (Liebau 1985).

Linkage within a ring can be illustrated conveniently by splitting the framework into two infinite layers (Figs. 2a, b). In a ring of each type, there are six Si–O–B angles. The *UDUDUD* ring has point symmetry 3, and thus has two unique Si–O–B linkages: *Si*(1)–O(5)–*B*(3) and *Si*(1)–O(12)–*B*(3). The *UUDUDD* rings have six unique Si–O–B linkages. Thus there are nine unique Si–O–B linkages in one layer. The average Si–O–B angle is 130.5°, and there is only one angle, *Si*(3)–O(2)–*B*(2) = 139.6°, that deviates significantly from the mean value.

There are two types of channel that extend along the *c* axis: (1) stacking of *UUDUDD* rings produces small cages that contain Na in [6]-coordination; (2) stacking of *UDUDUD* rings produces large cages that contain Na in [9]-coordination. In accord with the ratio of 2:1 for the two types of rings, there are twelve octahedrally coordinated Na polyhedra and six [9]-coordinated Na polyhedra per unit cell in malinkoite. Tri-augmented antiprisms link *via* shared faces to form columns along [001]. Pairs of octahedra share a common face to form dimers. Figure 3a shows the arrangement of Na polyhedra in the crystal structure of malinkoite. Dimers of octahedra are attached to the columns of tri-augmented antiprisms through common O(6), O(8) and O(10) anions that serve as bridging O atoms for linkage of tetrahedra along the *c* axis (Fig. 3b).

COMPARISON OF MALINKOITE
WITH BERYLLONITE, $NaBePO_4$

Smith (1978) discussed the general relations among these types of framework silicate minerals. Here, we focus on the very close relation between malinkoite,
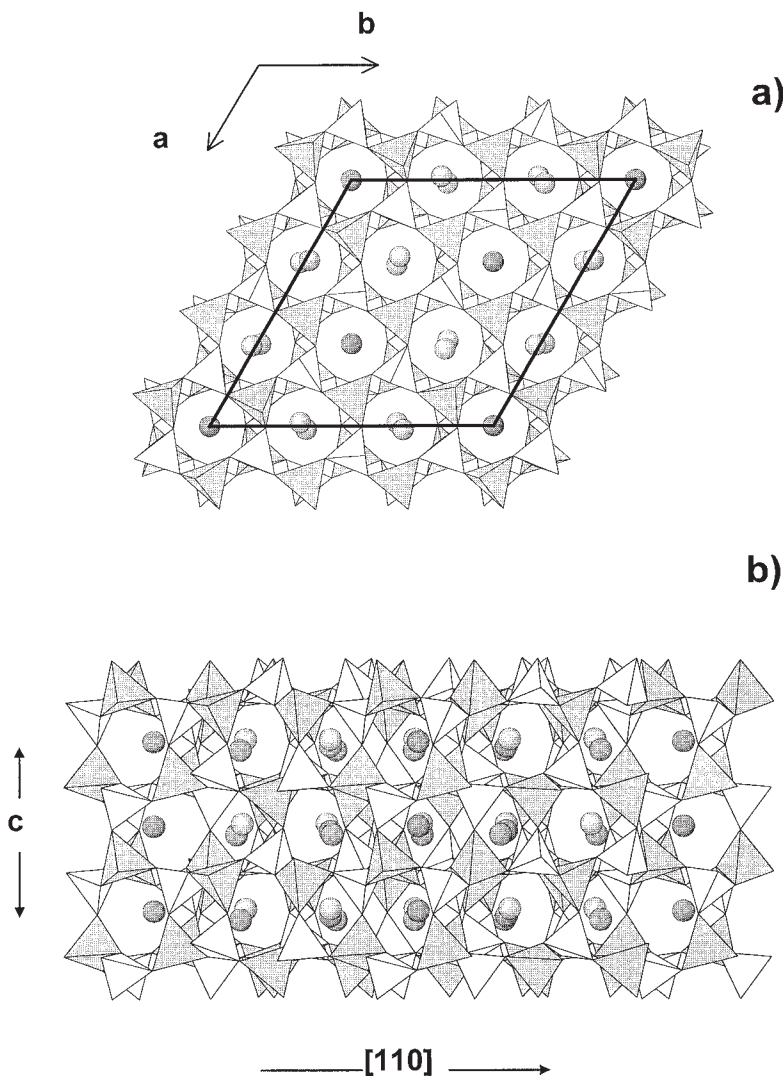
FIG. 1.   The crystal structure of malinkoite: (a) viewed down [001]; (b) projected along
[1$\bar{1}$0]; (SiO$_4$) tetrahedra are grey, (BO$_4$) tetrahedra are white, Na atoms are shown as
spheres.

NaBSiO$_4$, and beryllonite, NaBePO$_4$. Beryllonite is monoclinic, $P2_1/n$, a 8.178(3), b 7.818(2), c 14.114(6) Å, β 90.00(0)°, Z = 12 (Giuseppetti & Tadini 1973). The crystal structure of beryllonite is built of the same six-membered rings as malinkoite: *UDUDUD* and *UUDUDD* in a ratio of 1:2. In both malinkoite and beryllonite, the frameworks have a total negative charge of 9$^-$ per pair of tetrahedra: {(BeO$_4$)$^{6-}$ + (PO$_4$)$^{3-}$}$^{9-}$ in beryllonite and {(SiO$_4$)$^{4-}$ + (BO$_4$)$^{5-}$}$^{9-}$ in malinkoite. The coordination of Na in beryllonite is the same as that

in malinkoite. The ratio of tri-augmented antiprisms to octahedra per unit cell is 1:2, and the linkage of these polyhedra is similar in both structures.

The different topology of the two structures results from different linkage of the six-membered rings. In the structure of beryllonite, the tilting of tetrahedra within the *UDUDUD* rings is different from that in the structure of malinkoite. In malinkoite, tetrahedra of the same type within the *UDUDUD* rings are facing up and down within the same layer (Figs. 1a, 2a, b). In beryllonite,
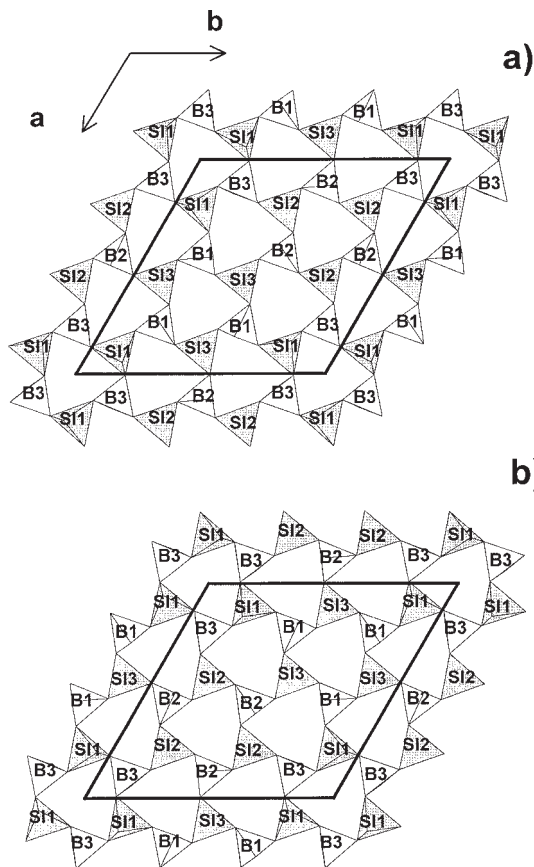
FIG. 2. The crystal structure of malinkoite: layers of (SiO$_4$) and (BO$_4$) tetrahedra at (a) $z \approx 0.54$, and (b) $z \approx 0.83$.
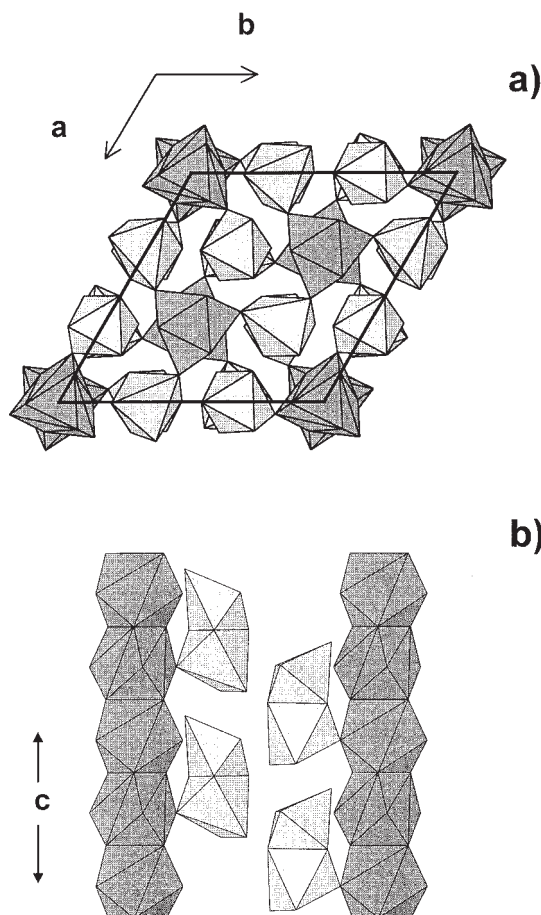

FIG. 3. Linkage of (NaO$_n$) polyhedra in the crystal structure of malinkoite: (a) projected down [001]; (b) viewed perpendicular to c, showing pairs of octahedra linked to columns of tri-augmented antiprisms.

tetrahedra of the same type within the *UDUDUD* rings are all facing the same way: within the same layer, they facing either up or down (Fig. 4), but never both. Linkage of two *UUDUDD* rings along [100] in malinkoite and [001] in beryllonite is identical.

The sequence of one *UDUDUD* and two *UUDUDD* rings accounts for the close values of a_{mal} = 13.8964(4) and c_{ber} = 14.114(6) Å. Linkage of the two types of rings perpendicular to a layer is identical in both structures. Two pairs of rings linked through bridging O atoms along [001] give rise to the similarity of the other two cell dimensions: c_{mal} = 7.7001(2), b_{ber} = 7.818(2) Å. Linkage of the two types of rings within a layer is different in each structure. The arrangement of the *UDUDUD* rings within a layer is identical in both structures: the rings link along [100] and [010] in malinkoite, and along [100] and [110] in beryllonite, in both cases through a common vertex. However, the arrangement of *UUDUDD* rings is different in malinkoite and beryllonite. There are two different orientations of the

UUDUDD rings: clockwise and anticlockwise. In the structure of malinkoite, clockwise and anticlockwise *UUDUDD* rings alternate along [100] and [010], forming a zig-zag chain (Fig. 5a). In the structure of beryllonite, analogue zig-zag chains extending along [100] are formed either by clockwise, or by anticlockwise, *UUDUDD* rings (Fig. 5b). The different linkages of six-membered rings within a layer result in a different topology for each framework, and consequently, different symmetries for malinkoite (hexagonal) and beryllonite (monoclinic).

THE STRUCTURE TOPOLOGY OF LISITSYNITE

In the crystal structure of lisitsynite [KBSi$_2$O$_6$, a 9.96304(4), b 10.4348(4), c 4.7044(2) Å, V 489.08(5)
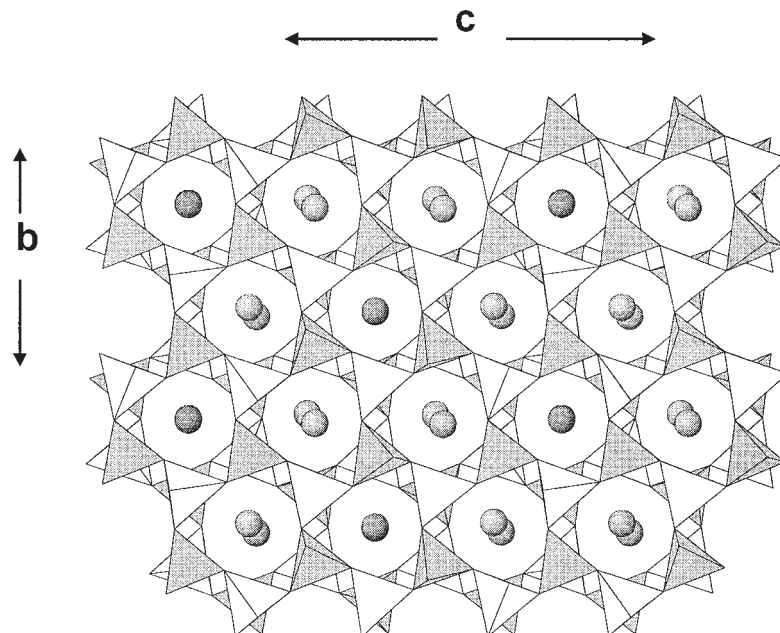
FIG. 4.   The crystal structure of beryllonite projected onto the (100) plane; (PO$_4$) tetrahe-
dra are grey, (BeO$_4$) tetrahedra are white, and Na atoms are shown as spheres.
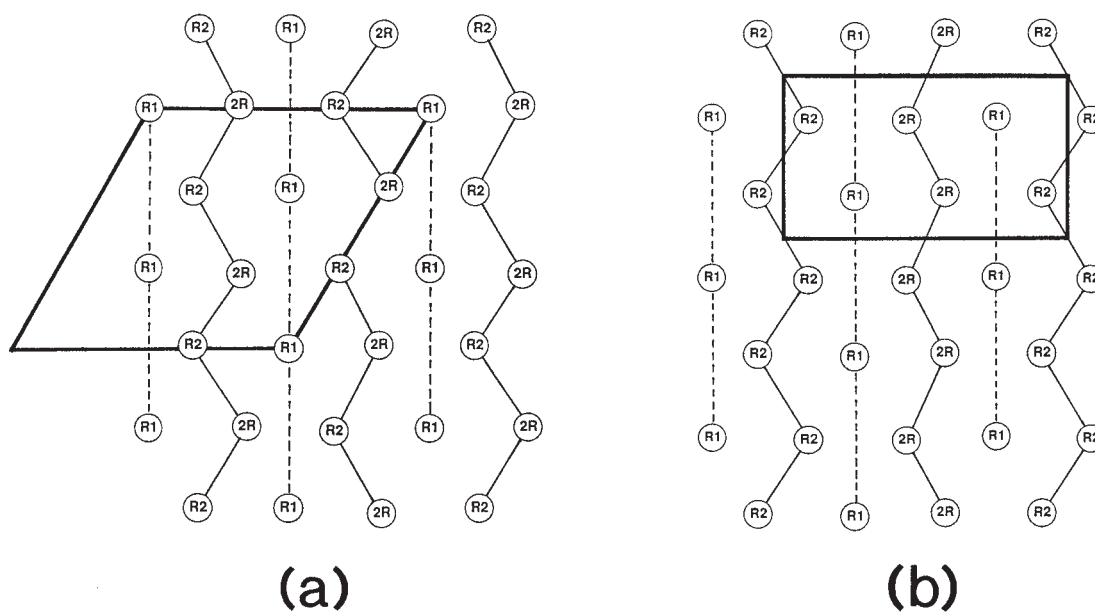

FIG. 5.   The arrangement of six-membered *T*-rings of two types: R1 (*UDUDUD*) and R2 (*UUDUDD*) in the crystal structures of
(a) malinkoite and (b) beryllonite; the symbols R2 and 2R correspond to clockwise and anticlockwise orientations of the
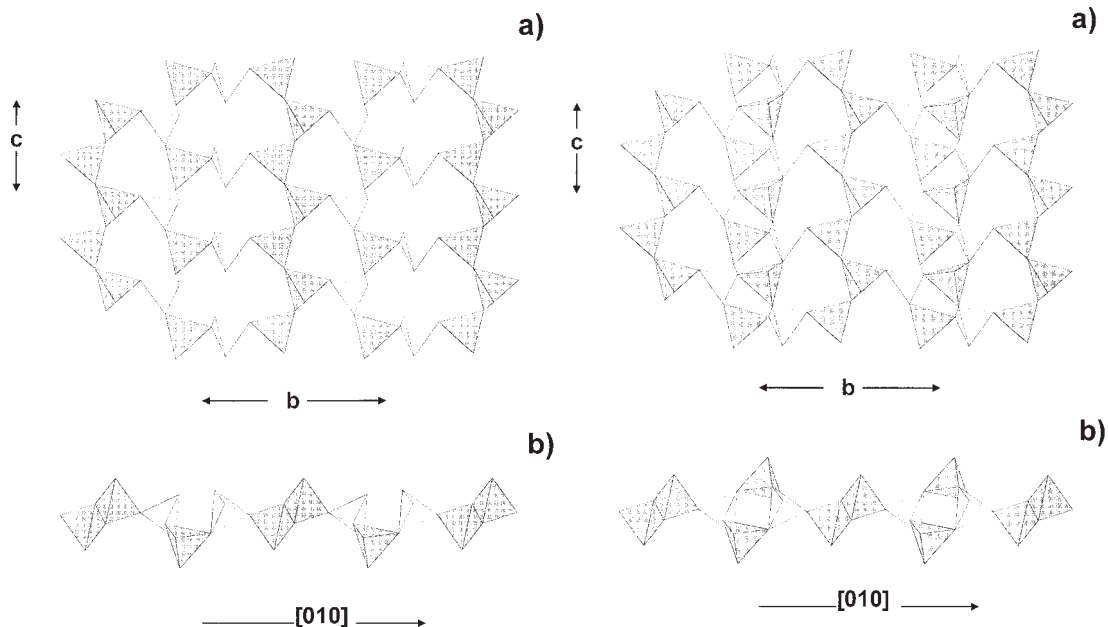*UUDUDD* rings, respectively.

a)

b)

FIG. 6. A fragment of the crystal structure of lisitsynite: sheet of tetrahedra consisting of six-membered (4Si + 2B) and eight-membered (5Si + 3B) rings: (a) projected onto (100); (b) viewed down [001]; (SiO$_4$) tetrahedra are grey, (BO$_4$) tetrahedra are white.
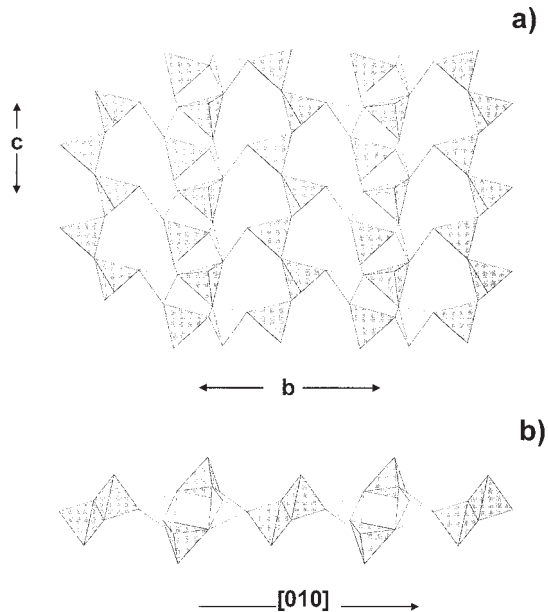
a)

b)
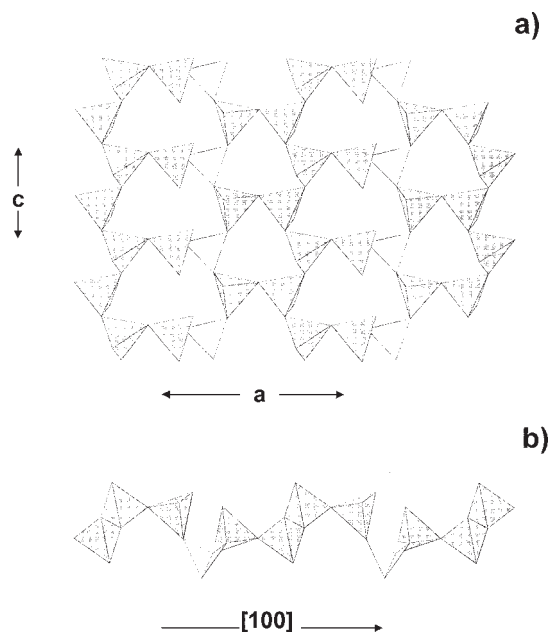
FIG. 7. A fragment of the crystal structure of lisitsynite: a sheet of tetrahedra consisting of six-membered (5Si + B) and eight-membered (6Si + 2B) rings: (a) projected onto (010); (b) viewed down [001]; legend as for Figure 6.

a)

b)

FIG. 8. A fragment of the crystal structure of lisitsynite: a sheet of four-membered and six-membered rings: (a) projected onto (100); (b) viewed down [001]; legend as for Figure 6.

Å^3, $P2_12_12_1$, $Z = 4$, D = 2.745 g cm^{-3}, Sokolova *et al.* 2000], the main building units of the borosilicate framework are four-, six- and eight-membered rings of alternating (SiO$_4$) and (BO$_4$) tetrahedra. Four-membered rings are formed by alternating (SiO$_4$) and (BO$_4$) tetrahedra, and have four Si–O–B linkages. There are two types of both six-membered and eight-membered rings in the structure of lisitsynite (Figs. 6, 7). There are six-membered rings, consisting of four (SiO$_4$) and two (BO$_4$) tetrahedra, [(4Si + 2B) rings], and eight-membered rings, consisting of five (SiO$_4$) and three (BO$_4$) tetrahedra [(5Si + 3B) rings]. Linkage of (4Si + 2B) and (5Si + 3B) rings produces a continuous sheet of tetrahedra parallel to (100) (Fig. 6). Within this sheet, (SiO$_4$) tetrahedra share common vertices to form a pyroxene-like [Si$_2$O$_6$]$^{4-}$ chain along [001].

Six-membered (5Si + B) rings, consisting of five (SiO$_4$) and one (BO$_4$) tetrahedra, and eight-membered (6Si + 2B) rings of six (SiO$_4$) and two (BO$_4$) tetrahedra, form another sheet parallel to (010) (Fig. 7a). In this sheet, a pyroxene-like chain of (SiO$_4$) tetrahedra can be also traced along [001]. Linkage of this chain with adjacent tetrahedra is different for each type of sheet. In the (100) sheet, (SiO$_4$) tetrahedra share common vertices with (BO$_4$) tetrahedra; in the (010) plane, they share vertices directly with other (SiO$_4$) tetrahedra (Figs. 7a, b). Thus, for this type of sheet, the ratio Si:B is 4:1.

FIG. 10. The crystal structure of lisitsynite projected onto (001): (SiO$_4$) tetrahedra are grey, (BO$_4$) tetrahedra are white, K atoms are shown as grey spheres.
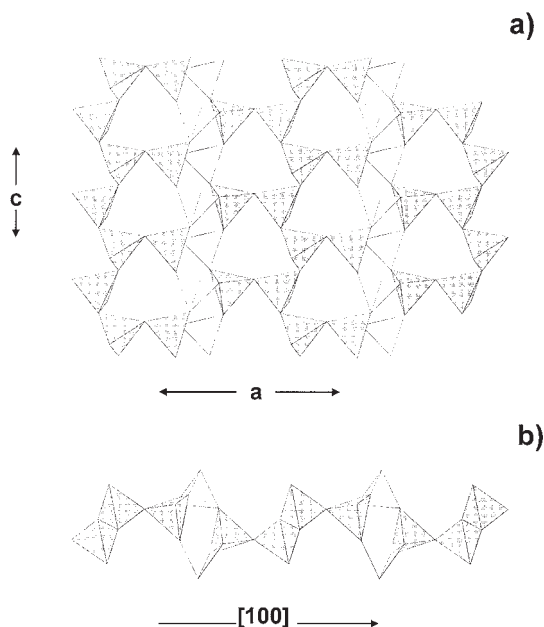

FIG. 9. A fragment of the crystal structure of lisitsynite: a sheet of four-membered and six-membered rings: (a) projected onto (010); (b) viewed down [001]; legend as for Figure 6.

The (100) sheet can be described as combination of zig-zag chains of four-membered rings and pyroxene-like chains extending along [001] (Figs. 8a, 9a) and linked *via* bridging oxygen atoms (Fig. 8b). The (010) sheet shows the same zig-zag and pyroxene-like chains (Fig. 9).

In the three-dimensional borosilicate framework (Fig. 10), there are one-dimensional channels that extend along the *c* axis. The channels are, in cross-section, seven-membered rings of tetrahedra and host K atoms with a coordination number of ten. As noted above, no trace of H$_2$O or (OH) was found in the channels of the lisitsynite structure.

The translation of the pyroxene-like chain along [001] defines the value of the *c* cell-dimension: 4.7044(2) Å. This translation is similar to the dimension of a four-membered ring along [001]. Despite the similar character of the (100) and (010) sheets, the difference in the *a* and *b* cell-dimensions results from different tilting of (SiO$_4$) and (BO$_4$) tetrahedra in each sheet. For the (100) sheet, <*T–T–T*> angles along [010] are ≥113°; for the (010) sheet, <*T–T–T*> angles along [100] are ≤113° (Figs. 6b, 7b). Thus the twisting of tetrahedra along [100] is more pronounced than along [010], and results in a smaller cell-dimension: *a* 9.9630(4) *versus b* 10.4348(4) Å.
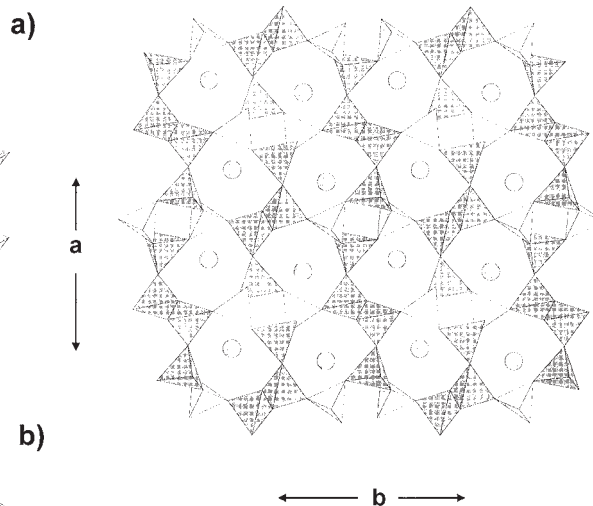
Related compounds

Lisitsynite, KBSi$_2$O$_6$, and synthetic "boroleucite", K[BSi$_2$O$_6$] = K[(Si$_2$B)O$_6$], *a* 12.618(4) Å, *I*43*d*, *Z* = 16) (Mikloš *et al*. 1992), have four- and six-membered rings of tetrahedra as main building-units, and the frameworks are topologically different. In synthetic "boroleucite", B and Si are randomly distributed over one unique tetrahedrally coordinated site (Si$_{0.67}$B$_{0.33}$). Lisitsynite and synthetic "boroleucite" may be regarded as polymorphs with different degrees of order of Si–B.

Lisitsynite and synthetic Li-A(BW) zeolite {Li[AlSiO$_4$] •H$_2$O, *a* 10.313(1), *b* 8.194(1), *c* 4.993(1) Å, *Pna*2$_1$, *Z* = 4; [Kerr (1974), Krogh Andersen & Ploug-Sørensen (1986)} have similar cell-dimensions and identical main building-units: four-, six- and eight-membered rings of tetrahedra and the same type of puckered-ladder arrangement of four-membered rings. However, because of the different connectivity of the rings, the topologies of lisitsynite and Li-A(BW) are different. The similarity of the shortest cell-dimension (corresponding to the one-dimensional channels in both structures), *c*$_{Li-A(BW)}$ 4.993(1), *c*$_{lis}$ 4.7044(2) Å, results from similar size of zig-zag chains extending along [001].

Prior to the discovery of lisitsynite, two zeolites, Li-A(BW) and bikitaite, LiAlSi$_2$O$_6$•H$_2$O (Kocman *et al*. 1974), had the highest framework-densities [the number of tetrahedrally coordinated *T* cations per 1000 Å^3] reported for zeolites: 20.2 for bikitaite and 19.0 for A(BW). The high framework-density of these materials is partly due to the fact that they are Li compounds. For

the novel zeolite, lisitsynite, the framework density is 24.5. The high value of the framework density may be explained by absence of H_2O and relatively small size of the channels.

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