

Crystal structure of KBSi_3O_8 isostructural with danburite

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Abstract

The crystal structure of KBSi_3O_8 (orthorhombic, *Pnam*, with $a = 8.683(1)$, $b = 9.253(1)$, $c = 8.272(1)$ Å, $V = 664.4(1)$ Å³, $Z = 4$) has been determined by the direct method applied to 3-dimensional reflection data. The structure of a microcrystal with the dimensions $20 \times 29 \times 37$ µm was refined to an unweighted residual of $R = 0.031$ using 386 non-zero structure amplitudes. KBSi_3O_8 adopts a structure essentially different from reedmergnerite NaBSi_3O_8 , with the low albite ($\text{NaAlSi}_3\text{O}_8$) structure, and isotypic with danburite $\text{CaB}_2\text{Si}_2\text{O}_8$ which has the same topology as paracelsian $\text{BaAl}_2\text{Si}_2\text{O}_8$. The chemical relationship between this sample and danburite gives insight into a new coupled substitution; $\text{K}^+ + \text{Si}^{4+} = \text{Ca}^{2+} + \text{B}^{3+}$ in the extraframework and tetrahedral sites. The present occupancy refinement revealed partial disordering of B and Si atoms which jointly reside in two kinds of general equivalent points, $T(1)$ and $T(2)$ sites. Thus the expanded crystal-chemical formula can be written in the form $\text{K}(\text{B}_{0.44}\text{Si}_{0.56})_2(\text{B}_{0.06}\text{Si}_{0.94})_2\text{O}_8$.

The systematic trend among crystalline compounds with the $M^+T^{3+}T^{4+}_3\text{O}_8$ formula suggests that they exist in one of four structural types; the feldspar structures with T^{3+}/T^{4+} ordered and/or disordered forms, and the paracelsian and the hollandite structures.

KEYWORDS: danburite, crystal structure, feldspar, paracelsian, hollandite, reedmergnerite.

Introduction

THE intracrystalline cation partitioning in feldspars has attracted considerable attention in recent years (Henderson, 1986; Smith and Brown, 1988; Kimata, 1988). Among the minor cation constituents in natural feldspars, field occurrences of B^{3+} indicate its widespread distribution and heterogeneity. The latter had been highlighted by the discovery of reedmergnerite NaBSi_3O_8 from various occurrences (Milton *et al.*, 1960; Dusmatov *et al.*, 1967; Khomyakov *et al.*, 1979). The polymerisation of Ca and B cations within silicates dictates the formation of danburite and datolite. Playing a structural role, however, is each coordination state of K and B cations; the former is much the larger cation than the latter with the smallest ionic radius except for H^+ .

Research on synthesising KBSi_3O_8 hydrothermally (Eugster and McIver, 1959) showed that it melts incongruently to quartz + glass, but its mineralogical properties have not been published until now. Without adducing sufficient evidence, however, their study abstracted that an orthorhombic feldspar, structurally similar to danbur-

ite, was synthesised on the join NaBSi_3O_8 – KBSi_3O_8 . Hydrothermal syntheses of the series KAlSi_3O_8 – KBSi_3O_8 (Martin, 1971) showed incomplete substitution of B for Al in K-feldspar structures.

A major focus of the present work is to evaluate the behaviour of B^{3+} cation in the structure of as-synthesized KBSi_3O_8 microcrystals by X-ray diffraction, using Raman and IR spectroscopic data, and to assess its crystal-chemical significance.

Preparation of single crystals

Single crystals of KBSi_3O_8 have been hydrothermally synthesised in a silver tube from a mixture of K_2CO_3 , H_3BO_3 and SiO_2 gel corresponding to the composition KBSi_3O_8 in a Morey-type autoclave at 430 °C, 430 kg/cm² and for 90 days. The chemical composition was determined by electron microprobe analysis (JEOL JXA-50A). Several silicates analysed, such as reedmergnerite NaBSi_3O_8 (B_2O_3 ; 14.27 wt.%), danburite $\text{CaB}_2\text{Si}_2\text{O}_8$ (27.80 wt.%), and adularia were used as probe standards of B_2O_3 , SiO_2 and K_2O . Although EPMA quantitative analysis of

boron is poor, zoning or other inhomogeneities containing K and Si cations could not be detected in the crystal. Based on the B_2O_3 concentration estimated on the assumption that the crystal is an anhydrous compound, the electron microprobe analysis yielded SiO_2 66.0, B_2O_3 15.0, K_2O 19.0, total = 100.0 wt.%. The composition computed on the basis of 32 oxygens, albeit of tolerable accuracy, gives the structural formula $K_{1.06}B_{1.13}Si_{2.85}O_8$. Inasmuch as this chemical formula indicated an analogy with feldspar, the starting composition in the structure determination was assigned to $KBSi_3O_8$ of the ideal stoichiometric type.

Refractive indices for this sample (Table 1) were measured in sodium light under the microscope, using immersion in calibrated oils (estimated error = ± 0.001). These indices are smaller than $n(\alpha)$ 1.554 and $n(\gamma)$ 1.573(1) of reedmergerite (Milton *et al.*, 1960). Application of the advanced Galdstone-Dale rule (Mandarin, 1981) to the idealised $KBSi_3O_8$ results in the mean calculated index, $\langle n \rangle = 1.5417$, which is in good agreement with the mean observed value 1.542.

Contribution of IR and Raman spectra to the structure determination

Prior to the structure determination by X-ray diffraction, IR and Raman spectra of this crystal were examined in order to elicit some topochemical information relating to the crystal structure in question.

For determination of the coordination number of boron in this silicate, measurements of the IR spectra by the KBr pellet technique were made with a Hitachi Infra-red Spectrophotometer type

260-30. The infrared spectrophotometer tracing for the sample $KBSi_3O_8$ is shown in Fig. 1, together with the spectra of danburite and reedmergerite. The $KBSi_3O_8$ sample has no absorption band around 1350 cm^{-1} which is assigned to BO_3 stretching vibration (Nakamoto, 1986). From comparison with the spectrum of tourmaline with 3-coordinated boron, it has been concluded that silicates with tetrahedrally-coordinated boron have a few broad bands between 800 and 1000 cm^{-1} (Farmer, 1972). Consequently the boron contained in the crystal in question can be characterised as surrounded by four oxygens.

Raman spectra of three alkali borosilicates are shown in Fig. 2. The analytical conditions for Raman microprobe with a multichannel detector (Japan Spectroscopic Co. Ltd., NR-1000) involved excitation by the 514.5-nm line of an Ar^+ laser, with approximately 10-mW laser power and counting times of 500 s per point. Characteristic strong bands appear at 537 and 218 cm^{-1} in $KBSi_3O_8$ and at 614 and 260 cm^{-1} in danburite, while the spectrum of reedmergerite is obviously different from those of the above two crystals. The entire spectrum of crystalline $KBSi_3O_8$ shows some resemblance to that of danburite. The observations by IR and Raman spectroscopies demonstrate that $KBSi_3O_8$ with tetrahedrally-coordinated boron is isostructural with danburite.

Unit-cell and intensity-data collection

Three-dimensional X-ray diffraction data on a single crystal of $KBSi_3O_8$ were collected at room temperature using an automated RIGAKU four-circle diffractometer with graphite-monochromatised $Cu-K\alpha$ radiation ($\lambda = 1.54178\text{ \AA}$) at 50 kV

Table 1. Crystal and diffraction data for $KBSi_3O_8$.

K-danburite			
Formula	$KBSi_3O_8$	Refractive index	(α) 1.534 (β) 1.542 (γ) 1.549
Molar wt.	262.16		
Symmetry	orthorhombic		
S.G.	Pnam	Radiation	Rotaflex generator
a	8.683(1) \AA	Wavelength	1.54178A(CuK α)
b	9.253(1) \AA	Monochromator	graphite
c	8.272(1) \AA	μ	127.36
V	664.4(1) \AA^3	2 θ range	<120
Z	4	Observed reflections (with F>3 σ F)	386
Crystal size	20x29x37 μ m	R(unweighted)	4.0
D _{cal.}	2.620g/cm ³	R _w (weighted)	3.1
F(000)	520		

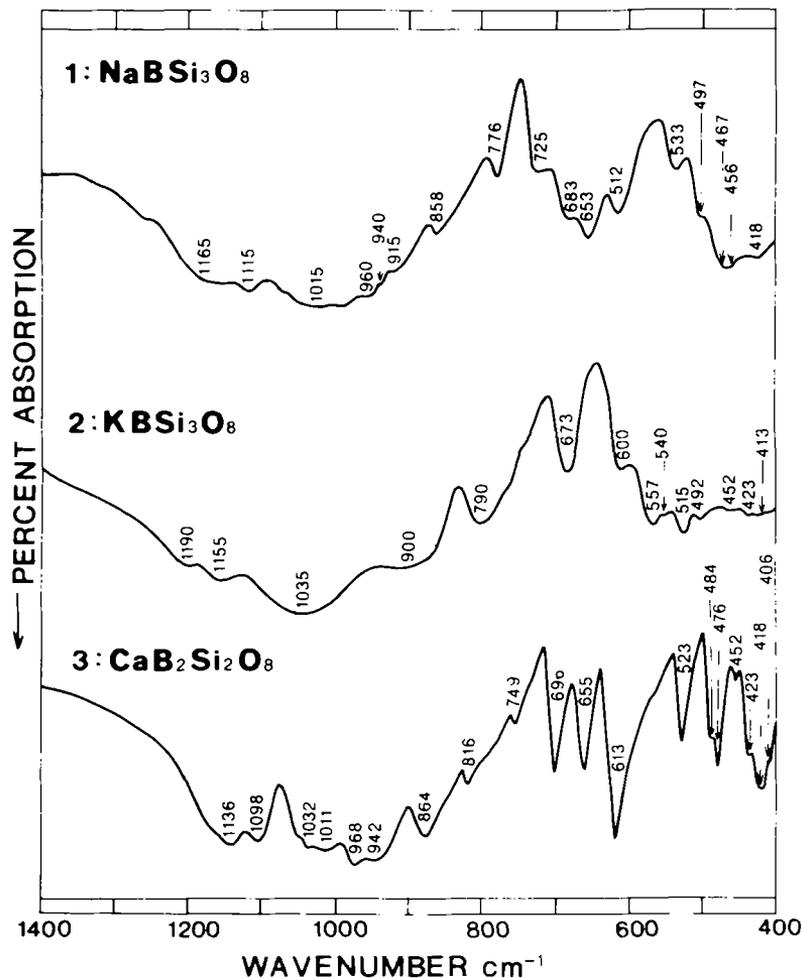


FIG. 1. Infrared absorption spectra of three borosilicate minerals; (1) reedmergnerite (NaBSi₃O₈), (2) the present sample (KBSi₃O₈), and (3) danburite (CaB₂Si₂O₈).

and 140 mA. The dimensions of the orthorhombic unit cell were determined by least-squares refinement of the diffraction angles of 25 reflections in the 2θ range of 20 to 25°. The cell parameters determined (Table 1) are contrasted with those of danburite; $a = 8.038(3)$, $b = 8.752(5)$ and $c = 7.730(3)$ Å (Phillips *et al.*, 1974). Furthermore, using a RIGAKU powder diffractometer with Ni-filtered Cu-K α radiation, the X-ray powder-diffraction pattern of this KBSi₃O₈ was measured and indexed (Table 2). A silicon internal standard was employed. Cell parameters calculated from the X-ray powder diffraction lines and from the single-crystal reflection data match well.

The intensity data were measured using the θ -

2θ scan mode ($4.6^\circ < 2\theta < 120^\circ$). Three standard peaks were measured every 50 reflections, and no significant change in their intensities was observed during data collection. The intensities were corrected for background, Lorentz and polarization effects. No absorption correction was made for the small crystal sizes. Additional experimental details are listed in Table 1.

Structure determination

The solution of the structure was begun using direct methods [the MULTAN 80 package]. Statistics produced by MULTAN indicated the structure to be centrosymmetric, thus fixing the space group as *Pnam* which is the symmetry of

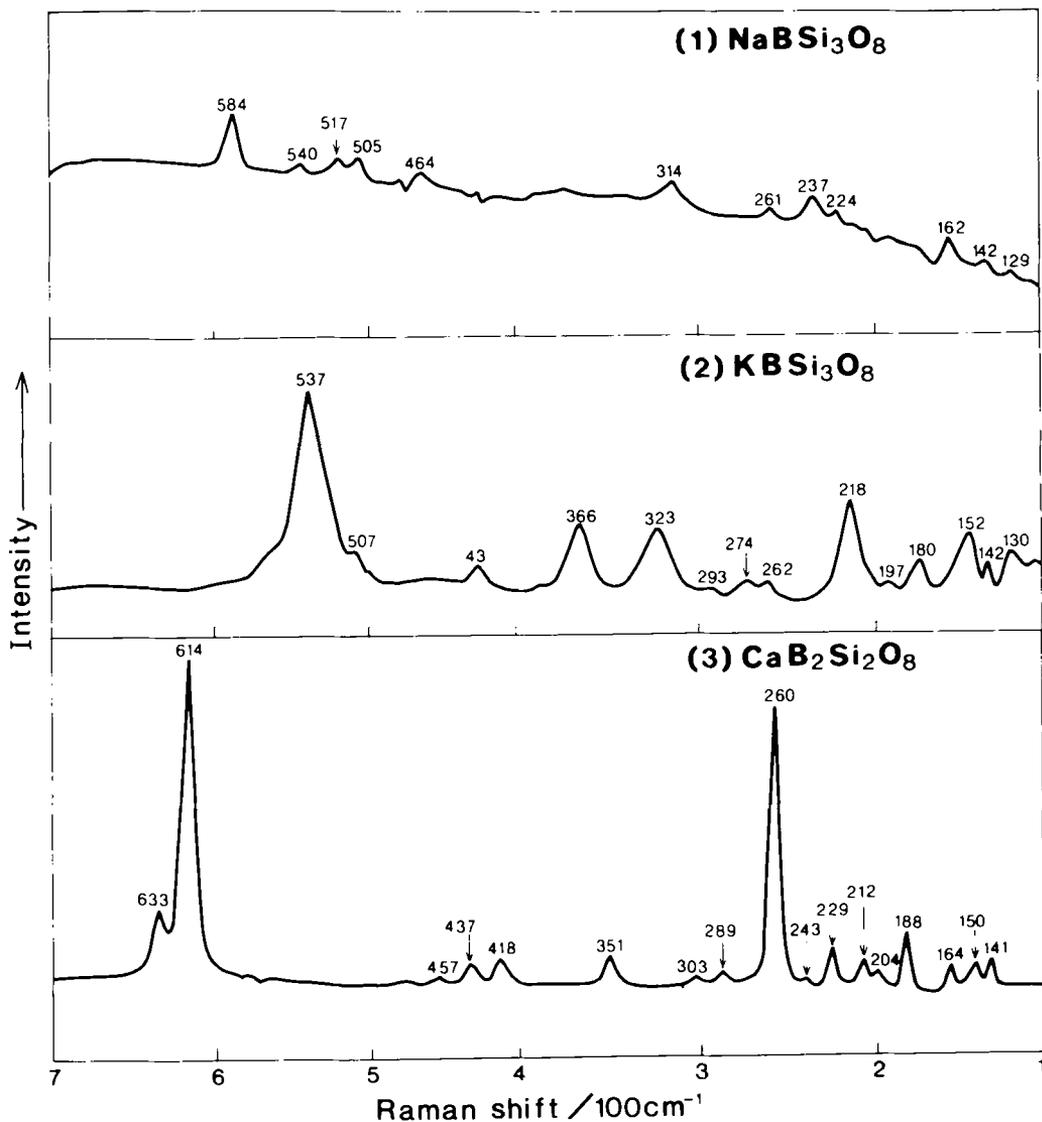


Fig. 2. Raman spectra of three borosilicate minerals: (1) reedmergnerite (NaBSi_3O_8), (2) the present sample (KBSi_3O_8), and (3) danburite ($\text{CaB}_2\text{Si}_2\text{O}_8$).

danburite. Reference of the above IR and Raman data to the present X-ray diffraction information uses the structure of danburite as a guide.

The refinements were carried out using the least-squares program RFINE2 (Finger, 1969). Scattering factors for neutral atoms with corrections for anomalous dispersion were taken from International Tables for X-ray Crystallography (1974, p. 99 and 149). The atomic parameters of danburite given by Phillips *et al.* (1974) were used

for the refinement. The composition of the crystal was constrained to the ideal stoichiometric type, KBSi_3O_8 . The final refinement cycles varied one overall scale factor, and positional and anisotropic temperature factors together with occupancy factors for $T1$ and $T2$. The fractional coordinates and anisotropic temperature coefficients are listed in Table 3. Thermal ellipsoids and interatomic angles are listed in Tables 4 and 5, respectively.

Table 2. X-ray powder diffraction data for synthetic KBSi_3O_8 .

hkl	d_{obs} (Å)	d_{calc} (Å)*	Int.	hkl	d_{obs} (Å)	d_{calc} (Å)*	Int.
110	6.330	6.330	17	040	2.313	2.313	9
111	5.030	5.028	7	312	2.298	2.297	5
020	4.627	4.626	5	123	2.288	2.286	6
200	4.343	4.340	2	140	2.235	2.235	2
002	4.137	4.138	25	232	2.150	2.148	4
120	4.080	4.082	17	330	2.110	2.110	22
210	3.931	3.929	22	223	2.080	2.079	7
201	3.844	3.843	56	004	2.069	2.069	5
121	3.661	3.661	25	240	2.043	2.045	6
211	3.548	3.549	14	241	1.982	1.982	1
112	3.462	3.463	22	420	1.965	1.964	1
220	3.161	3.165	100	313	1.951	1.951	2
022	3.081	3.084	6	421	1.911	1.911	1
202	2.992	2.995	4	332	1.880	1.880	1
130	2.901	2.906	37	323	1.833	1.833	2
031	2.890	2.890	25	150	1.809	1.809	7
212	2.846	2.849	13	422	1.774	1.775	8
131	2.739	2.747	4	431	1.735	1.735	2
013	2.642	2.643	4	403	1.704	1.705	3
311	2.620	2.619	13	333	1.676	1.676	6
113	2.529	2.529	11	342	1.655	1.656	4
222	2.514	2.514	13	423	1.600	1.600	4
320	2.454	2.453	19	350	1.559	1.559	2
132	2.379	2.378	1	205	1.546	1.546	5
203	2.329	2.328	7				

Note: $\text{CuK}\alpha$ radiation.* Refined cell parameters: $a = 8.679(2)$, $b = 9.252(2)$,
 $c = 8.275(1)$ Å.Table 3. Positional parameters and temperature factors for KBSi_3O_8 .

Atom	Positional parameters			$B(\text{Å}^2)$
	x	y	z	
K	0.4002(3)	0.0760(3)	0.25	1.71
T1	0.2818(3)	0.4071(3)	0.4231(3)	1.09
T2	0.0759(2)	0.1916(2)	-0.0662(2)	0.91
O1	0.1998(5)	0.0667(4)	-0.0288(5)	1.28
O2	0.1528(5)	0.3457(5)	-0.0373(5)	1.17
O3	0.4302(5)	0.3215(5)	0.0535(5)	1.28
O4	0.4847(7)	0.6796(7)	0.25	1.00
O5	0.2224(7)	0.3863(7)	0.25	1.47

Atom	Anisotropic temperature factors ($\times 10^4$)					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	54(4)	48(4)	68(3)	-4(3)	0	0
T1	38(5)	30(5)	40(4)	4(4)	1(4)	12(4)
T2	33(3)	30(3)	26(2)	3(3)	1(3)	5(2)
O1	48(7)	23(7)	58(7)	-8(6)	-11(6)	2(6)
O2	30(7)	44(7)	40(7)	2(6)	-16(6)	-1(6)
O3	47(7)	48(7)	28(6)	0(6)	-7(6)	6(6)
O4	26(10)	47(10)	21(9)	7(10)	0	0
O5	23(11)	55(12)	66(11)	-17(9)	0	0

Results and discussion of the structure

A conventional polyhedral diagram for the structure of KBSi_3O_8 is shown by projecting it along the a -axis, as shown in Fig. 3. The KBSi_3O_8 borosilicate features a framework consisting of $(\text{B},\text{Si})_2\text{O}_7$ and Si_2O_7 tetrahedra alternated with Ca in an irregular coordination polyhedron, which is different from the crystal structure of reedmergnerite NaBSi_3O_8 (Appleman and Clark, 1965). KBSi_3O_8 can be identified as crystal-chemically isotypic with danburite $\text{CaB}_2\text{Si}_2\text{O}_8$ (Phillips *et al.*, 1974), belonging to the paracelsian groups. The structural trend that crystalline compounds with the $M^+T^{3+}T^{2+}_3\text{O}_8$ formula can form with the paracelsian structure has been

emphasised by structure refinement of the present KBSi_3O_8 in a single crystal. Moreover the K cation occupying the extra-framework site of the former structure is the largest alkali cation already observed in a borosilicate (Povarennykh, 1972; Liebau, 1985; Wells, 1984) in reference to $\text{Ba}(1)-\text{O}$, 2.911 Å, in silicoborate mineral, garrelsite, $\text{Ba}_3\text{NaSi}_2\text{B}_7\text{O}_{16}(\text{OH})_4$ (Ghose *et al.*, 1976).

The coordination number of Ca in danburite was considered by Lindbloom *et al.* (1974). It was found by following their illustration that a 7-fold coordination model for the K cation in KBSi_3O_8 is inconsistent with several minerals of similar structure types. Table 6 shows that an 8-fold coordination model for the K atom can be electrostatically defined based on consideration of bond strength (Brown, 1981). This definition implies that eight nearest-neighbouring oxygens control both the magnitude of the apparent 'thermal' vibration parameter and the variation of K-O bond-lengths.

Significance of the present KBSi_3O_8 phase

$\text{CaB}_2\text{Si}_2\text{O}_8$ (danburite) and KBSi_3O_8 have been found to be isostructural, resulting from the coupled substitution, $\text{K}^+ + \text{Si}^{4+} = \text{Ca}^{2+} + \text{B}^{3+}$, occurring when the extra-framework and tetrahedral sites are filled. The framework of danburite, however, consists of complete ordering of tetrahedral B and Si cations, while the present occupancy refinement has led to $(\text{B}_{0.44}\text{Si}_{0.559})$ for the $T(1)$ site and $(\text{B}_{0.059}\text{Si}_{0.941})$ for $T(2)$. This framework reveals partial disordering of the B and Si atoms which jointly reside in two kinds of

Table 4. Thermal ellipsoid data for KBSi_3O_8 .

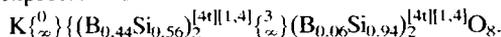
Atom	Ellipsoid axis	R.M.S. displacement (Å)	Angles to crystal axes (degrees)		
			x	y	z
K	1	0.13924(1)	44.83(7)	45.17(7)	90
	2	0.14908(1)	134.95(7)	44.95(7)	90
	3	0.16338(2)	90	90	0
T1	1	0.09341(708)	100(2)	42(1)	130(2)
	2	0.1196(4)	158(6)	84(2)	69(6)
	3	0.1359(45)	71(6)	49(1)	48(2)
T2	1	0.0907(37)	81.8(2)	113(7)	25(6)
	2	0.1103(11)	149(8)	65(10)	71.8(6)
	3	0.1195(18)	60(8)	35(3)	74(8)
O1	1	0.0944(11)	71(5)	20(7)	87(13)
	2	0.1250(35)	133(4)	74(12)	133(2)
	3	0.1647(22)	131(2)	79(6)	42.8(7)
O2	1	0.0827(6)	39.1(1)	92(6)	51.0(4)
	2	0.1334(56)	58(7)	121(24)	133(15)
	3	0.1407(50)	70(9)	31(23)	112(21)
O3	1	0.0940(39)	76(2)	100(10)	17(4)
	2	0.1360(9)	161(1)	105(6)	78(5)
	3	0.1458(34)	102(4)	18(10)	77(10)
O4	1	0.08559(1)	90	90	0
	2	0.09687(1)	165.91(1)	75.91(1)	90
	3	0.14534(2)	75.91(1)	14.09(1)	90
O5	1	0.07911(1)	21.30	68.70	90
	2	0.15168(2)	90	90	180
	3	0.16252(2)	111.30	21.30	90

Table 5. Interatomic distances and angles in KBSi_3O_8 .

T-O distances (Å)	O-O distances (Å)	O-T-O angles (°)
T1-O1 1.538(5)	O1-O2 2.474(6)	105.4(3)
O2 1.571(5)	O1-O3 2.542(6)	112.2(3)
O3 1.525(5)	O1-O5 2.567(6)	113.4(3)
O5 1.534(4)	O2-O3 2.532(6)	109.8(3)
mean 1.542	O2-O5 2.480(5)	106.0(3)
	O3-O5 2.501(6)	109.7(3)
T2-O1 1.609(5)	O1-O2 2.614(6)	109.5(2)
O2 1.592(5)	O1-O3 2.649(6)	110.7(2)
O3 1.611(5)	O1-O4 2.646(6)	110.5(3)
O4 1.612(3)	O2-O3 2.587(6)	107.7(2)
mean 1.606	O2-O4 2.624(6)	109.9(3)
	O3-O4 2.617(4)	108.6(3)
K-O distances (Å)	[Mult.]	T-O-T angles (°)
K-O1 2.890(4)	[2]	T1-O1-T2 135.2(3)
O2 2.802(5)	[2]	T1-O2-T2 135.5(3)
O3 2.805(5)	[2]	T1-O3-T2 141.3(3)
O5 2.819(7)	[1]	T2-O4-T2 141.1(4)
O5 3.260(7)	[1]	T1-O5-T1 137.9(2)
		mean 138.2
O2 3.314(4)	[2]	

general equivalent points, $T(1)$ and $T(2)$. For reedmergnerite, KBSi_3O_8 (Appleman and Clark, 1965), complete order was demonstrated on the basis of both its occupancy refinement and the mean distance of 1.465 Å in a tetrahedral site corresponding to boron, and that of 1.615 Å in other tetrahedral sites corresponding to silicon. Because Si is expected to occupy the $T(2)$ site, the mean distance of 1.606(4) Å for $T(2)$ must indicate a significant topochemical contribution that changes the size of the $T(1)$ and $T(2)$ sites. The mean T-O distances for the $T(1)$ and $T(2)$ sites, 1.542(5) and 1.606(4) Å respectively, indicate 0.487 B and 0.060 B, respectively, inter-

olated from the 1.465–1.615 linear relation. These calculated values are reliably consistent with the refined occupancies, $\text{B}_{0.441}\text{Si}_{0.559}$ for the $T(1)$ site and $\text{B}_{0.059}\text{Si}_{0.941}$ for the $T(2)$ site. Since the refined values attain the charge-balance to maintain stability of the structure, the expanded crystal-chemical formula can be written in the form $\text{K}(\text{B}_{0.44}\text{Si}_{0.56})_2(\text{B}_{0.06}\text{Si}_{0.94})_2\text{O}_8$. Following the Nomenclature of inorganic structure types (Lima-de-Faria *et al.*, 1990), the above formula is expressed as



The present KBSi_3O_8 species is the second borosilicate with the B/Si disordering; cf. synthetic reedmergnerite NaBSi_3O_8 (Kimata, 1977, and Mason, 1980). However, inferring a substitutional scheme for B incorporation is premature for some silicates (Grew *et al.*, 1991); it seems that only a few of the stereochemically possible compounds are able to simultaneously carry both K cations of a larger ionic radius and B ones of the smallest except for H^+ . The connection between their structures and paragenesis, remain as yet unanswered questions, but combination of these atoms seems to dictate saline or evaporitic environments.

The differences between the paracelsian and feldspar structures arise from the manner in which the double-crankshaft chains are cross-linked to generate the three-dimensional frameworks (Smith and Brown, 1988). Therefore crystal chemical properties of cations constituting

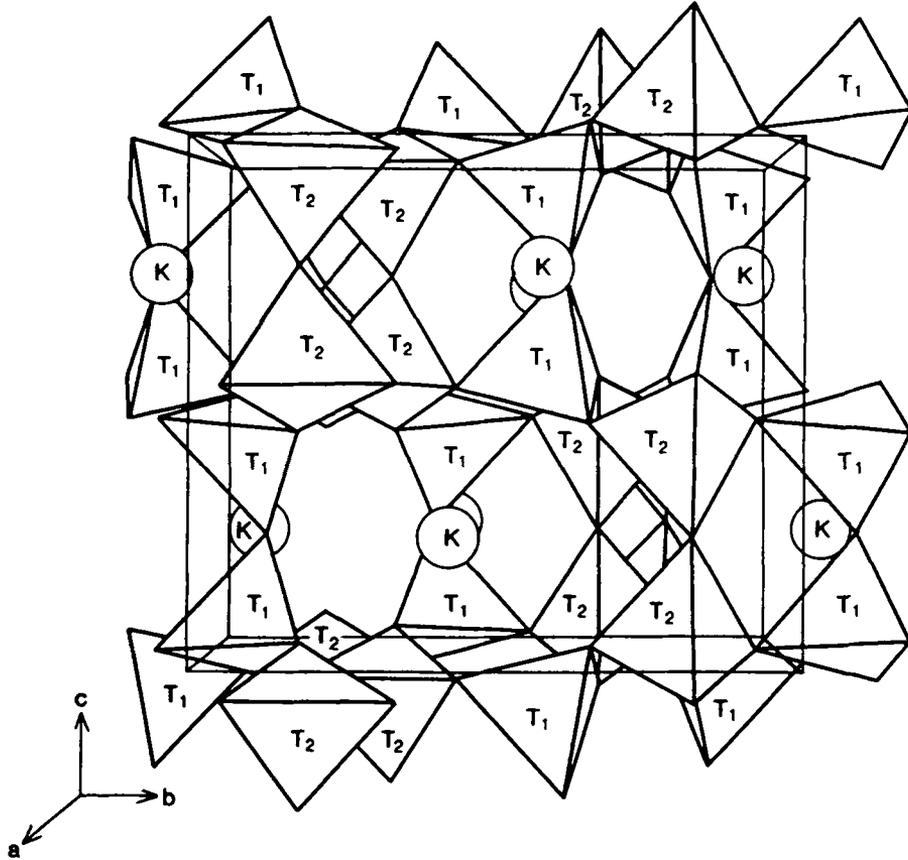


Fig. 3. A conventional polyhedral diagram for the structure of KBSi_3O_8 depicted by projecting it along a axis.

Table 6. Examination of coordination number of K cation in KBSi_3O_8 .

Mineral	M-cation	CN*	Bond valence**
KBSi_3O_8	K	7	0.971
		8	1.009
$\text{CaB}_2\text{Si}_2\text{O}_8$	Ca	7	1.779
		9	1.947
NaBSi_3O_8	Na	7	1.022
		9	1.076

* Coordination number

** The Bond-Valence Method (Brown, 1981)

these tetrahedral frameworks furnish a key to building either structure. The chemical formula of the $M^{2+}T^{3+}_2T^{4+}_2\text{O}_8$ type is common to both the feldspar and paracelsian structures (Smith and Brown, 1988), whereas after additional consideration of albite polymorphs with Al/Si-order and -disorder a $M^+T^{3+}T^{4+}_3\text{O}_8$ formula admitted only the former. Understanding the crystal chemical

behaviour of monovalent alkali cations, coupled with structure refinement of this KBSi_3O_8 compound, does not establish critical constraints for construction of the paracelsian structure with the formula $M^+T^{3+}T^{4+}_3\text{O}_8$. Consideration of both natural occurrences and syntheses leads to the conclusion that crystalline compounds with the chemical formula $M^+T^{3+}T^{4+}_3\text{O}_8$ can form four structural types; feldspar structure with either T^{3+}/T^{4+} -order or -disorder, the paracelsian and the hollandite structures.

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[Manuscript received 10 April 1990;
revised 9 March 1992]