tion with metal ions and the transport of these ions across biological membranes. Such a model system designed to simulate various biological functions appears to be feasible. The structural results for the monomer of a cyclic peptide indicate that the proposed conformation for a cylindrical peptide can be largely achieved and that the cavities created by the stacked rings are large enough to accommodate metal ions.

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The Structures of (Sr,Ba)[(Al,Ga)₂(Si,Ge)₂O₈].
I. The Crystal Structures of the Synthetic Feldspars SrGa₂Si₂O₈ and BaGa₂Si₂O₈

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The crystal structures of the synthetic feldspars $SrGa_2Si_2O_8$ and $BaGa_2Si_2O_8$ have been found from X-ray intensities, measured on a diffractometer, and refined by Fourier and least-squares methods. Both structures are similar to that of celsian, with space group $I2/c$ and 8 formula units per cell. There is complete Ga/Si order in $SrGa_2Si_2O_8$ ($\langle Si-O \rangle = 1\cdot614$, $\langle Ga-O \rangle = 1\cdot821$ Å) and probably also in $BaGa_2Si_2O_8$, even though here the mean tetrahedral distances would at first sight suggest some disorder ($\langle Si-O \rangle = 1\cdot634$, $\langle Ga-O \rangle = 1\cdot805$ Å). The divalent cations can be considered seven-coordinated. The deviations of T–O bonds from the expected single-bond values are examined.

Introduction

Compounds of the general formula $(Sr, Ba)[(Al, Ga)_2(Si, Ge)_2O_8]$ are characterized by two principal structure types. The first is monoclinic, body-centred, and has the topology of a feldspar (Megaw, 1974a). The second is pseudo-orthorhombic, primitive, and is similar to paracelsian (Smith, 1953; Bakakin & Belov, 1961). The isopolymorphic relationships, and the Al–Ga and Si–Ge substitution in the aluminosilicates of Sr and Ba, are discussed elsewhere (Gazzoni, 1973; Calleri & Gazzoni, in preparation). The present paper describes the structures of the feldspar modification of the Sr and Ba gallosilicates, leaving the paracelsian form of $SrGa_2Si_2O_8$ to a later paper.

Structure determination

Experimental results

For the X-ray analysis use was made of crystals synthesized by Gazzoni (1973) by crystallization from the melt. The crystal class and space group were determined from Weissenberg and precession photographs: both compounds were assigned to space group $I2/c$, assuming the presence of the centre of symmetry at (000) on the analogy with other 14 Å feldspars (*cf.* Newnham & Megaw, 1960). The spots on long-exposure single-crystal photographs of the crystals used for the present investigation did not present any kind of splitting or diffusion.

The unit-cell parameters were refined by a least-

squares procedure based on an adequate number of θ values (Cu $K\alpha$ radiation). For $BaGa_2Si_2O_8$ the θ values were measured on powder spectra obtained by a focusing camera, while for $SrGa_2Si_2O_8$ they were accurately measured on the diffractometer because here the polycrystalline specimens were less homogeneous and well crystallized.

The experimental results are as follows.

(1) Strontium gallosilicate

$SrGa_2Si_2O_8$, $M=411\cdot25$, monoclinic, $a=8\cdot481$ (2), $b=13\cdot142$ (2), $c=14\cdot444$ (3) Å, $\beta=115\cdot48$ (4)°; $U=1453\cdot29$ Å^3; $D_{calc}=3\cdot76$ g cm^{-3}; $Z=8$; space group: $I2/c$; $F(000)=1536$. Crystal dimensions: $0\cdot191$, $0\cdot106$ and $0\cdot067$ mm across the opposite faces of $\{100\}$, $\{001\}$ and $\{010\}$ respectively. Linear absorption coefficient for Cu $K\alpha$ radiation, $\mu=231\cdot34$ cm^{-1}.

The intensities, on the same relative scale, were measured at room temperature with a G.E. automatic three-circle diffractometer (Cu $K\alpha$ β-filtered radiation) equipped with a Na(Tl)I scintillation counter. The θ–2θ scanning method of integration was employed with a scanning speed of $2°$ min^{-1} and increasing the integration interval with θ. The total number of reflexions explored was 1466 (within $2\theta=160°$) and they were all introduced in the analysis; the number of b-type difference reflexions (with $h+k$ odd, l odd) was 628. The observations were corrected for the Lorentz–polarization effect and for the absorption effect (Hamilton, 1966).

(2) Barium gallosilicate

$BaGa_2Si_2O_8$, $M=460\cdot98$, monoclinic, $a=8\cdot727$ (5), $b=13\cdot240$ (6), $c=14\cdot608$ (6) Å, $\beta=115\cdot00$ (6)°; $U=1530\cdot01$ Å^3; $D_{calc}=4\cdot00$ g cm^{-3}; $Z=8$; space group: $I2/c$; $F(000)=1680$. Crystal dimensions: $0\cdot130$, $0\cdot050$ and $0\cdot022$ mm across the opposite faces of $\{100\}$, $\{001\}$ and $\{010\}$ respectively. Linear absorption coefficient for Mo $K\alpha$ radiation, $\mu=129\cdot08$ cm^{-1}.

The intensities were collected at room temperature with a Philips four-circle automatic diffractometer, equipped with a graphite monochromator, using the θ–2θ step-scanning technique (Mo $K\alpha$ radiation). The integration speed was $0\cdot05°$ s^{-1} and the integration interval $1\cdot2°$. The weaker reflexions were scanned four times and the measurements were averaged. The intensities of over 2000 independent reflexions were measured (within $2\theta=30°$). After rejecting the reflexions whose amplitudes were not significantly larger than the standard deviations based on counting statistics, the number of reflexions available was 1579; the number of b-type reflexions was 648. Corrections for Lorentz–polarization and absorption effects were applied.

Initial model and refinement procedure

For the structure analysis we used the system of programs written by G. Sheldrick and included in the library of the Computing Centre of Cambridge Uni-

versity. The computation of the atomic scattering factors employed the exponential function $f(s_x)=\sum_{i=1}^{4} a_i \exp(-b_i s_x^2)+C$, where $s=\sin\theta/\lambda$; to the coefficients a_i, b_i and to the constant C were assigned the values calculated by Cromer & Waber (1965). All the atoms were considered neutral except Sr and Ba which were assumed to be doubly ionized. The correction for the anomalous dispersion of Sr,Ba,Ga and Si (Cromer, 1965) was introduced right from the beginning. The b-type reflexions were included in the F_o sets throughout the analysis.

For both structures the coordinates of celsian (Newnham & Megaw, 1960) were used as a starting model; the initial agreement between F_o and F_c's was rather poor for the strontium compound, but much better for the barium compound. The gallium atoms were assumed to be in sites T(1) ($0z00$) and T(2) (0000)* and the choice was confirmed by two subsequent Fourier syntheses, followed by a computation of bond lengths, for each structure. At this stage, with an average vibrational parameter $B=1$ Å^2, the agreement between F_o and F_c's was worse for the b-type than for the a-type reflexions. However, a few cycles refining the individual vibrational isotropic parameters greatly improved the agreement for both types of reflexions. Five cycles reduced the overall R value to $8\cdot9\%$ for $SrGa_2Si_2O_8$ and to $7\cdot9\%$ for $BaGa_2Si_2O_8$. The B values were $0\cdot4$–$0\cdot5$ Å^2 for the Ga and Si atoms and ~1 Å^2 for the divalent cations. For the oxygen atoms, in the strontium compound they ranged between $0\cdot7$ Å^2 for $O(A1)$ and $O(A2)$ and $1\cdot3$ Å^2 for $O(B)$ (0), $O(C)$ (0) and $O(D)$ (0), while in the barium compound they were higher, ranging between $1\cdot08$ Å^2 for $O(A1)$ and $O(D)$ (z) and $\sim1\cdot55$ Å^2 for $O(A2)$, $O(C)$ (0) and $O(D)$ (0). In the Fourier maps the peaks of the oxygen atoms had noticeably elliptical sections in the xz plane, and for the barium compound the gallium atoms also showed a slight ellipticity at this stage.

The anisotropic full-matrix refinement was carried out as follows. Two cycles were run refining anisotropically the gallium and silicon atoms, with all the other atoms fixed; in two subsequent cycles the divalent cations were also refined anisotropically, with $O(A1)$ and $O(A2)$ still fixed and the other oxygens allowed to refine isotropically; then all the variables were introduced in a fully anisotropic refinement. Fudge factors between $0\cdot7$ and $0\cdot5$ were used and the scale factor was always considered as a variable. Operating in this way the refinement proceeded smoothly and the few correlation matrix elements with values as high as $0\cdot55$–$0\cdot62$ were those between thermal parameters of the same atom.

The weighting scheme used in the final stage of refinement was: $10/(2A+F_o+2F_o^2/B)$. The coefficients A and B were optimized after each cycle and their

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* Use will be made throughout this paper of the notation proposed by Megaw (1955).

final values were $A=0.89$, $B=682$ for $SrGa_2Si_2O_8$; $A=17.4$, $B=814$ for $BaGa_2Si_2O_8$. Such a scheme gives a relatively high weight to the weaker reflexions (and therefore to most of the b-type reflexions); among the various kinds of weightings we tried it was that which gave the best constancy of $\langle w\Delta^2\rangle$ values when the reflections were batched in several ways.

For $BaGa_2Si_2O_8$ the refinement was pursued until the ratios of shift to e.s.d. value were less than 0.15 for all the atoms. The final R value was 4.7% ($wR=5.2\%$) for the 1463 reflexions (592 of b-type) used throughout the refinement; 116 weak reflexions had been, in fact, progressively eliminated because of their very poor agreement, and were never reintroduced.

In the final stage of the refinement of $SrGa_2Si_2O_8$ a correction was introduced for secondary extinction, since several of the strongest reflexions were clearly affected by this. In the set of programs we had been using, the secondary extinction is treated as a parameter of the Zachariasen type (cf. Zachariasen, 1968). This parameter is set equal to $200(r^*)$, where r^* is the mean domain path as defined by Larson (1970), and refined. Five final cycles in which this extinction parameter and the anisotropic parameters of all the atoms were allowed to refine together gave convergence with significant improvement in F_o/F_c agreement and in the standard deviations. The average shift to e.s.d. value

was less than 0.15. The final R value was 7.8% ($wR=8.4\%$) for all the 1466 reflexions or 5.6% ($wR=6.4\%$) excluding 107 reflexions to which zero weight had been progressively assigned because they were presumably affected by casual experimental errors. The b-type reflexions left with a weight different from zero were 574. The final value of the extinction parameter was 0.11.

Fourier syntheses were computed, at the end of the refinement, for both compounds. They showed the persistence of the ellipsoidal character of several oxygen peaks, already noticed in the course of the refinement. This was particularly apparent for $O(A1)$, $O(B)$ (0), $O(B)$ (z) and $O(D)$ (0) of $BaGa_2Si_2O_8$ and $O(B)$ (z), $O(C)$ (0), $O(C)$ (z) and $O(D)$ (0) of $SrGa_2Si_2O_8$. We had applied the test proposed by Ribbe, Megaw & Taylor (1969) for verifying whether the models with two 'half-atoms' and one anisotropic atom were distinguishable. With a separation $2d$ of 0.4–0.5 Å, the largest splittings that may be assigned here to any of the oxygen atoms, the two models are indistinguishable provided that the difference $B_{max}-B_{min}$ for an ellipsoid does not exceed ~4.5 Å^2. In our case the differences never exceed 1.6 Å^2; hence the models are indistinguishable, and the simpler model with single anisotropic atoms was therefore adopted.

Table 1. *Fractional coordinates and vibrational parameters* ($\times 10^4$) *of* $SrGa_2Si_2O_8$ *with the significant figures of the standard deviations in parentheses*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr (0000)	2668 (1)	−34 (0)	664 (1)	124 (4)	132 (4)	153 (4)	−24 (2)	54 (4)	−3 (2)
Si(1) (0000)	72 (2)	1721 (1)	1057 (1)	109 (8)	58 (9)	85 (9)	−17 (6)	38 (7)	−13 (6)
Ga(1) (0z00)	9999 (1)	1788 (1)	6193 (1)	150 (5)	55 (4)	96 (5)	−5 (3)	69 (4)	−11 (3)
Ga(2) (0000)	6943 (1)	1232 (1)	1702 (1)	140 (5)	55 (5)	89 (5)	−5 (3)	61 (4)	−4 (3)
Si(2) (0z00)	6797 (2)	1107 (1)	6712 (1)	72 (8)	41 (8)	63 (8)	6 (6)	21 (6)	−11 (6)
O(A1) (0000)	47 (5)	1244 (4)	1 (3)	112 (27)	101 (25)	144 (28)	−3 (15)	49 (23)	−14 (14)
O(A2) (0000)	5853 (8)	3 (3)	1427 (4)	219 (27)	38 (24)	147 (27)	18 (14)	93 (24)	11 (15)
O(B) (0000)	8325 (7)	1229 (4)	1014 (4)	196 (26)	165 (25)	203 (26)	−30 (19)	87 (21)	−42 (19)
O(B) (0z00)	7961 (8)	1245 (4)	6098 (4)	224 (26)	161 (25)	214 (28)	−22 (21)	112 (23)	−69 (21)
O(C) (0000)	69 (7)	2942 (4)	1137 (4)	236 (25)	147 (26)	155 (25)	−35 (19)	81 (21)	−44 (21)
O(C) (0z00)	115 (7)	3151 (4)	6308 (4)	144 (22)	83 (23)	169 (25)	−29 (18)	44 (19)	−28 (17)
O(D) (0000)	1852 (8)	1255 (4)	1906 (4)	249 (28)	166 (25)	82 (23)	−40 (17)	47 (21)	30 (20)
O(D) (0z00)	2001 (7)	1156 (4)	7060 (4)	201 (25)	160 (25)	146 (25)	−50 (20)	80 (20)	−17 (21)

Table 2. *Fractional coordinates and vibrational parameters* ($\times 10^4$) *of* $BaGa_2Si_2O_8$ *with the significant figures of the standard deviations in parentheses*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba (0000)	2807 (1)	3 (0)	653 (0)	77 (3)	194 (3)	126 (3)	−10 (2)	14 (2)	5 (2)
Si(1) (0000)	83 (2)	1809 (2)	1069 (2)	59 (9)	76 (9)	24 (8)	4 (8)	8 (7)	−29 (7)
Ga(1) (0z00)	50 (1)	1845 (1)	6188 (1)	42 (4)	78 (5)	14 (4)	−5 (4)	9 (3)	−11 (4)
Ga(2) (0000)	7071 (1)	1253 (1)	1737 (1)	45 (5)	78 (5)	23 (5)	5 (3)	2 (4)	1 (4)
Si(2) (0z00)	6954 (2)	1135 (2)	6741 (2)	56 (9)	63 (9)	39 (8)	2 (7)	11 (7)	3 (7)
O(A1) (0000)	38 (6)	1334 (4)	2 (4)	176 (34)	129 (34)	54 (28)	35 (20)	35 (20)	59 (14)
O(A2) (0000)	6151 (8)	6 (4)	1446 (4)	119 (34)	111 (34)	298 (33)	11 (15)	−3 (21)	5 (15)
O(B) (0000)	8374 (8)	1318 (5)	1078 (5)	187 (34)	259 (35)	189 (33)	−50 (21)	117 (18)	−47 (21)
O(B) (0z00)	8091 (8)	1341 (5)	6123 (5)	150 (30)	218 (29)	248 (36)	−8 (21)	126 (19)	−39 (20)
O(C) (0000)	126 (8)	3021 (6)	1155 (5)	174 (30)	175 (26)	179 (33)	−65 (18)	63 (19)	−77 (18)
O(C) (0z00)	212 (8)	3172 (6)	6332 (5)	113 (29)	202 (25)	173 (32)	8 (19)	30 (19)	−3 (18)
O(D) (0000)	1833 (8)	1327 (6)	1901 (5)	163 (31)	414 (38)	65 (29)	1 (20)	10 (17)	30 (24)
O(D) (0z00)	1950 (8)	1191 (6)	7052 (5)	116 (28)	251 (30)	38 (26)	−3 (20)	−36 (19)	16 (21)

The final parameters of the two gallosilicates are listed in Tables 1 and 2; the thermal parameters U_{ij} are the coefficients of the expression:

$$\exp \left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^* +2U_{13}hla^*c^*+2U_{12}hka^*b^*)\right].$$
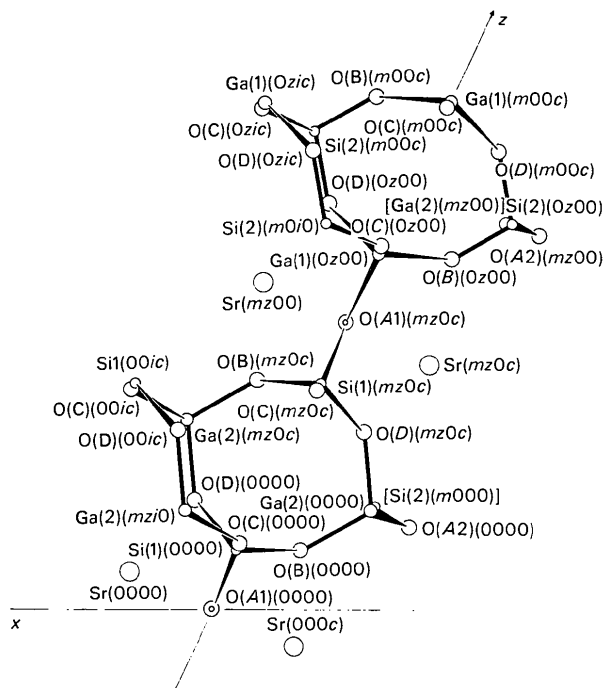
Two points may be noted about the standard deviations which were derived from full-matrix least-squares computations refining all the variables simultaneously. First, although the R value for the barium feldspar is significantly smaller than for the strontium feldspar, the standard deviations of the lighter atoms are not. The effect may be attributed to the overwhelming contribution of the heavy barium cation to the structure amplitudes, which prevents a better determination of the light-atom parameters. Furthermore, the standard deviations of the oxygen parameters are larger than those obtained from recent refinements of other feldspars (Wainwright & Starkey, 1971; Prince, Donnay & Martin, 1973; Brown, Hamilton, Prewitt & Sueno, 1974). This does not necessarily imply that our intensity measurements have been less accurate, but it may be due to the presence of the heavier atoms, Ga in place of Al and Sr or Ba in place of Ca or (Na, K), and to the procedure, found necessary in another study (Wainwright & Starkey, 1971), of subdividing the parameters for the refinement, which obviously gives underestimated standard deviations.*

Description and discussion of the structures

The tetrahedral framework

The results for the tetrahedral bond angles and distances are given in Tables 3, 4, 5 and 6. Some of the essential features of the framework of the two gallosilicates are shown in Figs. 1 and 2 which are

Fig. 1. Orthographic projection along [010] of a portion of the unit-cell content of $SrGa_2Si_2O_8$; the atoms belonging to the lower rings are distinguished by labels between square brackets.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30702 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Tetrahedral bond distances* (Å) *and angles* (°) *for* $SrGa_2Si_2O_8$

(a) Tetrahedral interatomic distances with the significant figures of the e.s.d.'s in parentheses

Si(1) (0)—O(A1) (0000)	1·642 (5)		Ga(2) (0)–O(A2) (0000)	1·819 (5)
O(B) (0000)	1·594 (6)		O(B) (0000)	1·835 (6)
O(C) (0000)	1·608 (6)		O(C) (mzi0)	1·805 (6)
O(D) (0000)	1·602 (6)		O(D) (mz0c)	1·823 (5)
Ga(1) (z)–O(A1) (mz0c)	1·851 (5)		Si(2) (z)—O(A2) (mz00)	1·631 (5)
O(B) (0z00)	1·821 (6)		O(B) (0z00)	1·596 (7)
O(C) (0z00)	1·798 (5)		O(C) (m0i0)	1·616 (6)
O(D) (0z00)	1·820 (6)		O(D) (m00c)	1·624 (6)

(b) Bond angles at tetrahedral sites (e.s.d. ≤ 0·3°)

	O(A)–O(B)	O(A)–O(C)	O(A)–O(D)	O(B)–O(C)	O(B)–O(D)	O(C)–O(D)	Mean
Si(1) (0)	99·7	116·7	101·3	112·2	115·4	110·9	109·4
Ga(1) (z)	98·0	116·5	96·0	114·2	116·5	113·2	109·1
Ga(2) (0)	105·2	99·8	104·3	113·6	114·4	117·1	109·0
Si(2) (z)	108·3	100·8	108·7	113·1	110·8	114·4	109·3

(c) Oxygen–oxygen distances in tetrahedra (e.s.d. ≤ 0·008 Å)

	O(A)–O(B)	O(A)–O(C)	O(A)–O(D)	O(B)–O(C)	O(B)–O(D)	O(C)–O(D)	Mean
Si(1) (0)	2·473	2·766	2·509	2·657	2·701	2·643	2·625
Ga(1) (z)	2·772	3·107	2·728	3·039	3·096	3·019	2·960
Ga(2) (0)	2·903	2·771	2·875	3·045	3·073	3·094	2·960
Si(2) (z)	2·616	2·501	2·645	2·680	2·650	2·722	2·636

Table 4. *Tetrahedral bond distances* (Å) *and angles* (°) *for* $BaGa_2Si_2O_8$

(a) Tetrahedral interatomic distances with the significant figures of the e.s.d.'s in parentheses

Si(1) (0)—O(A1) (000)	1·666 (6)	Ga(2) (0)-O(A2) (0000)	1·807 (6)
O(B) (0000)	1·632 (6)	O(B) (0000)	1·776 (7)
O(C) (0000)	1·609 (8)	O(C) (mzi0)	1·819 (7)
O(D) (0000)	1·628 (8)	O(D) (mz0c)	1·809 (7)
Ga(1) (z)-O(A1) (mz0c)	1·836 (6)	Si(2) (z)—O(A2) (mz00)	1·645 (6)
O(B) (0z00)	1·800 (7)	O(B) (0z00)	1·622 (7)
O(C) (0z00)	1·769 (7)	O(C) (m0i0)	1·656 (8)
O(D) (0z00)	1·822 (7)	O(D) (m00c)	1·614 (7)

(b) Bond angles at tetrahedral sites (e.s.d. ≤ 0·3°)

	O(A)-O(B)	O(A)-O(C)	O(A)-O(D)	O(B)-O(C)	O(B)-O(D)	O(C)-O(D)	Mean
Si(1) (0)	101·4	116·1	101·2	112·8	114·2	110·4	109·4
Ga(1) (z)	98·9	116·6	98·2	113·9	115·2	112·7	109·2
Ga(2) (0)	103·9	98·0	106·5	113·6	115·6	116·1	109·0
Si(2) (z)	107·6	101·0	108·6	113·0	112·4	113·5	109·4

(c) Oxygen–oxygen distances in tetrahedra (e.s.d. ≤ 0·008 Å)

	O(A)-O(B)	O(A)-O(C)	O(A)-O(D)	O(B)-O(C)	O(B)-O(D)	O(C)-O(D)	Mean
Si(1) (0)	2·552	2·779	2·546	2·700	2·737	2·658	2·662
Ga(1) (z)	2·763	3·068	2·766	2·987	3·059	2·989	2·939
Ga(2) (0)	2·820	2·736	2·897	3·014	3·034	3·079	2·930
Si(2) (x)	2·636	2·545	2·645	2·733	2·688	2·734	2·663

projections along [010] drawn to scale. The pairs of four-membered rings of tetrahedra, cross-linked through O(A2), which are nearly orthogonal to [010], would overlap in these projections; therefore, we drew the upper rings only, for clarity, labelling also, however, the positions of atoms Si(2) (m000) and Ga(2) (mz00) that belong to the lower rings of the pairs. Also, we have shown on one side only of the figures the four-membered rings, approximately orthogonal to the plane of drawing, that involve O(C) and O(D). The two compounds obviously have a very similar framework.

Table 5. *Tetrahedral means and r.m.s. values of the deviations for a tetrahedron* $\varepsilon_t(r)$

	$SrGa_2Si_2O_8$		$BaGa_2Si_2O_8$	
	Mean	$\varepsilon_t(r)$	Mean	$\varepsilon_t(r)$
Si(1) (0)	1·611 (3) Å	0·018 Å	1·634 (4) Å	0·020 Å
Ga(1) (z)	1·822 (3)	0·019	1·807 (3)	0·025
Ga(2) (0)	1·820 (3)	0·012	1·803 (3)	0·016
Si(2) (z)	1·617 (3)	0·011	1·634 (4)	0·017

Table 6. *Silicon–oxygen–gallium bond angles* (e.s.d. ≤ 0·4°)

	$SrGa_2Si_2O_8$	$BaGa_2Si_2O_8$
Si(1)-O(A1)-Ga(1)	134·8°	136·2°
Si(2)-O(A2)-Ga(2)	126·3	132·9
Si(1)-O(B)—Ga(2)	141·1	145·5
Si(2)-O(B)—Ga(1)	142·9	145·4
Si(1)-O(C)—Ga(2)	127·2	123·4
Si(2)-O(C)—Ga(1)	129·7	128·0
Si(1)-O(D) -Ga(2)	138·4	137·4
Si(2)-O(D)—Ga(2)	137·1	136·4

Inspection of Tables 3–6 and comparison with similar tables for celsian and anorthite (Newnham & Megaw, 1960; Megaw, Kempster & Radoslovich, 1962) shows a general systematic trend in the deviations of bond angles and bond lengths from the ideal in all four structures and agrees with the suggestion of Megaw *et al.* (1962) that such deviations are characteristic of the linkage scheme of the feldspar structure. The strains in tetrahedral bond angles of the present gallosilicates are, in general, larger than in celsian. The angles vary between 96 and 117° for $SrGa_2Si_2O_8$, as in anorthite, and between 98 and 116° in $BaGa_2Si_2O_8$ Nevertheless, the strains at T atoms of the same topological type show a marked similarity irrespective of the chemical type of the tetrahedral cations [*cf.* Tables 3(b) and 4(b)]. In short, the two gallosilicates have a feldspar framework in every respect.

In the structure of $SrGa_2Si_2O_8$ (*cf.* Table 5), the mean Si–O length, 1·614 (3) Å, is equal, within the e.s.d., to the value 1·615 Å, at present accepted as the pure Si–O bond length in tectosilicates and found in the fully ordered structures of reedmergnerite (Appleman & Clark, 1965) and anorthite (Wainwright & Starkey, 1971). The mean Ga–O length, 1·821 (3) Å, is close to 1·83 Å, which seems to be the value accepted for the pure Ga–O tetrahedral bond length (*cf. e.g.* Stewner & Hoppe, 1971; Cotton & Wilkinson, 1972, p. 263). Therefore the Ga/Si distribution is apparently ordered.

In $BaGa_2Si_2O_8$, on the contrary, both the mean Si–O and the mean Ga–O distances, 1·634 (4) and 1·805 (3) Å respectively, differ significantly from those for pure Si–O and Ga–O bonds. At first sight this suggests that some Ga/Si disorder exists, in spite of the appreciable difference between the radii involved.

There are, however, arguments for questioning such a conclusion. First, the temperature factors of the tetrahedral cations are small (smaller than in anorthite) and similar to each other, although the large difference in the atomic numbers of Ga and Si implies that even a limited disorder should have appreciably increased the vibrational parameters of Ga and depressed those of Si unless appropriate scattering factors had been used. Secondly, we must look critically at the assumption that tetrahedral means are strictly constant for a given T atom, varying only with the atomic composition ratio. It is now generally agreed that individual T–O bond lengths, statistically considered, are significantly dependent on the type of linkage (Si–O–Si or Si–O–Al) and also on the M cation and its coordination (cf. Phillips, Ribbe & Gibbs, 1973). Moreover, they may also show structural strain effects of different intensity in different structures or different parts of a structure (cf. Fleet, Chandrasekhar &

Megaw, 1966). Hence variations in tetrahedral means are to be expected, statistically predictable from the root-mean-square deviations of the individual bonds (for a full discussion see Megaw, Kempster & Radoslovich (1962) pp. 1022-1023). The observed variations in tetrahedral means are actually much less than those predicted, both in these structures (cf. Table 5, where the two independent Ga and Si tetrahedra in each structure are nearly identical) and in celsian (Newnham & Megaw, 1960), anorthite and bytownite. Nevertheless it seems unsafe to deduce disorder from tetrahedral mean variations of the same order of magnitude as the root-mean-square deviations of the individual bonds (cf. Table 5). This is particularly true in making comparisons between different structures. We note, for example, that in the paracelsian modification of $SrGa_2Si_2O_8$ (results to be published), while the mean Ga–O distance is 1·829 Å, the mean Si–O distance is 1·626 Å, a combination which cannot be explained by the assumption that tetrahedral means are dependent on atomic composition only.

On the strength of the arguments outlined above, the postulate of disorder in $BaGa_2Si_2O_8$ does not seem necessary.

Environment of the M cation

The distances from Sr and Ba of the oxygen atoms included in a sphere with radius 3·40 Å are recorded in Table 7.

The M–O($A2$) distances are much shorter than the rest and this effect is known to occur in all feldspars. The Ba–O($A2$) distance is even shorter than in celsian: 2·646 against 2·667 Å. The M–O(C) distances, on the contrary, are longer than the others, particularly for $SrGa_2Si_2O_8$. Considering, moreover, that O($A2$) has a shielding effect on the O(C) atoms (cf. below), we are entitled to conclude that the latter atoms do not coordinate the cation. Therefore, the coordination turns out to be sevenfold for $SrGa_2Si_2O_8$ and $BaGa_2Si_2O_8$ (Table 7), as it is for celsian (Newnham & Megaw, 1960) and for $SrAl_2Si_2O_8$ (results to be published). The oxygen atoms involved are O($A2$), the two O(B) and O(D) and two centrosymmetric O($A1$) which are in the coordination group of two M cations (see Figs. 1 and 2). It is worth noting that the same seven atoms have been selected as the coordination group in the 7 Å monoclinic feldspars (Megaw, 1974b).
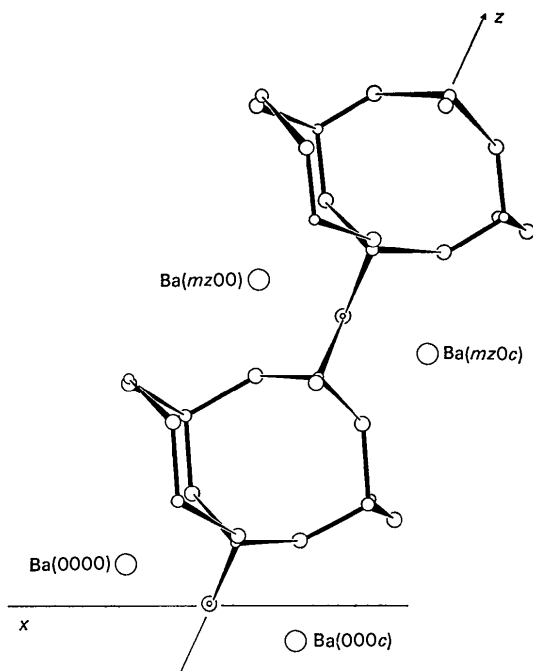

Fig. 2. Projection, as in Fig. 1, of a portion of the unit cell of $BaGa_2Si_2O_8$.

Table 7. *Environment of strontium and barium (within* 3·4 Å)

Sr(0000)–O($A1$)	(0000)	2·617 (5) Å	Ba(0000)–O($A1$)	(0000)	2·812 (5) Å
O($A1$)	(000c)	2·618 (5)	O($A1$)	(000c)	2·865 (5)
O($A2$)	(0000)	2·440 (7)	O($A2$)	(0000)	2·646 (7)
O(B)	(000c)	2·701 (6)	O(B)	(000c)	2·883 (6)
O(B)	(m00c)	2·902 (6)	O(B)	(m00c)	2·961 (8)
O(D)	(0000)	2·764 (6)	O(D)	(0000)	2·904 (7)
O(D)	(m000)	2·747 (6)	O(D)	(m000)	2·921 (7)
O(C)	(0zi0)	3·034 (6)	O(C)	(0zi0)	3·084 (8)
O(C)	(mzi0)	3·314 (6)	O(C)	(mzi0)	3·198 (8)

Fig. 3, a projection along x^*, shows the coordination around Ba; the radii have been reduced for clarity. Atoms O(B) and O(D) lie approximately on a plane; the elevation along x^* of atoms O(C) is slightly lower than that of O($A2$) (0000). A very similar packing obtains with the smaller Sr cation. The coordination polyhedron can be approximated, to use the words of Megaw *et al.* (1962), to 'a very distorted cube with one corner missing', but here the missing corner is O(C) instead of O(B) or O(D), and the corner O($A2$) is displaced to lie on the bisector of the angle between the two M–O($A1$) joins.

The atom O($A2$) has an appreciable shielding effect on atoms O(C). This can be proved by the method proposed in the Appendix to the article by Gait, Ferguson & Coish (1970), assuming for Sr and Ba ionic radii equal to 1·13 and 1·35 Å respectively, and for the oxygen atoms the radius 1·40 Å. This effect is consistent with the assumption that the oxygen atoms, and particularly O($A2$) and O($A1$), have a lone pair of electrons directed towards the M cation. The diameter of an oxygen lone pair can be estimated, with good approximation, to be 1·40 Å (*cf.* Gillespie, 1972, p. 38). From scale diagrams it is easily seen how the electron pair of O($A2$) neatly interposes between those of the O(C) atoms. The polarization effect ought to be more pronounced with the Sr ion which has a higher charge density. In fact, even though the M–O($A2$) distances are the shortest in the coordination group of all the feldspars, their values 2·440 and 2·646 Å (Table 7), are not exceptional for Sr and Ba in sevenfold coordination. Recent investigations on strontium and barium complexes and salts, showed that, when polarized oxygen atoms are involved, the Sr–O distance is commonly ~2·44 Å and the Ba–O distance ~2·64 Å [see *e.g.* Galigné (1971) and Hollander, Templeton & Zalkin (1973) for Sr in six- and sevenfold coordination, Mitsuda, Mori & Okazaki (1971) and, particularly, Dubler, Korber & Oswald (1973), for a review of Ba–O distances]. All this leaves open, of course, the question of the exact type of bonding which takes place between the O($A2$) oxygens and the M cations. The T–O($A2$)–T angles, 126·3 and 132·9° for SrGa$_2$Si$_2$O$_8$ and

BaGa$_2$Si$_2$O$_8$ respectively, are not too far from 120° and therefore it is presumable that the O($A2$) atoms are in an sp^2 hybridization state. The possibility of having covalent bonding with the large Sr and Ba cations looks however rather remote. The shortness of our M–O($A2$) distances, due to structural requirements (*cf.* Megaw, 1974a), can be better accounted for, as prompted above, by admitting an appreciable electrostatic polarization involving a lone pair of O($A2$).

The oxygen atoms O($A1$) (0000) and O($A1$) (000c) are rather far apart, 3·271 Å in the strontium compound and 3·534 Å in the barium compound. There is a gap left through which two centrosymmetric M cations face each other, but the O($A1$) atoms are the least involved in the formation of multiple bonding (see the following section) so that they have two lone pairs available which, if oriented towards the coordinated cations, produce a high electron concentration around the M–O($A1$) joins and then shield the cation–cation repulsion.

The M cations, in conclusion, appear to be situated in a rather large cavity, but they are tightly held in place by the strong electric field created by O($A1$) and O($A2$). The coordination of the two present compounds is therefore strictly similar to that described for Ba in celsian (Newnham & Megaw, 1960).

Bond length and bond character

It is now generally accepted that the T–O bonds are largely covalent and we thought it advisable to use the experimental bond distances to obtain information about the bond character. As is well known, π bonding plays an important role in determining the conformation of the tetrahedra not only in isolated silicate ions, but also tectosilicates. Experimental spectroscopic evidence actually exists which proves the presence of d–p π bonding in framework silicates and aluminosilicates (*e.g.* Brown, Gibbs & Ribbe, 1969). Several articles have been published recently describing the results obtained by applying quantitative molecular-orbital calculations, mainly of the Hückel type, to the tetrahedral frameworks of aluminosilicates (*e.g.* Gibbs, Louisnathan, Ribbe & Phillips, 1974). It has

Table 8. *Pauling n_π(T–O) bond order values*

SrGa$_2$Si$_2$O$_8$

	n_π		n_π		n_π		n_π
Si(1) (0)–O($A1$) (0000)	1·31	Ga(2) (0)–O($A2$) (0000)	1·16	Si(2) (z)–O($A2$) (mz00)	1·35	Ga(1) (z)–O($A1$) (mz0c)	1·08
O(B) (0000)	1·46	O(B) (0000)	1·13	O(B) (0z00)	1·46	O(B) (0z00)	1·15
O(C) (0000)	1·43	O(C) (mzi0)	1·20	O(C) ($m0i$0)	1·40	O(C) (0z00)	1·22
O(D) (0000)	1·44	O(D) (mz0c)	1·15	O(D) (m00c)	1·37	O(D) (0z00)	1·16

BaGa$_2$Si$_2$O$_8$

	n_π		n_π		n_π		n_π
Si(1) (0)–O($A1$) (0000)	1·26	Ga(2) (0)–O($A2$) (0000)	1·20	Si(2) (z)–O($A2$) (mz00)	1·31	Ga(1) (z)–O($A1$) (mz0c)	1·11
O(B) (0000)	1·34	O(B) (0000)	1·29	O(B) (0z00)	1·38	O(B) (0z00)	1·21
O(C) (0000)	1·43	O(C) (mzi0)	1·16	O(C) ($m0i$0)	1·30	O(C) (0z00)	1·31
O(D) (0000)	1·36	O(D) (mz0c)	1·19	O(D) (m00c)	1·40	O(D) (0z00)	1·15

been found that the T–O bond lengths are characterized by different overlap populations according to the oxygen-atom coordination and that correlations exist between the T–O, and O–T–O, angles and the population of T–O bonds, the stronger bonds tending to occur at larger angles.

In the present gallosilicates as in all the feldspars, the bond distances are significantly shorter than the expected single-bond lengths: Si–O 1·77, Ga–O 1·89 Å. These two values are derived by using for Si and Ga the covalent radii, 1·17 and 1·30 Å respectively, recommended by Gillespie (1972) and for oxygen the value 0·74 Å recommended by Pauling (1960) and then applying the Schomaker & Stevenson (1941) correction on the basis of the Pauling-type electronegativity values reported by Cotton & Wilkinson (1972, p. 215). Since the Pauling relationships based on the single-multiple bond resonance theory permit a satisfactory estimation of the per cent π-bond character, they will be applied here to the T–O bonds (Pauling, 1952, 1960). It is interesting to note that Louisnathan & Gibbs (1972) found a strong correlation between Pauling n_π(Si–O) bond order and the bond overlap population n(Si–O), calculated with Si(spd) basis sets.

The n_π(T–O) values calculated for $SrGa_2Si_2O_8$ and $BaGa_2Si_2O_8$ are recorded in Table 8. It is quite evident that the larger Ga atoms are less inclined than the Si atoms to form multiple bonds, as expected, although in $BaGa_2Si_8$ the difference between the Si and Ga tetrahedra is less marked. On average, the Si–O bonds present $\sim$40% π-bond character and the Ga–O bonds $\sim$20%. The differences between the individual bonds of the several columns of Table 8 are not very large, except for the T–O(A1) bonds. The heteropolar character of the bonds should maintain a net positive charge on the tetrahedral cations.
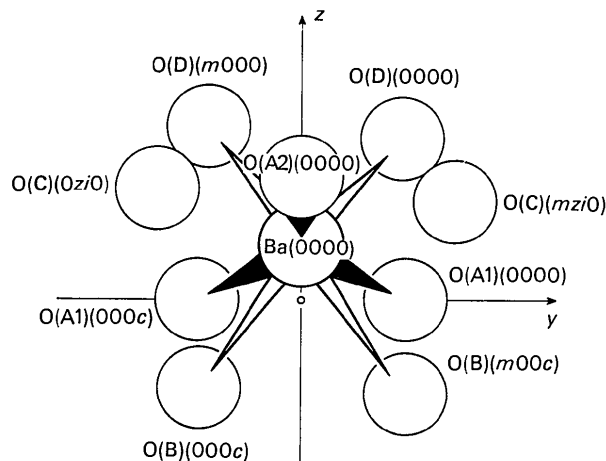
The T–O(A1) bonds present the smallest degree of π-bond order in both gallosilicates and this agrees with the fact that the O(A1) atoms coordinate two N cations. In view of the strong coordination exerted by the O(A2) atoms, we might expect that the relative n_π values would be next in increasing order of magnitude, but this prediction holds only approximately. The T–O(C) bonds, on the contrary, should present the highest n_π values, since the O(C) atoms are in the coordination group of neither compounds. This requirement is fulfilled only on average. The general trend of the n_π values is comparable with that found for the bond overlap populations of anorthite (Gibbs et al., 1974), considering, of course, those O(C) atoms that are not involved in the coordination of Ca. It has to be remembered that the dependence of the T–O lengths on the coordination number of oxygen had been pointed out previously by Megaw et al. (1962) (see also Fleet et al., 1966).

If the relation between the n_π(T–O) values of Table 8 and the T–O–T angles of Table 6 is examined by plotting n_π(T–O) against $-1/\cos$ (T–O–T), a linear trend is revealed, as predicted by molecular-orbital calculations (e.g. Gibbs et al. 1974) but the T–O(C)–T angles behave anomalously. These angles are closely similar, $\sim$130°, in all the feldspars, and are not the largest as they should be here. The system of strains and stresses necessary for the stability of the feldspar framework (Megaw et al., 1962) evidently prevails over the repulsion due to a 'concentration' of electrons along the T–O(C) bonds.

The study of the trend of the n_π values versus the O–T–O angles made it possible to ascertain the presence of an overall positive correlation also between these two quantities, both for the Si and Ga tetrahedra, but with the very large scatter of points which seems characteristic of this distribution (Gibbs et al., 1974).

We also calculated the bond-order values for celsian and for $SrAl_2Si_2O_8$. The comparison of the four sets of values indicates that the multiple-bond character decreases in the sense Si–O > Al–O > Ga–O, but that the difference between the Si and Al, or Ga, tetrahedra is certainly less accentuated in the two Ba feldspars. The availability of atoms O(A1) and O(A2) for multiple-bond formation is greater with the Ba compounds. Also, the smaller charge density of Ba, with respect to Sr, seems to affect the framework in the sense that the strains and stresses are less marked in $BaGa_2Si_2O_8$ and celsian [see Tables 3(b) and 4(b) and Newnham & Megaw, (1960)]. These differences are, however, only possibly significant.

Fig. 3. Projection along x^* of the arrangement of atoms around Ba in $BaGa_2Si_2O_8$, with radii reduced for clarity. The oxygen atoms of the coordination group are connected to the barium ion.

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