The Structures of (Sr,Ba)[(Al,Ga)₂(Si,Ge)₂O₈].
IV. The Crystal Structure of the Synthetic Feldspar BaGa₂Ge₂O₈

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The structure of the feldspar modification of $BaGa_2Ge_2O_8$ has been found from diffractometer intensities and refined by Fourier and least-squares methods. The structure is similar to that of celsian: space group $I2/c$, $Z=8$. The mean values for the four independent tetrahedra of the asymmetric unit are: $\langle Ge(1)\ (0)-O\rangle = 1\cdot74$, $\langle Ge(2)\ (z)-O\rangle = 1\cdot74$, $\langle Ga(1)\ (z)-O\rangle = 1\cdot81$, $\langle Ga(2)\ (0)-O\rangle = 1\cdot82$ Å. These figures are compatible with the postulate of nearly complete Ga/Ge order. The strains in the tetrahedral bond angles are very marked, the angles varying between 96 and 118°. The Ba ion can be considered seven-coordinated. The influence of different T and M cations on the framework of the 14 Å monoclinic feldspars is examined.

Introduction

The structural investigation of the feldspar form of $BaGa_2Ge_2O_8$ has been performed as part of a programme of research on the phases of compounds with the general formula $(Sr, Ba)[(Al, Ga)_2(Si, Ge)_2O_8]$. The present modification is metastable and was obtained only by cooling of the melt (Gazzoni, 1973); the structure of the stable, paracelsian-like, modification was described in part III of this series (Calleri & Gazzoni, 1976).

The structures of a few 14 Å monoclinic feldspars are known: synthetic $SrAl_2Si_2O_8$ (Chiari, Calleri, Bruno & Ribbe, 1975); synthetic $SrGa_2Si_2O_8$ and $BaGa_2Si_2O_8$ (Calleri & Gazzoni, 1975a); synthetic $BaGa_2Ge_2O_8$ (present work); natural celsian, $BaAl_2Si_2O_8$ (Newnham & Megaw, 1960). We intend therefore to compare some dimensional features of these compounds, as has been done for three paracelsian modifications (Calleri & Gazzoni, 1976), looking for a correlation with the dimensions of the cations.

Structure determination

Experimental results

Weissenberg and precession photographs showed only 'a-type' ($h+k$ even, l even) and 'b-type' ($h+k$ odd, l odd) reflexions and permitted the assignment of space group $I2/c$, assuming the presence of a centre of inversion at (000) by analogy with other 14 Å feldspars (for example see Newnham & Megaw, 1960). The cell parameters were refined by least squares from θ values measured on powder spectra taken with a focusing camera (Cu $K\alpha$ radiation).

The results are: $BaGa_2Ge_2O_8$, $M = 549\cdot98$, monoclinic, $a = 8\cdot896$ (6), $b = 13\cdot528$ (6), $c = 14\cdot906$ (6) Å, $\beta = 114\cdot87$ (6)°; $U = 1627\cdot5$ Å³; $D_c = 4\cdot49$ g cm⁻³; $Z = 8$; space group $I2/c$; $F(000) = 1968$. Crystal dimensions: $0\cdot160$ mm across the opposite faces of {100}, $0\cdot055$ mm across the opposite faces of {010}, $0\cdot115$ mm between (001) and (10$\bar{4}$); μ(Mo $K\alpha$) = 195·5 cm⁻¹.

The intensities accessible to Mo $K\alpha$ radiation, within $2\theta = 60°$, were collected at room temperature with a Philips four-circle diffractometer, equipped with a graphite monochromator, by the θ–2θ step-scanning technique. The integration speed was $0\cdot025°$ s⁻¹ and the integration interval $1\cdot5°$; 1405 reflexions, out of 2164 explored, had $I \geq 2\sigma(I)$ and were included in the analysis; there were 420 b-type reflexions. The weaker reflexions were scanned four times and the measurements were averaged. The reflexions with $I \geq 4\sigma(I)$ were measured also with the ω step-scanning technique: integration speed $0\cdot05°$ s⁻¹, integration interval $2\cdot0°$. The number of reflexions was in this case 810, 164 of which were b-type. The amplitudes obtained from the two sets of intensities were averaged for the final stages of the refinement, after correction for absorption (Hamilton, 1966).

Starting model and refinement

For the initial stage of the analysis use was made of the 810 reflexions with $I \geq 4\sigma(I)$. The coordinates of celsian (Newnham & Megaw, 1960) were used as a starting model, assuming the Ga atoms to be in sites T(1) (z) and T(2) (0), according to the Megaw (1955) notation. The initial R was 0·31 which reduced to 0·05 after two Fourier syntheses and a few full-matrix least-squares cycles with all the atoms, except Ba, isotropic. All the atoms were considered neutral

except Ba which was assumed to be doubly ionized. The scattering factors were those of Cromer & Mann (1968) with an anomalous dispersion correction for Ba, Ga and Ge. The B values were 0·55 and 0·65 Å² for Ga and Ge respectively; for the O atoms they ranged between 1·2 for the O(B) atoms and 1·75 Å² for O($A2$) and O(D) (z); the equivalent B for Ba was 1 Å². In the Fourier maps the peaks showed the expected relative heights and a modest elliptical character in the xz plane.

For the anisotropic refinement use was made of all 1405 reflexions with $I \geq 2\sigma(I)$. The full-matrix anisotropic refinement was carried out as in part I (Calleri & Gazzoni, 1975a). No correction for secondary extinction was required. The weighting scheme was ($|F_o|$ on absolute scale) $60/(A|F_o|^2 + B|F_o| + C)$; the coefficients were finally: $A = 0·0070$, $B = 1·00$, $C = 60·00$.

At convergence R was 0·068 ($wR = 0·078$) for the 1343 reflexions (397 of b-type) used throughout the analysis; 62 reflexions were progressively given zero weight because of poor agreement (total $R = 0·072$). The final R is relatively high, but in order to have a fairly large number of b-type reflexions we had to introduce all the reflexions with intensity just above background.

The fractional coordinates and vibrational parameters are given in Table 1; the latter parameters are the coefficients of the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.*

It may be noted that the Ba cation is displaced very little out of the mirror plane of the 'average structure', with $C2/m$ symmetry, here, in celsian and in BaGa₂Si₂O₈ (Newnham & Megaw, 1960; Calleri & Gazzoni, 1975a); larger shifts were found for the smaller Sr cation in SrGa₂Si₂O₈ and SrAl₂Si₂O₈ (Calleri & Gazzoni, 1975a; Chiari et al., 1975).

The root-mean-square displacements along the ellipsoid axes are given in Table 2 with the angles that these axes make with the cell axes. The thermal mo-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31795 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

tion is not very marked, but the anisotropy is appreciable and greater than for the gallosilicates of Sr and Ba. The ellipsoids of the cations have their longest axis parallel to one of the cell axes as in the paracelsian modification of BaGa₂Ge₂O₈ (Calleri & Gazzoni, 1976).

R after the full anisotropic refinement is higher than that based on the 810 strongest reflexions; the standard

Table 2. *Parameters characterizing the vibrational ellipsoids referred to their own principal axes*

	Axis	R.m.s.d. (Å)	α_{ix}	α_{iy}	α_{iz}
Ba	1	0·130	132°	86°	17°
	2	0·185	87	4	94
	3	0·073	42	90	73
Ge(1)	1	0·086	15	87	129
	2	0·159	94	6	92
	3	0·074	76	85	39
Ga(1)	1	0·086	7	85	119
	2	0·166	96	7	92
	3	0·052	86	85	29
Ga(2)	1	0·097	154	90	39
	2	0·151	92	3	92
	3	0·047	64	87	51
Ge(2)	1	0·089	135	93	20
	2	0·155	92	3	88
	3	0·055	45	90	70
O($A1$)	1	0·169	12	78	117
	2	0·202	102	17	95
	3	0·120	90	78	27
O($A2$)	1	0·182	94	6	84
	2	0·232	118	96	7
	3	0·106	29	89	86
O(B) (0)	1	0·161	83	73	36
	2	0·217	112	26	92
	3	0·148	24	71	126
O(B) (z)	1	0·161	47	80	69
	2	0·220	113	25	71
	3	0·110	128	113	29
O(C) (0)	1	0·178	21	111	109
	2	0·204	93	84	23
	3	0·092	69	21	103
O(C) (z)	1	0·166	123	33	76
	2	0·198	126	113	28
	3	0·139	53	68	67
O(D) (0)	1	0·168	139	65	39
	2	0·230	66	26	107
	3	0·097	59	96	56
O(D) (z)	1	0·168	153	75	44
	2	0·229	70	23	89
	3	0·113	73	107	45

Table 1. *Fractional coordinates and vibrational parameters* ($\times 10^4$) *with the significant figures of the e.s.d.'s in parentheses*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba (0000)	2755 (1)	3 (1)	670 (1)	19 (1)	37 (1)	13 (0)	1 (1)	−1 (1)	−1 (0)
Ge(1) (0000)	32 (2)	1799 (2)	1083 (1)	20 (3)	27 (1)	6 (1)	−3 (1)	4 (1)	−1 (1)
Ga(1) (0z00)	13 (2)	1821 (2)	6155 (1)	20 (2)	29 (1)	3 (1)	−5 (1)	2 (1)	−2 (1)
Ga(2) (0000)	6989 (2)	1222 (2)	1739 (1)	16 (3)	24 (1)	4 (1)	−1 (1)	−2 (1)	−1 (1)
Ge(2) (0z00)	6911 (2)	1152 (2)	6732 (1)	11 (2)	26 (1)	6 (1)	0	0	1 (1)
O($A1$) (0000)	19 (24)	1268 (11)	−10 (12)	82 (20)	42 (8)	17 (6)	−8 (15)	12 (9)	−5 (8)
O($A2$) (0000)	6005 (16)	−2 (15)	1467 (11)	34 (16)	36 (8)	47 (9)	0	4 (9)	−2 (9)
O(B) (0000)	8282 (21)	1242 (14)	1056 (13)	85 (25)	46 (11)	29 (9)	−17 (13)	25 (12)	−4 (8)
O(B) (0z00)	8040 (21)	1306 (14)	6033 (11)	82 (24)	45 (10)	22 (8)	−13 (12)	23 (12)	8 (7)
O(C) (0000)	86 (21)	3066 (12)	1195 (12)	95 (30)	13 (7)	44 (11)	−11 (10)	32 (15)	3 (6)
O(C) (0z00)	95 (21)	3131 (13)	6296 (13)	68 (26)	30 (9)	31 (8)	−3 (12)	8 (11)	−6 (7)
O(D) (0000)	1884 (19)	1314 (14)	1939 (11)	54 (23)	52 (11)	16 (7)	16 (13)	−4 (11)	−1 (7)
O(D) (0z00)	1881 (21)	1244 (14)	6992 (11)	77 (26)	51 (11)	17 (7)	21 (14)	8 (12)	9 (7)

deviations from the former, however, are smaller owing to the greater number of reflexions used. The coordinates from the two refinements were practically identical for the cations whilst the differences for the O atoms were all within twice the standard deviations. The conclusion is that the number of b-type reflexions required for attaining a correct model is relatively small and that the introduction of thermal anisotropy does not cause significant improvement (Phillips, Colville & Ribbe, 1971).

The standard deviations for the O atoms are rather large (Table 1) as is to be expected in the presence of Ga, Ge and Ba.

Comparative description and discussion

Bond distances and interbond angles

The bond angles and distances are given in Tables 3, 4 and 5. The O–T–O angles (Table 3b) show the very large deviations from the ideal which are characteristic of the feldspar framework, but the trend of tensions and compressions agrees well with the scheme proposed by Megaw (1974a); here, however, the deviations from the mean values are larger than for the gallosilicates of Sr and Ba and much larger than for the aluminosilicates (Table 4b).†

The main cause of the strains and stresses in the bond angles may be traced in the row of atoms, O($A2$)–M–O($A2$), along x^*, which forms one of the peculiarities of the feldspar structure; the repulsion between neighbouring M cations produces a thrust

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† The references for the structures of the 14 Å monoclinic feldspars are given in Table 4 and will not be quoted further except to avoid confusion. It has to be noted that the specimens used for the investigation of celsian showed an appreciable substitution of K for Ba (and of Si for Al). Since we aim at a general comparison of the different compounds, this should not be of great importance.

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

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

Ge(1) (0)–O($A1$) (0000)	1·777 (18)	Ga(2) (0)–O($A2$) (0000)	1·837 (19)
–O(B) (0000)	1·715 (19)	–O(B) (0000)	1·830 (19)
–O(C) (0000)	1·721 (16)	–O(C) ($mzi0$)	1·817 (18)
–O(D) (0000)	1·733 (17)	–O(D) ($mz0c$)	1·801 (17)
Ga(1) (z)–O($A1$) ($mz0c$)	1·853 (18)	Ge(2) (z)–O($A2$) ($mz00$)	1·720 (19)
–O(B) ($0z00$)	1·826 (19)	–O(B) ($0z00$)	1·737 (18)
–O(C) ($0z00$)	1·783 (18)	–O(C) ($m0i0$)	1·758 (19)
–O(D) ($0z00$)	1·785 (18)	–O(D) ($m00c$)	1·753 (17)

(b) Bond angles at tetrahedral sites (e.s.d. ≤0·8°)

	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
Ge(1) (0)	98·3	118·7	99·2	115·3	115·1	109·1	109·3
Ga(1) (z)	96·4	119·6	96·7	112·4	118·4	111·9	109·2
Ga(2) (0)	104·1	96·4	107·4	115·4	114·6	116·0	109·0
Ge(2) (z)	107·7	98·3	109·1	112·7	113·4	114·3	109·2

(c) Oxygen–oxygen distances in tetrahedra (e.s.d. ≤0·027 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
Ge(1) (0)	2·643	3·010	2·673	2·903	2·909	2·814	2·825
Ga(1) (z)	2·743	3·142	2·718	2·999	3·101	2·956	2·943
Ga(2) (0)	2·891	2·724	2·932	3·083	3·056	3·068	2·959
Ge(2) (z)	2·792	2·631	2·829	2·910	2·917	2·948	2·838

Table 4. *Tetrahedral bond-length means with the r.m.s. deviations* (Å) *for a tetrahedron,* $\varepsilon_t(r)$; *tetrahedral* O–T–O *means with r.m.s. deviations* (°) *for a tetrahedron,* $\varepsilon_t(T)$

(a) Bond lengths

	$SrAl_2Si_2O_8$[a]		$BaAl_2Si_2O_8$[b]		$SrGa_2Si_2O_8$[c]		$BaGa_2Si_2O_8$[c]		$BaGa_2Ge_2O_8$[d]	
	Mean	$\varepsilon_t(r)$	Mean	$\varepsilon_t(r)$	Mean	$\varepsilon_t(r)$	Mean	$\varepsilon_t(r)$	Mean	$\varepsilon_t(r)$
T(1) (0)	1·627 (3)	0·013	1·639 (4)	0·008	1·611 (3)	0·018	1·634 (4)	0·020	1·736 (8)	0·025
T(1) (z)	1·723 (3)	0·015	1·717 (4)	0·011	1·822 (3)	0·019	1·807 (3)	0·025	1·812 (9)	0·029
T(2) (0)	1·736 (3)	0·003	1·712 (6)	0·013	1·820 (3)	0·012	1·803 (3)	0·016	1·821 (9)	0·014
T(2) (z)	1·630 (3)	0·013	1·635 (6)	0·011	1·617 (3)	0·011	1·634 (4)	0·017	1·742 (9)	0·015

(b) Interbond angles

	$SrAl_2Si_2O_8$		$BaAl_2Si_2O_8$		$SrGa_2Si_2O_8$		$BaGa_2Si_2O_8$		$BaGa_2Ge_2O_8$	
	Mean	$\varepsilon_t(T)$	Mean	$\varepsilon_t(T)$	Mean	$\varepsilon_t(T)$	Mean	$\varepsilon_t(T)$	Mean	$\varepsilon_t(T)$
T(1) (0)	109·4 (1)	5·71	109·5 (1)	5·00	109·4 (1)	6·52	109·4 (1)	5·90	109·3 (1)	7·97
T(1) (z)	109·3 (1)	7·14	109·3 (1)	5·62	109·1 (1)	8·63	109·2 (1)	7·63	109·2 (1)	9·88
T(2) (0)	109·2 (1)	5·03	109·3 (1)	4·46	109·0 (1)	6·29	109·0 (1)	6·72	109·0 (1)	7·15
T(2) (z)	109·4 (1)	3·68	109·4 (1)	3·61	109·3 (1)	4·40	109·4 (1)	4·34	109·2 (1)	5·43

a Chiari, Calleri, Bruno & Ribbe (1975); b Newnham & Megaw (1960); c Calleri & Gazzoni (1975a); d present work.

outward on the O($A2$) atoms (Megaw, 1974a). It has been deduced by Megaw (1974a) that in an ideal framework the T–O($A2$)–T angle should be 110°, but the angle is much larger in actual structures and increases with the size of the M cation. In the alkali feldspars it opens from 130° for low albite to 141° for RbAl₂Si₂O₈ (Megaw, 1974b). In the alkaline-earth

feldspars it is 124·5° (mean) in anorthite (Megaw, Kempster & Radoslovich, 1962) and the values for the Sr and Ba monoclinic feldspars can be found in Table 5, with the other T–O–T angles. Hence the T–O($A2$)–T angle is regularly smaller when a divalent cation is present and the smaller the cation, and the greater the charge density, the smaller is the angle.

Table 5. *T–O–T bond angles* (°)

E.s.d. $\leq 1\cdot0°$ for BaAl₂Si₂O₈ and BaGa₂Ge₂O₈; $\leq 0\cdot4°$ for the other compounds.

	SrAl₂Si₂O₈	BaAl₂Si₂O₈	SrGa₂Si₂O₈	BaGa₂Si₂O₈	BaGa₂Ge₂O₈
T(1) (0)–O($A1$)——T(1) (z)	137·8	139·4	134·8	136·2	132·4
T(2) (0)–O($A2$)——T(2) (z)	127·7	135·2	126·3	132·9	129·1
T(1) (0)–O(B) (0)–T(2) (0)	144·4	150·2	141·1	145·5	140·4
T(1) (z)–O(B) (z)–T(2) (z)	145·6	149·6	142·9	145·4	139·5
T(1) (0)–O(C) (0)–T(2) (0)	129·6	127·0	127·2	123·4	123·6
T(1) (z)–O(C) (z)–T(2) (z)	132·3	130·2	129·7	128·0	125·3
T(1) (0)–O(D) (0)–T(2) (0)	139·7	139·4	138·4	137·4	138·7
T(1) (z)–O(D) (z)–T(2) (z)	138·1	138·1	137·1	136·4	139·1
Mean	136·9	138·6	134·7	135·6	133·5

Table 6. *Environment of the* M *cations* (*within* 3·4 Å)

	SrAl₂Si₂O₈	BaAl₂Si₂O₈	SrGa₂Si₂O₈	BaGa₂Si₂O₈	BaGa₂Ge₂O₈
M–O($A1$) (0000)	2·630 (5)	2·854 (7)	2·617 (5)	2·812 (5)	2·795 (18)
–O($A1$) (000c)	2·650 (5)	2·848 (7)	2·618 (5)	2·865 (5)	2·825 (18)
–O($A2$) (0000)	2·445 (5)	2·667 (7)	2·440 (7)	2·646 (7)	2·624 (15)
–O(B) (000c)	2·746 (5)	2·927 (11)	2·701 (6)	2·883 (6)	2·884 (19)
–O(B) (m00c)	2·855 (5)	2·939 (7)	2·902 (8)	2·961 (8)	2·924 (17)
–O(D) (0000)	2·769 (5)	2·909 (7)	2·764 (6)	2·904 (7)	2·925 (18)
–O(D) (m000)	2·743 (5)	2·902 (7)	2·747 (6)	2·921 (7)	2·937 (18)
Mean	2·691	2·863	2·684	2·856	2·845
M–O(C) (mzi0)	3·229 (5)	3·135 (10)	3·314 (6)	3·198 (8)	3·220 (18)
–O(C) (0zi0)	3·010 (5)	3·112 (10)	3·034 (6)	3·084 (8)	3·160 (17)

Table 7. *Interatomic distances* (Å) *defining the dimensions of the four-rings and of the coordination polyhedron with the significant figures of the e.s.d.'s in parentheses*

	SrAl₂Si₂O₈	BaAl₂Si₂O₈	SrGa₂Si₂O₈	BaGa₂Si₂O₈	BaGa₂Ge₂O₈
(*a*) Four-rings parallel to ($\bar{2}$13)					
(1) T(1) (0000)–T(1) (00ic)	4·774 (2)	4·732 (5)	4·880 (3)	4·870 (4)	5·012 (3)
(2) T(2) (mzi0)–T(2) (mz0c)	3·948 (2)	3·931 (6)	3·930 (1)	3·876 (2)	4·024 (3)
(3) T(2) (m0i0)–T(2) (m00c)	4·078 (2)	4·015 (6)	4·204 (3)	4·136 (4)	4·199 (3)
(4) T(1) (0z00)–T(1) (0zic)	4·666 (2)	4·683 (5)	4·693 (1)	4·705 (2)	4·909 (3)
(1)/(2)	1·209	1·204	1·242	1·256	1·245
(4)/(3)	1·144	1·166	1·116	1·138	1·169
(*b*) Four-rings parallel to (010)					
(1) T(1) (mzi0)–T(1) (00ic)	4·091 (2)	4·116 (6)	4·224 (3)	4·245 (4)	4·248 (2)
(2) T(2) (mzi0)–T(2) (00ic)	4·655 (2)	4·593 (4)	4·686 (1)	4·634 (1)	4·862 (3)
(3) T(2) (0z00)–T(2) (m00c)	4·790 (2)	4·677 (4)	4·909 (3)	4·819 (3)	4·987 (3)
(4) T(1) (0z00)–T(1) (m00c)	3·835 (2)	3·969 (6)	3·777 (1)	3·871 (2)	4·019 (2)
(2)/(1)	1·138	1·116	1·109	1·092	1·144
(3)/(4)	1·249	1·178	1·300	1·245	1·242
(*c*) Coordination polyhedron					
O($A1$) (0000)–O($A1$) (000c)	3·346 (7)	3·606 (13)	3·271 (8)	3·534 (7)	3·433 (22)
O(B) (000c)–O(B) (m00c)	3·287 (7)	3·597 (13)	3·273 (5)	3·532 (9)	3·454 (27)
O(D) (0000)–O(D) (m000)	3·161 (5)	3·302 (13)	3·177 (8)	3·340 (11)	3·462 (27)
O($A1$) (000c)–O(B) (000c)	2·525 (6)	2·569 (10)	2·473 (7)	2·552 (9)	2·643 (28)
O($A1$) (0000)–O(B) (m00c)	2·656 (6)	2·682 (10)	2·772 (8)	2·763 (9)	2·743 (28)
O($A1$) (000c)–O(D) (m000)	2·662 (5)	2·673 (18)	2·728 (7)	2·766 (9)	2·718 (25)
O($A1$) (0000)–O(D) (0000)	2·545 (5)	2·566 (18)	2·509 (7)	2·546 (8)	2·673 (25)
O($A2$) (0000)–O(D) (0000)	4·099 (7)	4·509 (9)	4·089 (8)	4·454 (9)	4·391 (23)
O($A2$) (0000)–O(B) (m00c)	4·094 (7)	4·417 (13)	4·039 (9)	4·379 (9)	4·324 (24)
O(B) (000c)–O(D) (m000)	4·319 (6)	4·435 (15)	4·330 (8)	4·464 (10)	4·485 (25)
O(B) (m00c)–O(D) (0000)	4·384 (6)	4·422 (14)	4·410 (8)	4·447 (9)	4·459 (24)

Similarly, given a divalent cation, the angle narrows when the size of the T cation increases; the effect is particularly apparent for the Ba compounds (Table 5). However, to the shrinkage of T–O($A2$)–T do not correspond smaller distortions of the O–T–O angles:
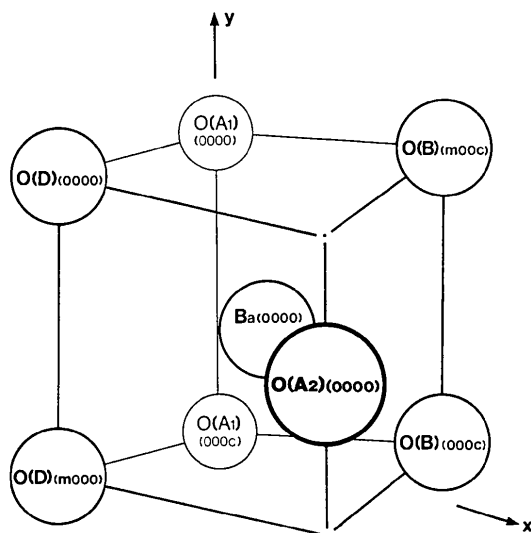

Fig. 1. Projection of the coordination polyhedron of BaGa$_2$Ge$_2$O$_8$ on (211).

BaGa$_2$Ge$_2$O$_8$, with the smallest T–O($A2$)–T, shows the largest deviations from the mean (Table 4b). The same trend of T–O($A2$)–T angles is shown, to varying extents, by the other T–O–T angles; the T–O(C)–T angles, however, decrease progressively with increasing size both of the M and T cations. It is interesting to note (Table 5) that for BaGa$_2$Ge$_2$O$_8$ they are both significantly narrower than 131° which seems to be the value preferred by the natural feldspars (Megaw, 1974b).

From the results obtained for the stability conditions of the feldspar and paracelsian forms (Gazzoni, 1973; Calleri & Gazzoni, 1975b), we may infer that a narrower ⟨T–O–T⟩ corresponds to a smaller stability field of the feldspar form.

The individual T–O bonds also show significant scatterings from the mean values, both for BaGa$_2$Ge$_2$O$_8$ (Table 3a) and for the other Sr and Ba feldspars, but they do not show the one-to-one correspondence shown by the T–O–T angles. On average the T–O($A1$) and T–O($A2$) bonds are longer than the rest and the T–O(C) bonds are shorter, which agrees with the type of coordination around the M cations.

A calculation of bond strengths from the Brown & Shannon (1973) formula suggests that the Ga/Ge distribution of the present compound is essentially ordered with ideal lengths Ga–O = 1·822 and Ge–O =
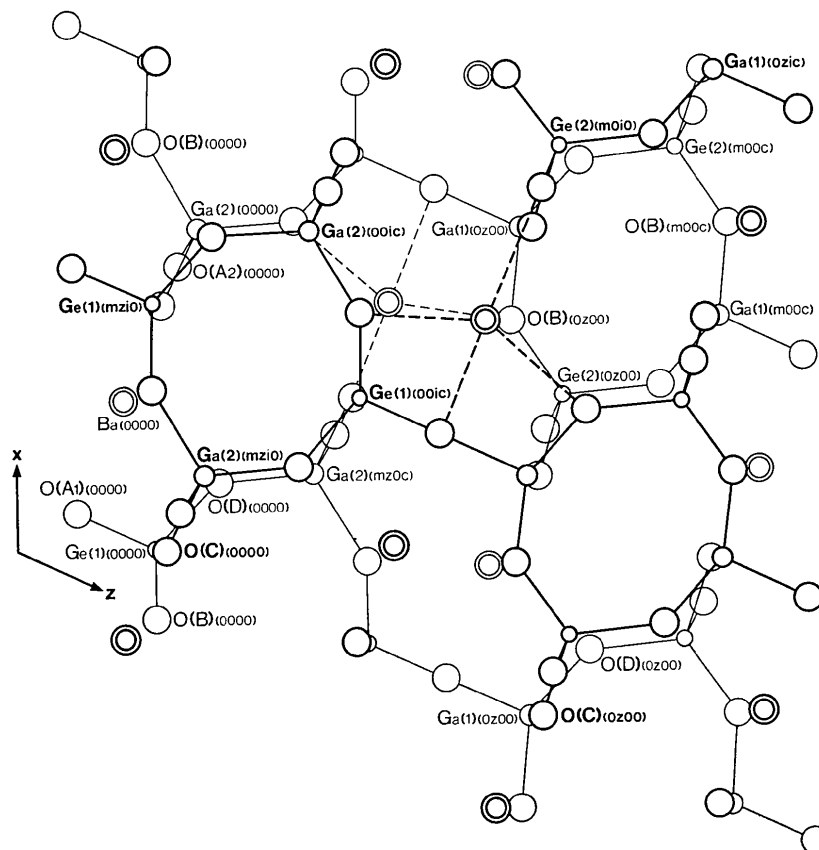

Fig. 2. Projection along [010] of the portion of the structure of BaGa$_2$Ge$_2$O$_8$ comprised between the planes $y = 0·0$ and $y = 0·5$.

1·735 Å. A comparison of the bond strengths, calculated from different T–O ideal values, for the several feldspar and paracelsian modifications would be interesting; we prefer, however, to defer it until completion of the analyses of other title compounds. It may be noted for the present that structural requirements affect the tetrahedral means. The grand means for the Ga–O bonds are 1·814 (3) and 1·826 (3) Å for the feldspar and paracelsian forms respectively (Table 4a; Calleri & Gazzoni, 1976).

Environment of the M cation

There are seven O atoms, within 3 Å of M (Table 6), which may be assumed to form the coordination group both here and for the other 14 and 7 Å monoclinic feldspars (Megaw, 1974b; Calleri & Gazzoni, 1975a). The coordination polyhedron of $BaGa_2Ge_2O_8$ is shown in Fig. 1. We may describe it as a distorted cube with two corners missing, the O(C) atoms of Table 6, and with O(A2), which shields the O(C) atoms, on the bisector of the angle O(A1) (0)–M–O(A1) (c) (cf. Megaw et al., 1962). The cube edges are approximately parallel to [010], [101] and [$\bar{1}$01]. The same disposition was found for the other feldspars of Table 6, but the coordination becomes slightly tighter, on average, with increasing size of the T cations. The short Ba–O(A2) distance, in particular, decreases regularly with increasing T cation size and becomes very short for $BaGa_2Ge_2O_8$: 2·62 (1) Å. The shortest Ba–O distances known so far, generally involving polarizable O atoms, are in fact about 2·64 Å (e.g. see Dubler, Korber & Oswald, 1973; Martin, Tordjman & Durif, 1975). The two M–O(A1) distances are shorter than the rest so that the Ba cation is held in place very tightly by the triangle of atoms O(A1) (0), O(A2), O(A1) (c), in the x^*y plane (Fig. 1). A similar behaviour is shown by the O(A1) (0)---O(A1) (c) edge, shared between two coordination polyhedra (Table 7c), whilst, on the other hand, the distance between nearest neighbour Ba cations is 4·416 (1) for celsian, 4·444 (1) for $BaGa_2Si_2O_8$ and 4·449 (1) Å for $BaGa_2Ge_2O_8$. All this attenuates the repulsion between neighbouring M cations of the present feldspar modification which is, nonetheless, everywhere metastable, the stable form being the paracelsian. The paracelsian framework with Ga and Ge is more suited for accommodating Sr and Ba since it allows a more regular, even though tighter, coordination: none of the Sr–O distances are shorter than 2·56 and none of the Ba–O distances shorter than 2·65 Å (Smith, 1953; Phillips, Kroll, Pentinghaus & Ribbe, 1975; Calleri & Gazzoni, 1976).

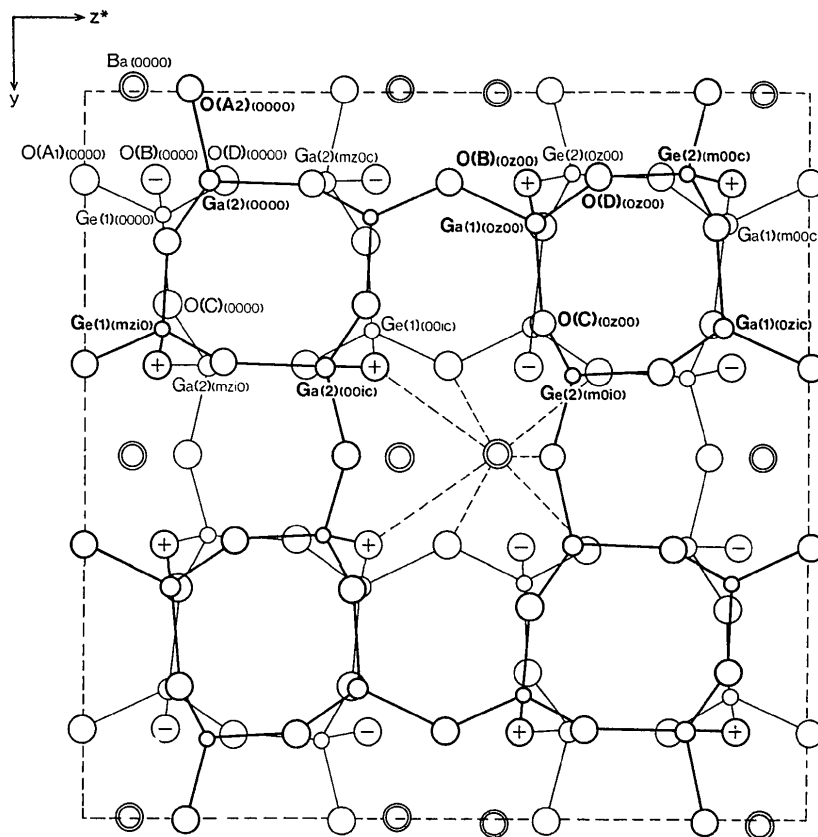The other four atoms of the coordination group

Fig. 3. Projection along [100] of the portion of the structure of $BaGa_2Ge_2O_8$ comprised between the planes, of Fig. 2, ($10\bar{1}$) through the origin and through the point $\frac{1}{2},0,0$.

O(B) (000c), O(B) (m00c), O(D) (0000), O(D) (m000), form a parallelogram parallel to the yz plane with the M cation slightly out of their plane (Megaw, 1974b; Bruno & Facchinelli, 1974). From the results of Table 7(c) we may note that the sides (Fig. 1) O(B) (c)--- O(D) (m), O(B) (m00c)--- O(D) (0) and O(D) (0)--- O(D) (m) lengthen as the size of the M or T cations increases; the side O(B) (c)--- O(B) (m00c) lengthens when M increases, but shortens when the T cations increase. The two sides O(B) (c)--- O(B) (m00c) and O(D) (0)--- O(D) (m) are very different for celsian while they become identical for $BaGa_2Ge_2O_8$ (Table 7). The M cation lies approximately in the centre of the parallelogram only in the structure of celsian where the two O(B)--- O(D) diagonals are very similar. For the other compounds of Table 6 the O(B) (c)--- O(D) (0) diagonal is shorter than the other and, finally, for all these compounds, except $BaGa_2Ge_2O_8$, O(B) (m00c) is the farthest from the M cation. We find an interesting parallelism with the 7 Å triclinic feldspars (Megaw, 1974b, pp. 106–108): in the structures where the m plane, orthogonal to [010], is no longer present, the M cation tends to move so as to get three equidistant neighbours in the (100) plane and to 'loose' the O(B) (m) atom. The effect is less marked with the large Ba ion which lies close to the mirror plane.

The effect of the T cation size on the framework

It is well known that in the feldspar framework there are two families of four-rings of tetrahedra: the rings of one type are centred on the diad axes at $z = 0.25$, 0·75; those of the second type are generated by the operation of the inversion centres at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ and $\frac{1}{4},\frac{1}{4},\frac{3}{4}$. The rings of the first type are easily seen in the projection of Fig. 2. The mean planes through the groups of four T cations are orthogonal to [010]. The rings of the second type are better discernible in the projection of Fig. 3; here the groups of four T cations, strictly coplanar since formed by pairs of centrosymmetric atoms, lie approximatly on plane ($\bar{2}$13). The four-rings show quasi-elliptical sections in the projections along [010] and [100] and, as has been done for some paracelsian modifications (Calleri & Gazzoni, 1976), we may compare the relative positions of the T cations, defining empirically a 'degree of ellipticity' as [T(2)–T(2)]/[T($\bar{1}$)–T($\bar{1}$)] for the rings orthogonal to the y axis and as [T($\bar{1}$)–T($\bar{1}$)]/[T(2)–T($\bar{2}$)] for the other rings. In this way the degree of ellipticity is always > 1 as can be seen from Table 7(a) and (b) where there are also reported the T–T distances between the atoms of type (0000), rows (1) and (2), and of type (0z00), rows (3) and (4).

From the results of Table 7 we deduce that, in general, the introduction of larger T cations at the ends of the 'major axes' reduces the ellipticity, while their introduction at the ends of the 'minor axes' emphasizes it and *vice versa* for smaller cations (Figs. 2 and 3). These contractions and expansions take place

in the expected senses when assuming that the four-rings must be elliptical even when the tetrahedral sites are topochemically equivalent, as in sanidine (Taylor, 1933), and that the substitution of different TO_4 groups occurs with an expansion of the framework not accompanied by very large tilts of the tetrahedra.

Considering more generally the whole of the trends, we may note from Table 7 that for each of the two chains of four-rings along [100], Fig. 2, which are formed by the alternation of a 'more elliptical' with a 'more rounded' ring, to an increase of the ellipticity for the former corresponds a decrease for the latter ring. Precisely, among the first four compounds of Table 7, for the chains formed by the rings of type T(0) the ellipticity of the rings nearly parallel to ($\bar{2}$13) increases with increasing T dimensions and that of the rings orthogonal to [010] decreases; the opposite holds for the chains of type T(z). For $BaGa_2Ge_2O_8$ the inclination towards an intermediate degree of ellipticity of the four independent rings, which is to be expected since the dimensions of Ga and Ge are closer than those of Al, or Ga, and Si, only manifests itself in a greater ellipticity of the more rounded rings and the rings as a whole show a large degree of deformation. Therefore the metastability of the feldspar form (Gazzoni, 1973) is accompanied by a greater elliptical character of the four-rings.

Within the rings orthogonal to [010], the distances T(1) (mzi0)--- T(1) (00ic) and T(1) (0z00)--- T(1) (m00c) increase very little, or really decrease, with increasing size of the M and T cations; the lengthening of the **c** parameter of the unit cell as a function of the cation size is due essentially to the presence of longer T–O(A1) bonds along the z axis (Fig. 2). The diagonals T(2)--- T(2), on the other hand, increase progressively with the T dimensions (Table 7). As a consequence the M cation is pushed in the x^*z plane towards O(A2) and the M–O(A2) distance shortens progressively becoming too short for $BaGa_2Ge_2O_8$ (Table 6).

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On the Conformational Varieties of Adrenaline: the Free Molecule and the Molecule in the Crystal

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Refined quantum-mechanical computations invariably predict that the preferred conformers of free androgenic phenethylamines or hallucinogenic indolalkylamines should correspond to values of the torsion angles $\tau_1 \simeq \pm 90°$ and τ_2 close to ± 60 or $180°$. X-ray crystallographic studies indicate that most such compounds exist in these conformations (in particular with $\tau_1 \simeq 90$, $\tau_2 \simeq 180°$) in the crystals. In some cases, however, the crystalline conformer corresponds to $\tau_1 \simeq 0$, $\tau_2 \simeq 180°$, an arrangement which does not even correspond to a local energy minimum on the conformational energy map for the free molecule. Such is, for example, the case for adrenaline in adrenaline hydrogen tartrate. Computations carried out for the lattice energy of this crystal and of the hypothetical crystals constructed with the usual conformers, by a procedure which uses intermolecular potential functions, show that the lattice energy of the 'experimental' crystal largely compensates for the loss in conformational energy of the constituent unit and represents a more stable arrangement than those obtained with conformers associated with $\tau_1 \simeq \pm 90°$.

1. Introduction

Many fundamental pharmacological compounds are composed of a conjugated ring with an attached ethylamine side chain (Pullman, 1976). Typical examples are the androgenic phenethylamines or the hallucinogenic indolalkylamines. In such molecules an essential conformational problem concerns the mutual orientation of the side chain and the ring. It is generally defined (Pullman, 1976) by reference to two torsion angles τ_1 and τ_2, illustrated in Fig. 1 for adrenaline. The first of these angles defines the overall orientation of the plane of the side chain with respect to the plane of the ring, the second the orientation of the cationic head with respect to the ring.

We recall that with the usual convention (Pullman, 1976) the torsion angle τ about the bond B–C in the sequence of atoms A–B–C–D is the angle through which the far bond C–D is rotated relative to the near

bond A–B. The *cis*-planar position of bonds A–B and C–D corresponds to $\tau = 0°$. The torsion angles are considered positive for a right-handed rotation: when looking along the bond B–C, the far bond C–D rotates clockwise relative to the near bond A–B. Alternatively, the positive angles are defined as 0 to 180°, measured for a clockwise rotation, and negative angles as 0 to $-180°$, measured for a counterclockwise rotation.

Conformational energy maps constructed for a large series of phenethylamines (Pullman, Coubeils, Courrière & Gervois, 1972; Pullman, Berthod & Courrière, 1974) and indolalkylamines (Pullman, Courrière & Berthod, 1974; Port & Pullman, 1974) by refined quantum-mechanical procedures lead to the prediction that the most stable conformations of these molecules, in the free state, should be associated with $\tau_1 \simeq \pm 90$ and $\tau_2 = \pm 60$ or $180°$, *i.e.* should correspond to a perpendicular arrangement of the C(1), C(7), C(8) plane of the side chain with respect to the plane of the