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The Structures of (Sr,Ba)[(Al,Ga)$_2$(Si,Ge)$_2$O$_8$]. V. The Crystal Structure of the Synthetic Feldspar BaAl$_2$Ge$_2$O$_8$

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The structural parameters of the feldspar modification of BaAl$_2$Ge$_2$O$_8$ were found from diffractometer intensities and refined by Fourier and least-squares methods to $R = 3{\cdot}6\%$. The space group is $I2/c$, $Z = 8$, $a = 8{\cdot}799$ (5), $b = 13{\cdot}371$ (6), $c = 14{\cdot}727$ (6) Å, $\beta = 114{\cdot}93$ (6)°. The mean T—O distances are: $\langle$Ge(1)—O$\rangle$ = 1·735, $\langle$Ge(2)—O$\rangle$ = 1·734, $\langle$Al(2)—O$\rangle$ = 1·743, $\langle$Al(1)—O$\rangle$ = 1·744 Å. The crystal is highly ordered. The Ba cation is seven coordinated, as are the other M cations of the title feldspars, $\langle$Ba—O$\rangle$ = 2·853 Å. Comparison with the results for other feldspars showed positive correlations of the $\langle$O—T—O$\rangle$ distortion, the $\langle T$—O—$T\rangle$ shrinkage and some significant ratios between T—T distances with the composition and, implicitly, with the relative stability of the feldspar and paracelsian modifications.

Introduction

The present investigation completes the study of the structures of the feldspar modification for all the end members of the title systems, except SrGa$_2$Ge$_2$O$_8$ which shows the paracelsian form only (Gazzoni, 1973) and SrAl$_2$Ge$_2$O$_8$ whose polymorphism is more complex; recently Kroll, Pentinghaus & Laves (1976) have illustrated in abstract form the structure of one of the polymorphs: an orthorhombic variant of the feldspar structure.

We extend here the comparisons between structural features, given in a preceding article (Calleri & Gazzoni, 1976*b*), to the results for the present feldspar, for the feldspar (Sr$_{0\cdot50}$Ba$_{0\cdot50}$)Ga$_2$Si$_2$O$_8$ (Calleri & Gazzoni, in preparation) and for a recently refined celsian (Griffen & Ribbe, 1976), with particular attention paid to the Ba feldspars. The relations between structural features and stability conditions are also briefly examined.

Experimental results

Sample preparation and lattice-parameter determination

The single crystals suitable for the X-ray analysis were selected from polycrystalline samples obtained by fusion and successive crystallization. Stoichiometric mixtures of fine-grained BaO, Al$_2$O$_3$ and GeO$_2$ were introduced into a silicon carbide resistivity furnace preheated to a temperature (~1550°C) slightly above the expected melting point (Gazzoni, 1973). The requirements of preventing the volatilization of GeO$_2$ and of obtaining good homogeneity were matched in the following way: the oxide mixture was kept at the melting temperature for a short time (~1 min), since the homogeneity is favoured here by the high fluidity of the melt, then quickly cooled to 1200°C and subsequently cooled very slowly to room temperature. Weighing before and after the thermal treatment did not indicate perceptible loss of GeO$_2$; this was confirmed by the purity of the powder spectrum indicating also the attainment of good and homogeneous crystallization.

The crystal class and space group were determined from Weissenberg and precession photographs which showed only '*a* type' ($h + k$ even, l even) and '*b* type' ($h + k$ odd, l odd) reflexions with no kind of splitting or diffuseness. Space group $I2/c$ was chosen with the inversion centre assumed to be at (000) by analogy with the other 14 Å monoclinic feldspars (Newnham & Megaw, 1960). The cell parameters were refined by least squares based on an adequate number of θ values measured on powder spectra taken with a focusing Guinier camera (Cu $K\alpha$). The results can be summarized as follows.

Crystal data

BaAl$_2$Ge$_2$O$_8$, M_r = 464·52, monoclinic, a = 8·799 (5), b = 13·371 (6), c = 14·727 (6) Å, β = 114·93 (6)°; V = 1571·6 Å^3; D_c = 3·93 g cm^{-3}; Z = 8; space group $I2/c$; $F(000)$ = 1680; linear absorption coefficient μ(Mo $K\alpha$) = 133·93 cm^{-1}.

Intensity collection and reduction

For the structural investigation a prismatic crystal was chosen having the dimensions 0·140, 0·051, 0·104 mm across the opposite faces of {100}, {010} and {001} respectively. The intensities accessible to Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å), within $2\theta = 60°$, were measured at room temperature on a Philips PW 1100 four-circle diffractometer equipped with a graphite monochromator. The conditions best suited to the measurement were θ–2θ step scan, scan rate 0·056° s^{-1} and scan range 1·7°. For the treatment of background, the calculation of net intensities and their standard deviations see, for example, Basso, Dal Negro, Della Giusta & Ungaretti (1975). The weaker reflexions were scanned four times and the measurements were averaged. Over 2000 reflexions were explored, 1726 of which had $I \geq 2{\cdot}5\sigma(I)$ and were included in the analysis; there were 700 *b*-type reflexions whose average intensity was slightly greater than for $BaGa_2Si_2O_8$ (Calleri & Gazzoni, 1975*b*). Corrections for the Lorentz–polarization effect for monochromatized radiation and for the absorption effect (Hamilton, 1966) were applied. A refinement of the unit-cell parameters was carried out with diffractometer observations and the results were identical, well within the standard deviations, with those reported above.

Initial model and refinement procedure

For the computation all the atoms were considered neutral except Ba (assumed to be doubly ionized). The scattering factors were those of Cromer & Waber (1965) with an anomalous dispersion correction for Ba, Al and Ge (Cromer, 1965). The coordinates of celsian (Newnham & Megaw, 1960) were used as a starting model with approximate *B* values deduced from the results for related compounds. The initial *R* was small, 0·18, and it reduced to 0·048 after one Fourier synthesis and a few isotropic cycles. It was manifest from the beginning that the *B* values for Al were unusually small: $B = 0{\cdot}15$ Å^2 for Al(1)(*z*) and 0·12 Å^2 for Al(2)(0) at the end of the isotropic refinement. The thermal parameters of the other atoms showed no unusual values. The refinement was completed by full-matrix cycles with *ORFLS* (Busing, Martin & Levy, 1962) refining anisotropically all the atoms except the *T* cations; within our experience, making these atoms anisotropic does not bring any improvement. The weighting scheme was ($|F_o|$ on an absolute scale): $w = 100/(A|F_o|^2 + B|F_o| + C)$, for $|F_o| \geq 54$; $w = K$, for $|F_o| < 54$; the coefficients were finally $A = 0{\cdot}0088$, $B = 1{\cdot}0$, $C = 50{\cdot}0$, $K = 0{\cdot}20$. No correction for secondary extinction was required. At convergence *R* was 0·036 (*wR* = 0·044) or 0·033 on excluding 78 reflexions (53 of *b* type) which were given zero weight because of poor agreement. The results of the refinement are given in Table 1,* from which it may be seen that the thermal parameters for the Al atoms are small – significantly smaller than those for the Ge atoms even though the latter are not particularly large. With the large difference between the atomic numbers of Al and Ge, a small amount of substitutional disorder should have the effect of increasing the vibrational parameters of Ge and suppressing those of Al unless appropriate scattering-factor curves had been used.† The equal radii of tetrahedrally coordinated Al^{3+} and Ge^{4+} (Shannon, 1976) and the small difference in π-bonding character between the AlO_4^{5-} and GeO_4^{4-} groups (Bruno & Pentinghaus, 1974) would not conflict with this. Slight deviations from the title stoichiometry, due

Table 1. *Results of the parameter refinement*

(*a*) Fractional coordinates and isotropic thermal parameters (all values $\times 10^4$) with the significant figures of the standard deviations in parentheses

	x	*y*	*z*	*B*
Ba(0000)	2776·5 (4)	4·2 (2)	663·1 (2)	
Ge(1)(0000)	47·8 (7)	1810·5 (4)	1107·3 (4)	5336 (104)
Al(1)(0*z*000)	45 (2)	1809 (1)	6134 (1)	2435 (201)
Al(2)(0000)	6986 (2)	1194 (1)	1732 (1)	1906 (195)
Ge(2)(0*z*000)	6958·2 (7)	1175·6 (4)	6733·1 (4)	4812 (101)
O(*A*1)(0000)	7 (4)	1328 (3)	−14 (2)	
O(*A*2)(0000)	6066 (6)	9 (3)	1461 (3)	
O(*B*)(0000)	8216 (5)	1320 (3)	1081 (3)	
O(*B*)(0*z*00)	8175 (5)	1315 (3)	6075 (3)	
O(*C*)(0000)	158 (5)	3092 (3)	1227 (3)	
O(*C*)(0*z*00)	163 (5)	3100 (3)	6270 (3)	
O(*D*)(0000)	1876 (5)	1263 (3)	1971 (3)	
O(*D*)(0*z*00)	1880 (5)	1245 (3)	6980 (3)	

(*b*) R.m.s. displacements for Ba with the angles α_{ij} between their directions and the cell axes

Axis	R.m.s.d.	α_{ix}	α_{iy}	α_{iz}
1	0·111 (1) Å	91°	7°	84°
2	0·119 (1)	113	96	7
3	0·088 (1)	23	92	92

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32691 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† We used considerations of this kind in the case of $BaGa_2Si_2O_8$ (Calleri & Gazzoni, 1975*b*) for opposing the obvious postulate of Ga/Si disorder which was not supported there by a difference in the thermal parameters. Griffen & Ribbe (1976) questioned their validity noting that the *B* values for the *T* cations of a natural celsian, 'necessarily partially disordered because of its composition', are small and not very different from each other. This is not surprising with nearly isoelectronic atoms like Si and Al; the expected effect is not related to disorder itself, but essentially to the atomic-number difference (*cf*. also Calleri & Gazzoni, 1974). Griffen & Ribbe (1976) have informed us that there are experimental results (to be published) proving that our $BaGa_2Si_2O_8$ synthetic feldspar shows some 10% disorder. We acknowledge the information, but still think it surprising that Ga/Si disorder has no effect on the thermal parameters.

to small losses of GeO_2 during the synthesis (Pentinghaus, 1976), also could affect the ordering and the thermal parameters. We note, however, that it is difficult to devise a Ge-defective model.

Looking for a rationalization of this anomaly, we introduced the occupancy factors of the T cations as variables. The results were as follows. The assignment of a fixed average B = 0·363 Å^2 (Table 1) to all four T cations and refinement, with no constraint on their site occupancy, along with the other variables resulted in the occupancy factors: 0·954 (2), 0·965 (2) for Ge(1)(0) and Ge(2)(z) and 1·065 (2), 1·045 (2) for Al(2)(0) and Al(1)(z) respectively; R improved to 0·035 (wR = 0·042), but the positional parameters were quite identical with those of Table 1. On refining simultaneously occupancy and B factors for the T atoms, we obtained site occupancy 0·98 and B = 0·46 Å^2 (mean) for Ge and 1·09, B = 0·52 Å^2 (mean) for Al. The B parameters, therefore, assumed their usual values, but the site-occupancy factors differed asymmetrically; the coordinates were, again, identical with those of Table 1 and R significantly improved to 0·033 (wR = 0·040).

Hence, in conclusion, the difference between the B values of Table 1 conceals a small electron deficiency at the Al sites and a small excess at the Ge sites. This may be justified, partially, if modest Al/Ge disorder is assumed, but more than one cause may be contributing (*e.g.* different formal charges at the Al and Ge sites). The overall effect is at any rate rather small and it will not be considered further.

The Ba cation is displaced very little out of the mirror plane of the 'average structure' with $C2/m$ symmetry (Table 1*a*), as in all Ba feldspars, and (Table 1*b*) its direction of minimum vibration appears to be along $\mathbf{x}^*$: the cation vibrates in the yz plane. The effect was noticed and explained by Newnham & Megaw (1960) for celsian; it is in agreement with the existence of the O(A2)—Ba···Ba—O(A2) row along $\mathbf{x}^*$, but, however, it is not so apparent for all the feldspars of the title series.

Description and discussion

Bond distances

From the revised set of ionic radii published by Shannon (1976), one may infer, using the value 1·36 Å for three-coordinated O, the following tetrahedral distances: Si—O = 1·62, Al—O = 1·75, Ga—O = 1·83, Ge—O = 1·75 Å. From the results so far available for

Table 2. *Tetrahedral bond distances* (Å) *and angles* (°)

(*a*) Tetrahedral distances with the e.s.d.'s in parentheses

Ge(1)(0)–O(*A*1)(0000)	1·759 (4)	Al(2)(0)–O(*A*2)(0000)	1·749 (4)
–O(*B*)(0000)	1·725 (5)	–O(*B*)(0000)	1·732 (5)
–O(*C*)(0000)	1·721 (4)	–O(*C*)(*mzi*0)	1·746 (5)
–O(*D*)(0000)	1·736 (5)	–O(*D*)(*mz*0*c*)	1·747 (5)
Mean	1·735 (3)	Mean	1·743 (3)
Ge(2)(*z*)–O(*A*2)(*mz*00)	1·738 (4)	Al(1)(*z*)–O(*A*1)(*mz*0*c*)	1·754 (4)
–O(*B*)(0*z*00)	1·730 (5)	–O(*B*)(0*z*00)	1·742 (5)
–O(*C*)(*m*0*i*0)	1·730 (4)	–O(*C*)(0*z*00)	1·738 (4)
–O(*D*)(*m*00*c*)	1·739 (4)	–O(*D*)(0*z*00)	1·742 (5)
Mean	1·734 (3)	Mean	1·744 (3)

(*b*) Bond angles at tetrahedral sites (e.s.d. ≤ 0·2°)

	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)	101·0	116·1	100·3	113·1	115·2	110·5	109·4
Al(1)(*z*)	99·5	116·8	99·3	113·1	116·3	110·9	109·3
Al(2)(0)	107·4	98·3	107·2	113·0	113·4	116·0	109·2
Ge(2)(*z*)	107·1	99·8	107·5	113·4	112·8	114·8	109·2

(*c*) Oxygen–oxygen distances in tetrahedra (e.s.d. ≤0·006 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)	2·688	2·952	2·682	2·875	2·921	2·839	2·826
Al(1)(*z*)	2·668	2·973	2·663	2·903	2·959	2·865	2·838
Al(2)(0)	2·804	2·643	2·813	2·899	2·906	2·961	2·838
Ge(2)(*z*)	2·790	2·652	2·803	2·892	2·890	2·922	2·825

(*d*) Tetrahedral bond-length r.m.s. deviations (Å) for a tetrahedron, ε_t (r); O—T—O r.m.s. deviations for a tetrahedron (°), ε_t (T)

	$\varepsilon_t(r)$	$\varepsilon_t(T)$		$\varepsilon_t(r)$	$\varepsilon_t(T)$
Ge(1)(0)	0·015	6·41	Ge(2)(*z*)	0·005	5·13
Al(2)(0)	0·007	5·78	Al(1)(*z*)	0·006	7·28

the feldspars, with the assumption that ⟨*T*—O⟩ variations are due to substitutional disorder only, slightly shorter distances may be inferred for the ideal *T*—O bonds: Si—O = 1·615, Al—O = 1·745, Ga—O = 1·82, Ge—O = 1·74 Å (Calleri & Gazzoni, 1976*b*; Smith & Isaacs, 1964; Wainwright & Starkey, 1971).

Table 3. *T—O—T bond angles* (°) (*e.s.d.* ≤0·3°)

Ge(1)(0)—O(*A*1)—Al(1)(*z*)	136·9
Al(2)(0)—O(*A*2)—Ge(2)(*z*)	130·8
Ge(1)(0)—O(*B*)(0)—Al(2)(0)	145·2
Al(1)(*z*)—O(*B*)(*z*)—Ge(2)(*z*)	143·9
Ge(1)(0)—O(*C*)(0)—Al(2)(0)	126·2
Al(1)(*z*)—O(*C*)(*z*)—Ge(2)(*z*)	127·0
Ge(1)(0)—O(*D*)(0)—Al(2)(0)	138·7
Al(1)(*z*)—O(*D*)(*z*)—Ge(2)(*z*)	138·1
Mean	135·8

Table 4. *Environment of* Ba *within* 3·2 Å

Ba—O(*A*1)(0000)	2·831 (4) Å	Ba—O(*B*)(*m*00*c*)	2·919 (5) Å
—O(*A*)(000*c*)	2·849 (4)	—O(*D*)(0000)	2·909 (4)
—O(*A*2)(0000)	2·626 (5)	—O(*D*)(*m*000)	2·906 (4)
—O(*B*)(000*c*)	2·934 (4)		
Mean	2·853 (1)		
Ba—O(*C*)(*mzi*0)	3·178 (4)	Ba O(*C*)(0*zi*0)	3·179 (4)

The present ⟨*T*—O⟩ (Table 2*a*) are nearly identical with the expected values and also the ⟨Ge—O⟩ distances are close to those of synthetic $BaGa_2Ge_2O_8$, which is highly ordered, and the ⟨Al—O⟩ values close to those of fully ordered anorthite (Calleri & Gazzoni, 1976*b*; Wainwright & Starkey, 1971). It is clear, at any rate, that the Al—O and Ge—O distances happen to be so close that it is impossible to use them for discussing Al/Ge disorder.

The r.m.s. deviations, $\varepsilon_t(r)$, for the tetrahedral bonds (Table 2*d*) are smaller here than for the other feldspars of the title series (Calleri & Gazzoni, 1976*b*); it may also be noted that the difference between the *T*(1) and *T*(2) sites is not everywhere significant, as regards the $\varepsilon_t(r)$ values.

The *T*—O—*T* bond angles are given in Table 3.

The Ba—O distances are given in Table 4 and other relevant distances within the coordination polyhedron (*cf.* Fig. 1 in Calleri & Gazzoni, 1976*b*) in Table 6(*c*); Table 5(*c*) shows the ⟨*M*—O⟩ means for the feldspar and paracelsian modifications. Among the Ba feldspars, ⟨Ba—O⟩ becomes slightly shorter with the expansion of the framework, although not all the differences are statistically significant: ⟨Ba—O⟩ = 2·863 (3) for celsian and 2·845 (7) Å for $BaGa_2Ge_2O_8$, whilst the intermediate terms $BaGa_2Si_2O_8$ and $BaAl_2Ge_2O_8$ show the intermediate values 2·856 (2) and 2·853 (1) Å respectively. Before proceeding in the examination of the

Table 5. O—*T*—O *distortions*

$\varepsilon[T(1)]$, $\varepsilon[T(2)]$: mean ε_t for one *T* site; $\langle\varepsilon(T)\rangle$: mean $\varepsilon_t(T)$ for one compound (°).

(*a*) Feldspars

	SrAlSi[a]	BaAlSi[b]	SrGaSi[c]	$(Sr_{0.50}Ba_{0.50})$GaSi[d]	BaGaSi[c]	BaAlGe[e]	BaGaGe[f]
$\langle\varepsilon(T)\rangle$	5·39	4·83	6·46	6·60	6·15	6·15	6·60
$\varepsilon[T(2)]/\varepsilon[T(1)]$	0·68	0·86	0·71	0·84	0·82	0·80	0·71

(*b*) Paracelsians

	BaAlSi[g]	SrGaSi[h]	SrGaGe[i]	BaGaGe[i]
$\langle\varepsilon(T)\rangle$	3·21	3·84	4·72	4·50
$\varepsilon[T(2)]/\varepsilon[T(1)]$	0·58	0·56	0·50	0·55

(*c*) Mean values of bonds and angles

	⟨⟨*T*—O⟩⟩	⟨M^{VII}—O⟩	⟨*T*—O—*T*⟩	⟨*M*—O⟩/⟨⟨*T*—O⟩⟩
$SrAl_2Ge_2O_8$(*F*)[j]	1·738 Å	2·696 Å	133·8°	1·57
$BaAl_2Ge_2O_8$(*F*)[e]	1·739	2·853	135·8	1·64
$BaGa_2Ge_2O_8$(*F*)[f]	1·778	2·845	133·5	1·60
$BaGa_2Ge_2O_8$(*P*)[i]	1·786	2·765	126·4	1·55
$SrGa_2Ge_2O_8$(*P*)[i]	1·788	2·625	123·0	1·47
$SrAl_2Si_2O_8$(*F*)[a]	1·681	2·691	136·9	1·60
$BaAl_2Si_2O_8$(*F*)[b]	1·678	2·862	138·4	1·71
$BaAl_2Si_2O_8$(*P*)[g]	1·682	2·802	133·2	1·67
$SrGa_2Si_2O_8$(*F*)[c]	1·717	2·684	134·7	1·56
$(Sr_{0.50}Ba_{0.50})Ga_2Si_2O_8$(*F*)[d]	1·722	2·764	134·8	1·60
$BaGa_2Si_2O_8$(*F*)[c]	1·719	2·856	135·6	1·66
$SrGa_2Si_2O_8$(*P*)[h]	1·727	2·621	125·7	1·52

References: (*a*) Chiari, Calleri, Bruno & Ribbe (1975); (*b*) Griffen & Ribbe (1976); (*c*) Calleri & Gazzoni (1975*a*); (*d*) Calleri & Gazzoni (to be published); (*e*) present work; (*f*) Calleri & Gazzoni (1976*b*); (*g*) Kroll & Phillips (1976); (*h*) Calleri & Gazzoni (1974); (*i*) Calleri & Gazzoni (1976*a*); (*j*) Pentinghaus & Laves (1976).

Table 6. *Significant T–T distances within the four-membered rings;* O–O *distances within the coordination polyhedron of* Ba; *e.s.d.'s in parentheses*

(*a*) *T* cations on (213) plane		(*b*) *T* cations on (010) plane	
(1) Ge(1)(0000)–Ge(1)(00*ic*)	4·892 (1) Å	(1) Ge(1)(*mzi*0)–Ge(1)(00*ic*)	4·139 (1) Å
(2) Al(2)(*mzi*0)–Al(2)(*mz*0*c*)	4·050 (2)	(2) Al(2)(*mzi*0)–Al(2)(00*ic*)	4·811 (2)
(3) Ge(2)(*m*0*i*0)–Ge(2)(*m*00*c*)	4·092 (1)	(3) Ge(2)(0*z*00)–Ge(2)(*m*00*c*)	4·855 (1)
(4) Al(1)(0*z*00)–Al(1)(0*zic*)	4·861 (2)	(4) Al(1)(0*z*00)–Al(1)(*m*00*c*)	4·059 (2)
(1)/(2)	1·208	(2)/(1)	1·162
(4)/(3)	1·188	(3)/(4)	1·196
(*c*) Coordination polyhedron			
O(*A*1)(0000)–O(*A*1)(000*c*)	3·551 (6) Å	O(*A*1)(0000)–O(*B*)(*m*00*c*)	2·668 (6) Å
O(*B*)(000*c*)–O(*B*)(*m*00*c*)	3·523 (6)	O(*A*1)(000*c*)–O(*D*)(*m*000)	2·663 (6)
O(*B*)(000*c*)–O(*D*)(*m*000)	4·470 (6)	O(*A*1)(0000)–O(*D*(0000)	2·682 (6)
O(*B*)(*m*00*c*)–O(*D*)(0000)	4·468 (6)	O(*A*2)(0000)–O(*D*)(0000)	4·395 (6)
O(*D*)(0000)–O(*D*)(*m*000)	3·354 (6)	O(*A*2)(0000)–O(*B*)(*m*00*c*)	4·379 (7)
O(*A*1)(000*c*)–O(*B*)(000*c*)	2·688 (6)		

coordination polyhedron a word of caution is necessary about the different topochemistry of the two intermediate terms just mentioned. $BaGa_2Si_2O_8$ is in fact characterized by the largest difference between the *T* cations, whilst the difference is negligible for $BaAl_2Ge_2O_8$. Therefore, these two compounds are not expected to behave alike. For instance, we found that, passing from synthetic $BaAl_2Si_2O_8$ to $BaGa_2Ge_2O_8$, the unit-cell volume increases regularly with the *T*-cation size and so does the density. However, the density for $BaAl_2Ge_2O_8$ is slightly smaller than for $BaGa_2Si_2O_8$ despite the former having a larger framework (Gazzoni, 1973). It is difficult to rationalize all the experimental results owing to the complexity of the feldspar structure both from the geometrical and bonding points of view; the following empirical considerations may be drawn at any rate.

Within the coordination polyhedron, two important features are the triangle formed approximately in the x^*y plane by the atoms O(*A*1)(0), O(*A*1)(*c*) and O(*A*2) and the quadrilateral formed in the *yz* plane by O(*B*)(*c*), O(*B*)(*m*00*c*), O(*D*)(0), O(*D*)(*m*) (Megaw, 1974). The *M* cations are held in place very tightly within the triangle in all feldspars and the coordination becomes significantly tighter with increasing *T*-cation size. With the Ba feldspars, in fact, the ⟨Ba–O(*A*)⟩ distances are: 2·789 (4) for celsian, 2·774 (4) for $BaGa_2Si_2O_8$, 2·768 (4) for $BaAl_2Ge_2O_8$ and 2·75 (1) Å for $BaGa_2Ge_2O_8$. With the Sr feldspars, ⟨Sr–O(*A*)⟩ = 2·575 (4) and 2·558 (4) Å for $SrAl_2Si_2O_8$ and $SrGa_2Si_2O_8$ respectively. In this instance, therefore, the tightening of the coordination complies regularly with the expansion of the framework. On the other hand, the mean *M*–O distance over the four atoms of the quadrilateral stays practically constant for the Ba feldspars, ~2·92, and for the Sr feldspars, ~2·78 Å (Table 4 and Calleri & Gazzoni, 1976*b*). Here we may note that O(*B*)(*m*00*c*) is everywhere the farthest from *M*, except for the present compound where, simultaneously, the two diagonals O(*B*)(*m*00*c*)···O(*D*)(*m*) and O(*B*)(*c*)···O(*D*)(0) have very close lengths, 5·634 (6) and 5·642 (6) Å; in the other feldspars of Table 5, O(*B*)(*m*00*c*)···O(*D*)(*m*) is significantly longer than O(*B*)(*c*)···O(*D*)(0), with the partial exception of celsian. This agrees with the dimensional equivalence of the AlO_4 and GeO_4 tetrahedra: the pairs of distances Ba–O(*A*1), Ba–O(*B*), Ba–O(*D*) (Table 4) are similar for the present compound, while they are significantly different for $BaGa_2Si_2O_8$, characterized by *T* cations with very different size.

Among the individual distances, Ba–O(*A*2), 2·626 (5) Å, is the same as for $BaGa_2Ge_2O_8$ and is very short in comparison with the other distances. This distance, which appears to be moderately affected by the framework topochemistry in general, has shown in one instance an appreciable variation for a small change of composition, involving, however, both the *M* and *T* cations. $Ba_{0\cdot84}K_{0\cdot18}Al_{1\cdot90}Si_{2\cdot11}O_8$ shows Ba–O(*A*2) = 2·667 (7) Å (Newnham & Megaw, 1960) and $Ba_{0\cdot95}K_{0\cdot05}Al_{1\cdot95}Si_{2\cdot05}O_8$ shows 2·641 (5) Å (Griffen & Ribbe, 1976). Among the other distances, we noticed that the edge O(*A*1)(0)···O(*A*1)(*c*), shared between two coordination polyhedra, widens with decreasing *T*-cation size whilst the distance between nearest-neighbour Ba ions shortens. This trend is somewhat surprising since it implies a greater repulsion between the centrosymmetric Ba ions on passing from $BaGa_2Ge_2O_8$, everywhere metastable at atmospheric pressure (Gazzoni, 1973), to the stable $BaAl_2Si_2O_8$. It is possible that the *M* cations are so far apart in all feldspars that the repulsion effect is of secondary importance in determining the stability conditions and that the mentioned trend is a consequence of the 'collapse' of the larger feldspar frameworks for accommodating the *M* cation even when it is as large as Ba. At any rate, the present compound fits the overall trend of the O(*A*1)···O(*A*1) edge (Table 6 and Calleri & Gazzoni, 1976*b*). However, the distance is here

3·551 (6) Å, shorter than for celsian, 3·602 (7) Å, but slightly longer than for $BaGa_2Si_2O_8$, 3·534 (7) Å, which has a smaller framework. The nearest Ba ions are at 4·431 (1) Å in the present feldspar; that is slightly closer than for $BaGa_2Si_2O_8$ and $BaGa_2Ge_2O_8$, 4·444 (1) and 4·449 (1) Å, respectively; they are at 4·419 (1) Å in celsian (Griffen & Ribbe, 1976).

Kroll & Phillips (1976) noted that the type of M cation does not affect the overall $\langle\langle T\text{—O}\rangle\rangle$ means. The effect is clearly confirmed by all the results given in Table 6; however, it cannot be considered unexpected: with essentially covalent bonds, the bond sum over given pairs of TO_4 groups must remain constant. For instance, the $\langle\langle T\text{—O}\rangle\rangle$ mean for an orthorhombic modification of $SrAl_2Ge_2O_8$, which is completely disordered, is 1·738 Å and is therefore identical with the value for the present compound (Kroll *et al.*, 1976). Even with a different framework like that of the paracelsians, where the $\langle M\text{—O}\rangle$ values are significantly smaller than for the feldspars, the corresponding $\langle\langle T\text{—O}\rangle\rangle$ values are just slightly longer (Table 5).

Interbond angles

Table 2 shows the O—T—O angles and Table 5(a) the root mean square angular deviations, $\varepsilon_t(T)$, for a series of feldspars and paracelsians.* The angular distortions are very large as for all feldspars; the present $\varepsilon_t(T)$ values are comparable to those of $BaGa_2Si_2O_8$ and less marked than those of $BaGa_2Ge_2O_8$. The T(1) tetrahedra are consistently more distorted than the T(2), both here and in all feldspars. The effect has been related (Kroll & Phillips, 1976) to the larger number of elements shared between a tetrahedron and the M polyhedron: two more for the T(1) tetrahedra of the 14 Å monoclinic feldspars and the corresponding paracelsians. The $\varepsilon[T(2)]/\varepsilon[T(1)]$ ratio (Table 5) displays larger variations for the feldspars than for the paracelsians and this effect has been related to the more irregular nature of the M polyhedron in the feldspars (Kroll & Phillips, 1976).

The M- and T-cation size is not without influence on the angular distortions (Table 5). The Ba feldspars are generally less distorted than the Sr feldspars. On the other hand, given the M-cation type, an increase in the average T-cation size corresponds to an increase of the distortion: the aluminosilicates show the smallest and the gallogermanates the largest distortions both among the feldspars and the paracelsians. Experimentally, we found also that an increasing overall angular distortion corresponds to a shrinking stability field for the feldspar modification. At atmospheric pressure the feldspar field is confined to progressively higher temperatures passing from an Al/Si to a Ga/Ge framework, the effect being precluded with the Sr cation: $SrGa_2Ge_2O_8$, in fact, shows the paracelsian form only (Gazzoni, 1973; Calleri & Gazzoni, 1975a). With increasing T-cation size the expanded feldspar frameworks have to distort themselves more and more to accommodate not only the relatively small Sr, but also the larger Ba ion; the paracelsian modification, whose framework provides a tighter coordination, becomes progressively favoured.

Our additional results confirm the deductions of Kroll & Phillips (1976) about the influence of chemically different T cations on the distortion: the Ga tetrahedra are more distorted in the presence of Ge than in the presence of Si (and we may add that the Al tetrahedra display a similar behaviour); the Si tetrahedra are more distorted in the presence of Ga than in the presence of Al (Table 2b and Calleri & Gazzoni, 1976b). It is therefore apparent that the angular distortion is not simply due to the T-cation size difference. Nonetheless, it would be unjustified to argue, on the strength of this, that the above trend is due to bonding properties alone. The same T-cation pairs are characterized by different features in the, different, paracelsian framework which shows smaller distortions (Table 5).

The mean values $\langle T\text{—O—}T\rangle$ (Table 3) show a progressive shrinkage with increasing T-cation size, given a divalent cation, as noted elsewhere (Calleri & Gazzoni, 1976b). Among the individual values, the T—O(A2)—T angle, of paramount importance for the feldspar framework, nicely fits the trend since we have the sequence 134–135, 133, 131 and 129° for the celsians, $BaGa_2Si_2O_8$, $BaAl_2Ge_2O_8$ and $BaGa_2Ge_2O_8$ respectively. The shrinkage is consistent with the contraction of the stability field of the feldspar form (Gazzoni, 1973).

The effect of the T-cation pairs on the framework

In the feldspar framework the tetrahedral four-membered rings centred on the diad axes at $z = 0{\cdot}25$, 0·75 show closed sections with an elliptical shape: these sections are formed by T—O(B), —O(D) groups. The mean planes through the four T cations or the four O atoms of any section are orthogonal to the y axis even though at different levels, the O groups being much more planar than the T groups. The four-membered rings generated by the inversion centres at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{1}{4},\frac{1}{4},\frac{3}{4})$ also show quasi-elliptical sections formed by T—O(D), —O(C) groups (Fig. 1). Here both the groups of O and T atoms are necessarily planar; the T groups lie approximately on the $(\bar{2}13)$ plane. All the above sections appear elliptical even when the T sites

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* In previous papers (Calleri & Gazzoni, 1974, 1976a) we used, for the T sites in the paracelsian framework, a notation different from that of Phillips, Kroll, Pentinghaus & Ribbe (1975). We labelled $T(1)(m)$ and $T(2)(0)$ the paracelsian sites allocating the trivalent T cations as for the feldspars. Phillips *et al.* (1975) and Kroll & Phillips (1976) use the symbols T(1) for the T sites displaying the larger angular distortions both in the feldspars and paracelsians. The latter choice is more sensible, perhaps, and we adopted it in Table 5.

are topochemically equivalent, as in sanidine. In order to follow the influence of different *T*-cation pairs on the framework we defined a 'degree of ellipticity' as [*T*(2)–*T*(2)]/[*T*(1)–*T*(1)] for the *T* groups parallel to (010) and as [*T*(1)–*T*(1)]/[*T*(2)–*T*(2)] for the *T* groups approximately parallel to ($\bar{2}$13) (Calleri & Gazzoni, 1976*b*). Similar axial ratios can be defined, obviously, for the O atoms, but we prefer to consider the *T*–*T* distances for several reasons: they show standard deviations constantly <0·005 Å; within the rings parallel to (010) they nearly coincide with the **x*** and **z** directions (Fig. 1); they sum up interdependent factors like the different *T*–O pair lengths and the corresponding angles at *T* and O. Therefore these *T*–*T* distances appear expedient for characterizing the framework with different *T* cations. The pertinent values are given in Table 6 and they are to be compared with those for the other feldspars (Calleri & Gazzoni, 1976*b*).

Among the four independent four-membered rings, the more elliptical sections are those through the *T*(0) cations parallel to ($\bar{2}$13) and through the *T*(*z*) parallel to (010) (Table 6; Fig. 1). We found experimentally that in general the introduction of larger *T* cations reduces the ellipticity when it occurs at the ends of the major axes and increases the ellipticity when it occurs at the ends of the minor axes; *vice versa* for smaller cations. This is to be expected, actually, if the angular conformation (∠O–*T*–O, ∠*T*–O–*T*) does not change too much. Comparing now the present $BaAl_2Ge_2O_8$ with $BaAl_2Si_2O_8$, the smaller SiO_4 is replaced by the larger GeO_4 group at the ends of the major axes and we should expect a reduction of the ellipticity for the above *T*(0) and *T*(*z*) groups. The expected reduction does not take place; on the contrary we note a slight increase for the *T*(*z*) groups (Table 6), examining either the former results for celsian (Newnham & Megaw, 1960) or the recent refinement (Griffen & Ribbe, 1976) which yield practically identical values for the ellipticity. Comparing, on the other hand, $BaAl_2Ge_2O_8$ with $BaGa_2Ge_2O_8$, the larger GaO_4 are substituted by the smaller AlO_4 groups at the ends of the minor axes and here the expected ellipticity decrease is very marked (Table 6 and Calleri & Gazzoni, 1976*b*).

The 'more rounded' sections are those through the *T*(*z*) groups parallel to ($\bar{2}$13) and the *T*(0) groups parallel to (010). Repeating the above comparisons, we have now the introduction of GeO_4 groups at the ends of the minor axes and of AlO_4 groups at the ends of the major axes. In both cases the ellipticity increase for the present compound confirms the general trend.

On considering the mean ellipticity, ⟨*e*⟩, over the four independent groups of *T* cations, we note a regular increase as a function of the framework expansion, with $BaAl_2Ge_2O_8$ lying between $BaGa_2Si_2O_8$ and $BaGa_2Ge_2O_8$. The mean ellipticity is actually a quasi-linear function of the overall *T*–O mean as shown in Fig. 2. The deviations from the respective mean ellipticities are the largest for $BaGa_2Si_2O_8$ and the smallest for the present $BaAl_2Ge_2O_8$. This seems justified, since GaO_4 and SiO_4 are dimensionally very different whilst AlO_4 and GeO_4 are nearly equidimensional.

The metastable $BaGa_2Ge_2O_8$ shows not only the largest mean ellipticity, but also a scatter from the mean larger than expected with the Ga/Ge pair, the two cations being dimensionally closer than Al/Ge or Ga/Si.

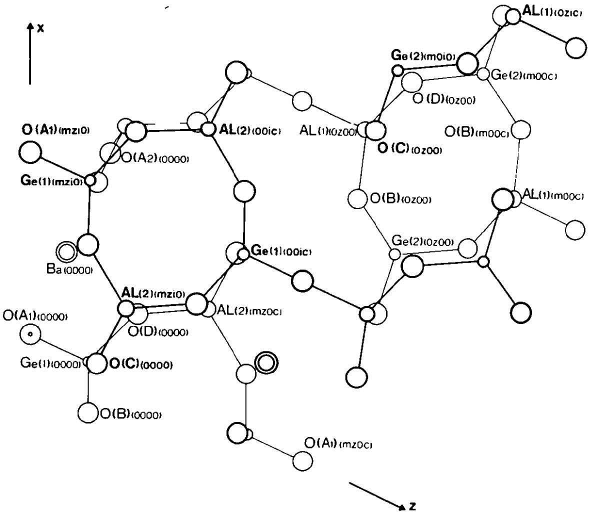

Fig. 1. Projection along [010] of a portion of the structure of $BaAl_2Ge_2O_8$ to show the atoms of Tables 1 and 6.

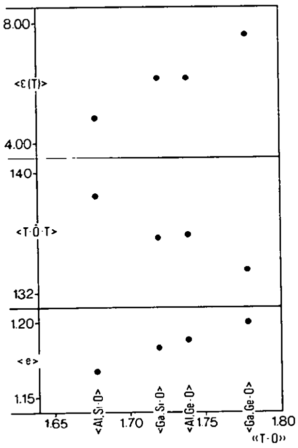

Fig. 2. Positive correlations *vs* the overall *T*–O means, for the Ba feldspars. From top to bottom: ⟨ε(*T*)⟩, overall r.m.s.d.'s for the O–*T*–O angles; ⟨*T*–O–*T*⟩, overall mean for the *T*–O–*T* angles; ⟨*e*⟩, mean ellipticity of the four-membered rings (see the text).

Conclusion

The results available so far warrant the following empirical conclusions. The M cation is very tightly coordinated by the triangle of atoms $O(A1)(0)$, $O(A1)(c)$, $O(A2)$; to the expansion of the framework (*e.g.* from $BaAl_2Si_2O_8$ to $BaGa_2Ge_2O_8$) corresponds a tightening of the coordination by these O atoms. At the same time the $\langle T{-}O{-}T\rangle$ angles shrink consistently and the overall r.m.s. deviations for the $O{-}T{-}O$ angles, $\langle\varepsilon(T)\rangle$, increase (Table 5). Since these trends are coupled with the progressive shrinkage of the stability field of the feldspar form in favour of the paracelsian form (Gazzoni, 1973) we may say that the 'instability' of the feldspar form is characterized by 'large distortions'.

The parameter $\langle M{-}O\rangle/\langle\langle T{-}O\rangle\rangle$, introduced by several authors (*e.g.* Kroll & Phillips, 1976), may be given a structural meaning in this context. It may be taken as a measure of the inverse of the volume that allocates the M cation. When the parameter becomes too small (the framework becomes too large) the feldspar structure is no longer stable, in the sense that it would require too large a 'collapse' of the framework, and the paracelsian structure becomes favoured at atmospheric pressure. From the experimental results we may tentatively fix 1·62 and 1·58 as critical $\langle M{-}O\rangle/\langle\langle T{-}O\rangle\rangle$ ratios for the Ba and Sr feldspars respectively (Table 5 and Calleri & Gazzoni, 1975*a*; Gazzoni, 1973). The feldspar $(Sr_{0.50}Ba_{0.50})Ga_2Si_2O_8$ shows the value 1·60, exactly intermediate between the above critical values. This is consistent with the results for the system $SrGa_2Si_2O_8$–$BaGa_2Si_2O_8$ which showed that this intermediate term is still characterized by a predominantly more stable paracelsian form.

Inserting in the diagram by Kroll & Phillips (1976, p. 291) the extra results of Table 5, it may be concluded that positive relations hold for $\langle T{-}O{-}T\rangle$ *vs* $\langle M{-}O\rangle/\langle\langle T{-}O\rangle\rangle$, but that they are only approximately linear. In particular, the feldspars $BaGa_2Si_2O_8$ and $BaAl_2Ge_2O_8$ are on opposite sides of the $BaAl_2Si_2O_8$–$BaGa_2Ge_2O_8$ line. We found the same situation for other positive relations that we noted.

Fig. 2 shows the correlations between the overall means, $\langle\varepsilon(T)\rangle$, of the r.m.s. deviations for the $O{-}T{-}O$ angles, and the $T{-}O{-}T$ means, and the overall $\langle\langle T{-}O\rangle\rangle$ means for the Ba feldspars; that is, these two diagrams show the trend of the angular distortions *vs* the composition.

The ratios between significant $T{-}T$ distances ('ellipticities') have been introduced for characterizing the influence of different T-cation pairs on the framework. The individual ratios are not a monotonic function of the T dimensions while the mean ratios are positively related to the $\langle\langle T{-}O\rangle\rangle$ means (or to the sum of the T-cation radii) (Fig. 2). Therefore, the progressive shrinkage of the stability field of the feldspar form is correlated also with the increase of the ellipticity of the four-membered rings. This has been verified for the Ba feldspars; the results for only two Sr feldspars have been published so far, but the above conclusions quite probably hold for the Sr feldspars too.

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