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The Structures of (Sr,Ba) [$(Al,Ga)_2(Si,Ge)_2O_8$]. III. The Crystal Structures of the Paracelsian-Like Modifications of Synthetic $SrGa_2Ge_2O_8$ and $BaGa_2Ge_2O_8$

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The structures of the title modifications of synthetic $SrGa_2Ge_2O_8$ and $BaGa_2Ge_2O_8$ have been determined from counter intensities and refined by Fourier and full-matrix least-squares methods. Both compounds crystallize in space group $P2_1/a$ with $Z=4$. The mean tetrahedral distances for $SrGa_2Ge_2O_8$ are: $\langle$Ge–O$\rangle$ = 1·748 (2), $\langle$Ga–O$\rangle$ = 1·829 (2) and for $BaGa_2Ge_2O_8$: $\langle$Ge–O$\rangle$ = 1·753 (4), $\langle$Ga–O$\rangle$ = 1·820 (4) Å. The two structures may be considered very highly, or completely, ordered. A comparison of the present results with those obtained for the paracelsian form of $SrGa_2Si_2O_8$ is given. The relations between the structural features and the stability conditions are briefly discussed.

Introduction

The isopolymorphism of the compounds with the general formula (Sr, Ba) [$(Al,Ga)_2(Si,Ge)_2O_8$] is characterized by two principal modifications (Smith, 1974): the first is similar to celsian (Newnham & Megaw, 1960), the second to paracelsian (Smith, 1953; Bakakin & Belov, 1961).

The present article is the third on these modifications and deals with the structure of the paracelsian forms of $SrGa_2Ge_2O_8$ and of $BaGa_2Ge_2O_8$ which were synthesized by Gazzoni (1973). The paracelsian modification turns out to be the more stable at atmospheric pressure, for both compounds.

The feldspar modification of the end members $SrGa_2Si_2O_8$ and $BaGa_2Si_2O_8$ was the subject of part I (Calleri & Gazzoni, 1975*a*) and the paracelsian modification of $SrGa_2Si_2O_8$ of part II (Calleri & Gazzoni, 1974). Part IV will deal with the structure of the feldspar form of $BaGa_2Ge_2O_8$. The structures of these end members have been recently illustrated at the Tenth International Congress of the IUCr (Calleri & Gazzoni, 1975*c*).

Structure determination

Experimental results

The analysis was based on crystals obtained from the melt and selected after examination under the microscope. Preliminary Weissenberg and precession photographs did not reveal any splitting or diffuseness of the spots. The systematic extinctions showed that both compounds belong to space group $P2_1/a$. The cell parameters were refined by a least-squares procedure based on θ values (Cu $K\alpha$ radiation) measured on powder spectra taken with a focusing camera. The intensities were measured on a diffractometer as explained below. The intensity difference between the reflexions of pairs hkl–$\bar{h}kl$ was, on average, less marked than for the paracelsian form of $SrGa_2Si_2O_8$ (Calleri & Gazzoni, 1974), but sufficient to confirm without ambiguity that the true symmetry of these compounds is monoclinic. The number of $0kl$ reflexions, with $k+l$ *odd*, having an intensity significantly different from zero, was here smaller than for $SrGa_2Si_2O_8$, which indicates that the two gallogermanates approach the symmetry *Pnam* (or $Pna2_1$) (*cf.* Smith, 1953).

(1) *Strontium gallogermanate*: $SrGa_2Ge_2O_8$, $M=500{\cdot}25$, monoclinic, $a=9{\cdot}210$ (8), $b=9{\cdot}666$ (8), $c=8{\cdot}570$ (7) Å, $\beta=90{\cdot}56$ (10)°; $U=762{\cdot}9$ Å^3; $D_c=4{\cdot}35$ g cm^{-3}; $Z=4$; space group $P2_1/a$; $F(000)=912$. Crystal dimensions: 0·100, 0·088, 0·134 mm across the opposite faces of {001}, {110} and {$\bar{1}$10} respectively. μ(Mo $K\alpha$) = 228·55 cm^{-1}.

The intensities were measured at room temperature with a Philips four-circle diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation). The conditions were: ω-step-scanning, integration speed 0·05° s^{-1}, integration interval 1·0°. The weaker reflexions were scanned four times and the measurements averaged. 1782 reflexions with $2\theta<60°$ had amplitudes significantly larger than the standard deviations based on counting statistics. Corrections for the Lorentz–polarization effects for monochromatized radiation and for absorption (Hamilton, 1966) were applied.

(2) *Barium gallogermanate*: $BaGa_2Ge_2O_8$, $M=549{\cdot}98$, monoclinic, $a=9{\cdot}349$ (6), $b=9{\cdot}903$ (6), $c=8{\cdot}770$ (5) Å, $\beta=90{\cdot}36$ (7)°; $U=811{\cdot}9$ Å^3; $D_c=4{\cdot}50$ g cm^{-3}; $Z=4$; space group $P2_1/a$; $F(000)=984$. Crystal dimensions:

0·087 mm along z (the elongation direction), with a cross-section 0·022 × 0·077 mm^2. μ(Mo $K\alpha$) = 195·80 cm^{-1}.

The intensities were measured as for the Sr compound but with the conditions: θ–2θ step-scanning, integration speed 0·06° s^{-1}, integration interval 1·2°. 1744 reflexions had amplitudes significantly above background. No correction was made for absorption because the crystal was bounded by rather small fracture facets difficult to index, even if idealized, and to measure accurately.

Structure solution and refinement

The structure of both compounds was solved by interpretation of sharpened Patterson syntheses (E maps) followed by computation of Fourier and difference syntheses. The Ge atoms occupy the tetrahedral sites of the Si atoms in $SrGa_2Si_2O_8$ (Calleri & Gazzoni, 1974).

Scattering factors were from Cromer & Mann (1968); the correction for anomalous dispersion by Sr, Ba, Ga and Ge was introduced from the beginning; all atoms were considered neutral except Sr and Ba which were assumed to be doubly ionized.

Refinement was started by block-diagonal isotropic least squares. The vibrational parameters at the end of the isotropic refinement were much smaller for the Sr than for the Ba compound. For the former, B was 0·4 for Sr, 0·22 for Ga and Ge, and ranged between 0·6 and 1·10 Å^2 for the O atoms; for the latter, B was 0·85 for Ba, 0·60 for Ga and Ge, and ranged between 0·92 and 1·13 for atoms of type O(1), O(2) and O(3), whilst it was 1·50 for O(4) and 1·58 Å^2 for O(5).

Since in the Fourier maps the peaks did not show undue ellipsoidal character, the refinement was completed by full-matrix anisotropic cycles with *ORFLS* (Busing, Martin & Levy, 1962) with minor modifications. No abnormal value was noticed among the correlation matrix elements throughout the refinement. The following weighting scheme was used ($|F_o|$ on absolute scale):

$$w = \frac{20}{A + |F_o| + B|F_o|^2} \quad \text{for } |F_o| \geq 20$$

$$w = K \quad \text{for } |F_o| \leq 20 \,.$$

The final values given to the coefficients were: $A = 25$; $B = 0{\cdot}0155$; $K = 0{\cdot}220$ for $SrGa_2Ge_2O_8$; $A = 25$; $B = 0{\cdot}0093$; $K = 0{\cdot}25$ for $BaGa_2Ge_2O_8$, which gave a satisfactory constancy of the $\langle |w\Delta^2| \rangle$ values when the reflexions were batched in several ways.

In the course of the refinement of $SrGa_2Ge_2O_8$ most of the strongest reflexions appeared affected by secondary extinction and were temporarily given zero

Table 1. *Fractional coordinates and vibrational parameters* (× 10^4) *of* $SrGa_2Ge_2O_8$ *with the significant figures of the standard deviations in parentheses*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sr	8853 (1)	4127 (1)	2498 (1)	25 (1)	15 (0)	18 (1)	1 (0)	−2 (0)	−1 (0)
Ge(1) (0)	564 (1)	1992 (1)	9411 (1)	14 (1)	11 (1)	11 (1)	−1 (0)	0	0
Ga(1) (*m*)	527 (1)	1942 (1)	5689 (1)	14 (1)	11 (1)	13 (1)	0	−1 (0)	1 (1)
Ga(2) (0)	2355 (1)	9243 (1)	9324 (1)	14 (1)	13 (1)	14 (1)	0	−1 (1)	−1 (1)
Ge(2) (*m*)	2427 (1)	9206 (1)	5621 (1)	12 (1)	13 (1)	13 (1)	1 (0)	1 (0)	1 (0)
O(1) (0)	1938 (5)	921 (5)	10175 (6)	24 (5)	27 (4)	28 (6)	9 (4)	−8 (4)	−9 (4)
O(1) (*m*)	1910 (5)	798 (5)	4844 (6)	25 (5)	17 (4)	38 (6)	7 (4)	5 (4)	10 (4)
O(2) (0)	1160 (5)	3708 (5)	9350 (6)	31 (5)	9 (4)	39 (6)	−7 (4)	−15 (4)	7 (4)
O(2) (*m*)	1184 (5)	3736 (5)	5681 (6)	26 (5)	18 (4)	31 (5)	−7 (3)	9 (4)	−7 (4)
O(3) (0)	9146 (5)	1971 (5)	10753 (6)	15 (4)	28 (5)	38 (6)	−7 (4)	3 (4)	−10 (4)
O(3) (*m*)	8999 (5)	1971 (5)	4310 (5)	23 (4)	27 (5)	24 (5)	−5 (4)	−7 (4)	9 (4)
O(4)	11 (6)	1362 (6)	7606 (5)	52 (6)	35 (5)	15 (5)	−16 (4)	6 (4)	−2 (4)
O(5)	3303 (5)	9248 (6)	7442 (6)	23 (5)	60 (6)	16 (5)	−3 (4)	1 (4)	−4 (5)

Table 2. *Fractional coordinates and vibrational parameters* (× 10^4) *of* $BaGa_2Ge_2O_8$ *with the significant figures of the standard deviations in parentheses*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	8912 (1)	4118 (1)	2502 (1)	18 (1)	21 (1)	46 (1)	2 (0)	−3 (1)	0
Ge(1) (0)	633 (1)	1963 (1)	9376 (1)	10 (1)	16 (1)	37 (1)	−1 (1)	−2 (1)	−1 (1)
Ga(1) (*m*)	609 (1)	1933 (1)	5700 (1)	8 (1)	13 (1)	38 (1)	0	−3 (1)	0
Ga(2) (0)	2306 (1)	9205 (1)	9330 (1)	9 (1)	18 (1)	41 (1)	0	−2 (1)	0
Ge(2) (*m*)	2352 (1)	9179 (1)	5633 (1)	9 (1)	19 (1)	39 (1)	1 (0)	−2 (1)	0
O(1) (0)	1990 (8)	883 (8)	10062 (9)	11 (7)	30 (7)	89 (12)	6 (5)	−15 (6)	−10 (7)
O(1) (*m*)	1974 (8)	789 (8)	4932 (9)	23 (7)	18 (6)	60 (10)	7 (5)	11 (6)	12 (7)
O(2) (0)	1218 (8)	3648 (8)	9420 (9)	23 (7)	33 (7)	51 (10)	2 (6)	−21 (6)	−2 (7)
O(2) (*m*)	1239 (8)	3657 (8)	5580 (9)	18 (7)	21 (7)	56 (10)	−2 (5)	16 (6)	−5 (7)
O(3) (0)	9231 (8)	1907 (8)	10689 (9)	24 (8)	35 (7)	34 (9)	−5 (6)	13 (6)	−4 (7)
O(3) (*m*)	9110 (8)	1928 (8)	4375 (9)	32 (8)	19 (7)	50 (9)	0	−7 (6)	5 (7)
O(4)	56 (9)	1471 (9)	7581 (9)	30 (8)	62 (9)	50 (10)	−24 (7)	−6 (7)	−1 (8)
O(5)	3146 (8)	9133 (8)	7442 (9)	16 (7)	48 (9)	62 (10)	−9 (6)	−10 (7)	4 (8)

weight. In the final stage of the refinement a correction for this effect was introduced with a program written by G. Chiari (personal communication); by a least-square procedure we deduced for the function:

$$I_c/I_o = K(1+gI_c)\ ,$$

$K=0·923$ and $g=1·747\times10^{-6}\ e^{-2}$. This correction greatly improved the overall agreement; at convergence R was 4·3%, or 4·1% ($wR=5·0$%) on excluding 60 reflexions, most of them very weak, with discrepancies >20% and which were given zero weight in the final cycles because they were probably affected by experimental errors. The final positional and vibrational parameters are listed in Table 1; the β_{ij} are the coefficients of the expression: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. No correction for secondary extinction was applied to $BaGa_2Ge_2O_8$ since the effect was very small: $K=0·996$, $g=0·96\times10^{-7}$. The final R was 6·6% or 5·8% ($wR=6·9$%) on excluding 97 reflexions with discrepancies >20%, which were given zero weight in the final cycles. R is therefore significantly greater than for the Sr compound. The effect may be ascribed, at least partly, to the failure to apply an absorption correction. In this connexion, we ran a refinement of the $SrGa_2Ge_2O_8$ parameters with the amplitudes not corrected for absorption: the positional parameters obtained did not differ significantly from those listed in Table 1 from which we presume that the correction for absorption is not of paramount importance in our case.

The final parameters for $BaGa_2Ge_2O_8$ are listed in Table 2. The standard deviations of the coordinates of the O atoms are larger than for the Sr compound, due, in part, to the presence of the heavier Ba cation. The effect of the heavy cations Ga, Ge, Sr and Ba on the accuracy of the parameters of the light O atoms has been already noted (Calleri & Gazzoni, 1975*a*).

The differences between the vibrational parameters of the two compounds reduced in the course of the anisotropic refinement, but the final thermal parameters of the Ba are greater than those of the Sr compound. In Table 3 are given the elements characterizing the vibrational ellipsoids referred to their own principal axes; as for the paracelsian form of $SrGa_2Si_2O_8$ (Calleri & Gazzoni, 1974), we report the root-mean-square displacements with the angles α_{ij} between

Table 3. *Parameters characterizing the vibrational ellipsoids referred to their own principal axes*

	Axis	$SrGa_2Ge_2O_8$ r.m.s.d. (Å)	α_{ix}	α_{iy}	α_{iz}
Sr	1	0·086	103°	21°	106°
	2	0·106	16	80	102
	3	0·080	82	72	21
Ge(1) (0)	1	0·070	74	21	103
	2	0·078	18	107	94
	3	0·064	83	79	13
Ga(1) (*m*)	1	0·074	66	34	68
	2	0·079	27	106	112
	3	0·067	79	119	31
Ga(2) (0)	1	0·077	41	131	90
	2	0·082	55	48	119
	3	0·068	72	69	29
Ge(2) (*m*)	1	0·071	32	121	81
	2	0·080	62	31	78
	3	0·068	104	96	15
O(1) (0)	1	0·088	119	43	61
	2	0·137	59	47	121
	3	0·084	45	90	46
O(1) (*m*)	1	0·101	31	84	121
	2	0·132	66	62	39
	3	0·070	109	29	111
O(2) (0)	1	0·088	43	92	47
	2	0·146	131	76	44
	3	0·055	79	14	99
O(2) (*m*)	1	0·090	131	82	42
	2	0·130	52	117	51
	3	0·079	65	28	79
O(3) (0)	1	0·101	110	53	43
	2	0·137	104	46	133
	3	0·070	24	66	85
O(3) (*m*)	1	0·094	38	54	100
	2	0·130	116	43	58
	3	0·078	65	110	33
O(4)	1	0·108	57	34	86
	2	0·165	34	124	84
	3	0·073	98	90	7
O(5)	1	0·099	5	85	88
	2	0·169	94	6	94
	3	0·077	93	86	4

	Axis	$BaGa_2Ge_2O_8$ r.m.s.d. (Å)	α_{ix}	α_{iy}	α_{iz}
Ba	1	0·103	72°	15°	88°
	2	0·135	98	90	8
	3	0·087	17	105	83
Ge(1) (0)	1	0·088	96	6	88
	2	0·120	96	92	6
	3	0·064	8	85	84
Ga(1) (*m*)	1	0·080	90	0·3	90
	2	0·123	97	90	7
	3	0·059	8	90	83
Ga(2) (0)	1	0·096	89	1	89
	2	0·127	94	91	4
	3	0·062	4	91	86
Ge(2) (*m*)	1	0·098	86	4	91
	2	0·124	95	88	5
	3	0·062	6	94	86
O(1) (0)	1	0·119	83	16	75
	2	0·193	102	103	18
	3	0·058	13	100	80
O(1) (*m*)	1	0·099	37	65	115
	2	0·163	72	71	26
	3	0·079	121	32	97
O(2) (0)	1	0·127	91	8	82
	2	0·159	120	98	31
	3	0·069	31	93	60
O(2) (*m*)	1	0·101	88	11	80
	2	0·158	68	100	25
	3	0·073	22	88	112
O(3) (0)	1	0·122	67	44	55
	2	0·142	118	46	122
	3	0·083	38	86	128
O(3) (*m*)	1	0·113	25	77	69
	2	0·147	113	80	25
	3	0·096	98	16	104
O(4)	1	0·141	99	98	12
	2	0·191	117	27	87
	3	0·086	29	64	78
O(5)	1	0·149	90	43	133
	2	0·166	107	49	46
	3	0·074	17	79	78

their directions and the cell axes. The thermal motion is small, particularly for $SrGa_2Ge_2O_8$ whose cations show also a modest degree of anisotropy. On the other hand, the anisotropy is marked for the cations of $BaGa_2Ge_2O_8$ whose ellipsoids are nicely oriented along the cell axes; it may be noted that the latter effect occurs also, to some extent, in danburite, $CaB_2Si_2O_8$, which has a similar framework (Phillips, Gibbs & Ribbe, 1974).*

Scrutiny of the structures

The framework

The distinctive features of the structures of the paracelsian modifications were illustrated elsewhere (Calleri & Gazzoni, 1974, 1975*b*). In this section we compare the conformational aspects of the framework of the paracelsian form of $SrGa_2Si_2O_8$, $SrGa_2Ge_2O_8$ and $BaGa_2Ge_2O_8$.

The corresponding atoms of the three compounds are characterized by similar fractional coordinates, [Tables 1 and 2 and the corresponding table in Calleri & Gazzoni (1974)], and the three unit cells show very similar axial ratios; hence a single figure is sufficient for the comparison and discussion of the results. Fig. 1 is the orthographic projection along [001] of the part of the structure bounded approximately by the planes $z=0{\cdot}25$ and $z=1{\cdot}0$. The atoms which form the tetrahedral layers nearly orthogonal to [001], linked by O(4) and O(5), have been distinguished* by the symbol 0 when they belong to the layer at $z\simeq 1$ (or zero) and by the symbol *m* when they belong to the layer at $z\simeq 0{\cdot}5$ (Tables 1 and 2 and Fig. 1). We note that the pairs of atoms of type 0 and *m* of the present gallogermanates are placed more symmetrically than those of $SrGa_2Si_2O_8$ with respect to the pseudo-symmetry planes at $z=\frac{1}{4},\frac{3}{4}$; the effect is more apparent for $BaGa_2Ge_2O_8$. Therefore the gallogermanates of Sr and Ba approach the orthorhombic symmetry, neglecting the alternation of Ga

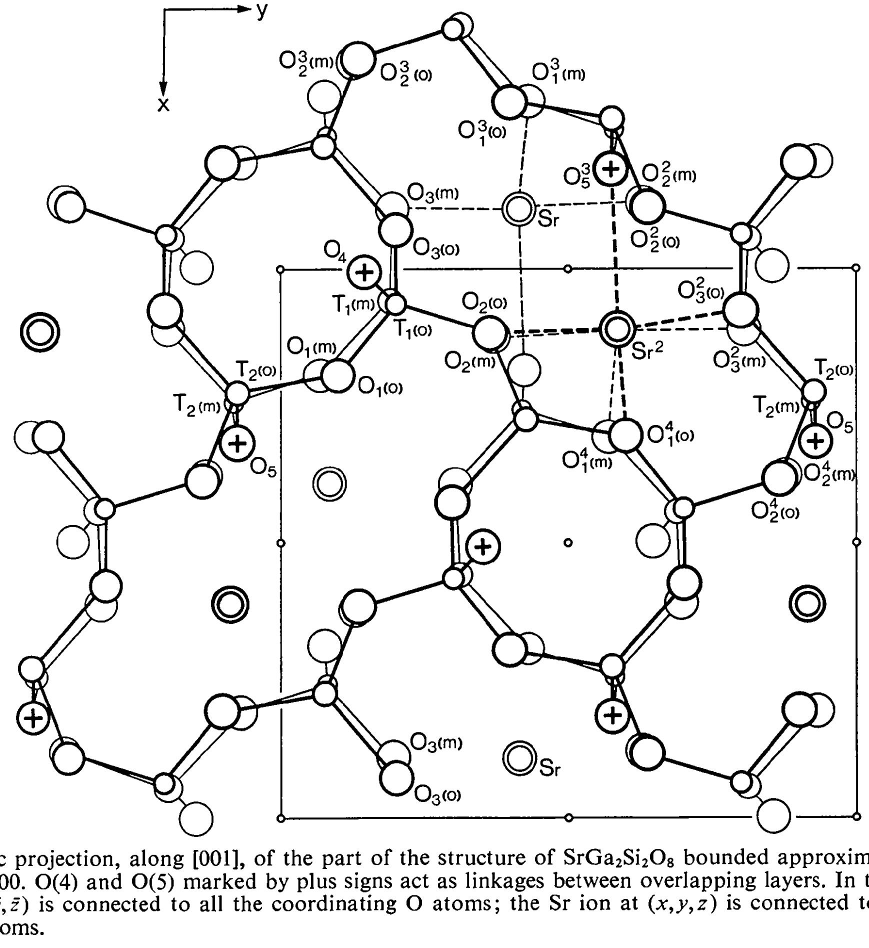

Fig. 1. Orthographic projection, along [001], of the part of the structure of $SrGa_2Si_2O_8$ bounded approximately by the planes $z=0{\cdot}25$ and $z=1{\cdot}00$. O(4) and O(5) marked by plus signs act as linkages between overlapping layers. In the upper right part the Sr ion at $(\bar{x},\bar{y},\bar{z})$ is connected to all the coordinating O atoms; the Sr ion at (x,y,z) is connected to a part only of the coordinating O atoms.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31385 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* The atoms have also been distinguished, when necessary, with superscripts which refer to the equivalent positions: $1=(x,y,z,$ of Tables 1 and 2); $2=(\bar{x},\bar{y},\bar{z})$; $3=(\frac{1}{2}+x,\frac{1}{2}-y,z)$; $4=(\frac{1}{2}-x,\frac{1}{2}+y,\bar{z})$. Translations of whole periods are not marked.

and Ge in the tetrahedral sites, more closely than the Sr gallosilicate. This is consistent with the values of the β angles of the respective unit cells and the relative intensity of the $0kl$ reflexions with $k+l$ *odd*. Fig. 1 is actually the projection of the structure of $SrGa_2Si_2O_8$ because it shows most clearly the departure from orthorhombic symmetry.

In the present gallogermanates the whole framework adapts itself to different divalent cations by only small readjustments of the tetrahedral groups; the interatomic distances most significant for following this adaptation are given in Table 4, which includes some results for $SrGa_2Si_2O_8$, not given in part II of this series (Calleri & Gazzoni, 1974). The cavities containing the divalent cations, which in Fig. 1 appear outlined by the eight-membered rings and which are better illustrated in Figs. 2 and 3, have in fact a very similar conformation (Table 4).

Table 4. *Interatomic distances* (Å) *defining the dimensions of the four- and eight-membered rings nearly orthogonal to z with the significant figures of the e.s.d.'s in parentheses*

The + signs distinguish the edges of the coordination polyhedron, formed by pairs of atoms coordinating the same divalent cation.

	$SrGa_2Si_2O_8$	$SrGa_2Ge_2O_8$	$BaGa_2Ge_2O_8$
$T_1^1(0)$—$T_1^2(0)$	4·069 (1)	4·117 (1)	4·212 (2)
$T_2^1(0)$—$T_2^2(0)$	4·519 (1)	4·733 (1)	4·747 (2)
$T_1^1(m)$–$T_1^2(m)$	3·944 (1)	4·052 (1)	4·177 (2)
$T_2^1(m)$–$T_2^2(m)$	4·742 (1)	4·836 (1)	4·813 (2)
$O_2^1(0)$–$O_2^2(0)$	3·467 (5)	3·477 (7)	3·664 (11)
$O_2^1(m)$–$O_2^2(m)$	3·426 (6)	3·470 (7)	3·668 (11)
$O_2^3(0)$–$O_2^4(0)$	9·818 (6)	10·126 (7)	10·157 (11)
$O_2^3(m)$–$O_2^4(m)$	9·844 (6)	10·154 (7)	10·151 (11)
$O_1^4(0)$–$O_2^1(0)$ +	2·810 (6)	2·792 (7)	2·812 (7)
$O_1^4(m)$–$O_2^1(m)$ +	2·523 (6)	2·697 (7)	2·732 (7)
$O_1^4(0)$–$O_3^2(0)$ +	2·870 (6)	2·918 (7)	3·077 (10)
$O_1^4(m)$–$O_3^2(m)$ +	2·911 (5)	2·929 (7)	3·058 (11)
$O_2^1(0)$–$O_3^2(0)$ +	4·141 (5)	4·187 (7)	4·424 (11)
$O_2^1(m)$–$O_3^2(m)$ +	4·122 (6)	4·152 (7)	4·385 (12)
$O_2^1(0)$–$O_2^1(m)$ +	3·196 (5)	3·145 (7)	3·369 (12)
$O_3^2(0)$–$O_3^2(m)$ +	3·084 (5)	3·053 (7)	3·236 (11)
$O_1^4(0)$–$O_1^4(m)$ +	4·001 (5)	4·003 (7)	4·273 (10)
$O_1^3(0)$–$O_1^3(m)$	4·428 (5)	4·571 (7)	4·500 (12)
$O_2^2(0)$–$O_2^2(m)$	5·213 (5)	5·426 (7)	5·403 (11)
$O_3^1(0)$–$O_3^1(m)$	5·346 (5)	5·522 (7)	5·539 (11)
M^1——M^2	4·977 (1) 4·892 (1)	5·083 (1) 5·052 (1)	5·153 (1) 5·126 (1)

The first M–M distance refers to cations related by the inversion centre at $(0,\frac{1}{2},1)$, the second distance to cations related by the centre at $(0,\frac{1}{2},\frac{1}{2})$.

The structure of the feldspar modification is characterized by two families of four-rings which are nearly orthogonal to y and to x of the feldspar cell; their conformation is not very different for the Sr and Ba compounds studied by us and listed in the *Introduction*. In the structure of the paracelsian modifications, the four-rings nearly parallel to z of the paracelsian cell (x of the feldspar cell; Gazzoni, 1973) are very distorted while the rings nearly orthogonal to this axis, which participate in the formation of the eight-membered rings (Fig. 1), retain a conformation comparable to that of the feldspars. It is interesting to follow the variations of these latter rings as a function of the dimensions of the tetrahedral (T) and divalent (M) cations.

The rings show a quasi-elliptical section and we may use the T–T distances for defining empirically the 'degree of ellipticity': $(T_2\text{–}T_2^2)/(T_1\text{–}T_1^2)$. The rings are elliptical also in paracelsian (Smith, 1953; Bakakin & Belov, 1961) and in danburite (Johansson, 1959; Phillips *et al.*, 1974).

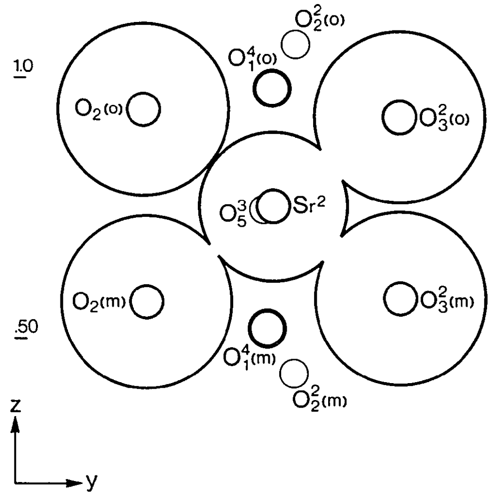

Fig. 2. Projection along [100] of the environment of the Sr ion of $SrGa_2Ge_2O_8$. The position of all the atoms is indicated by small circles; the atoms $O_2^2(0)$ and $O_2^2(m)$ do not coordinate the Sr ion. The atoms lying approximately on a plane normal to [100] are represented by large circles whose radii are proportional to the ionic radius of Sr or to the van der Waals radius of O.

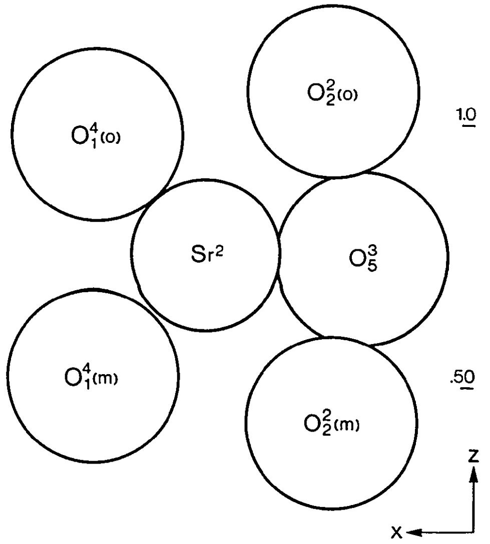

Fig. 3. Projection along [010] of the part of the environment of Sr of $SrGa_2Ge_2O_8$ formed by the atoms lying approximately on a plane normal to [010].

In Table 4 are given the T_1–T_1 and T_2–T_2 distances for the rings of type 0 and for the rings of type *m*. From the experimental results it is evident that the ellipticity varies between the rings of type 0 and *m* for the same compound and between the corresponding rings of the two gallogermanates. Assuming that these rings must be elliptical even when the tetrahedral sites are topochemically equivalent,* the introduction of larger T cations at the ends of the major axes, T_2–T_2, should reduce the ellipticity. If this is true, the rings of type 0 should be less elliptical than those of type *m* (Fig. 1). The $(T_2–T_2^2)/(T_1–T_1^2)$ ratios for the rings are:

	$SrGa_2Si_2O_8$	$SrGa_2Ge_2O_8$	$BaGa_2Ge_2O_8$
type 0	1·110	1·150	1·127
type *m*	1·202	1·193	1·152

The results are therefore consistent with the prediction. For $BaGa_2Ge_2O_8$ the two rings are more alike than expected, but $BaGa_2Ge_2O_8$ approaches orthorhombic symmetry more closely than the other two compounds.

When comparing the gallosilicate with the two gallogermanates, we would expect, since the dimensions of Ga and Ge are closer than those of Ga and Si, that the ellipticity for the 0 rings should increase and that of the *m* rings should decrease (Fig. 1), the two families of rings tending to an intermediate degree of ellipticity. The results show the expected trend with the possible exception of the *m* ring of $SrGa_2Ge_2O_8$ whose ratio is close to that for $SrGa_2Si_2O_8$.

Obviously, factors other than the tetrahedral cations must be taken into account for explaining the trend of

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* It may be noted that in the structure of danburite, where the corresponding sites at elevation 0 and ½ are topochemically equivalent, the rings should show a similar elliptical character; hey are actually identical, to attain the symmetry *Pnma* Phillips *et al.*, 1974).

Table 5. *Tetrahedral bond distances* (Å) *and angles* (°) *for* $SrGa_2Ge_2O_8$

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

Ge(1) (0) –O(1) (0)	1·757 (5)	Ga(1) (*m*)–O(1) (*m*)	1·841 (5)	Ga(2) (0)–O(1) (0)	1·821 (5)	Ge(2) (*m*)–O(1) (*m*)	1·742 (5)
–O(2) (0)	1·749 (5)	–O(2) (*m*)	1·837 (5)	–O(2) (0)	1·844 (5)	–O(2) (*m*)	1·765 (5)
–O(3) (0)	1·749 (5)	–O(3) (*m*)	1·830 (5)	–O(3) (0)	1·815 (5)	–O(3) (*m*)	1·740 (5)
–O(4)	1·734 (5)	–O(4)	1·805 (5)	–O(5)	1·842 (5)	–O(5)	1·751 (5)

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

	O(1)–O(2)	O(1)–O(3)	O(1)–O(4)	O(1)–O(5)	O(2)–O(3)	O(2)–O(4)	O(2)–O(5)	O(3)–O(4)	O(3)–O(5)	Mean
Ge(1) (0)	110·2	106·8	109·3		105·5	113·3		111·6		109·5
Ga(1) (*m*)	109·7	106·6	111·2		103·6	112·8		112·7		109·4
Ga(2) (0)	99·3	115·3		116·9	113·7		100·6		109·7	109·3
Ge(2) (*m*)	100·5	112·8		116·3	113·9		103·8		109·1	109·4

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

	O(1)–O(2)	O(1)–O(3)	O(1)–O(4)	O(1)–O(5)	O(2)–O(3)	O(2)–O(4)	O(2)–O(5)	O(3)–O(4)	O(3)–O(5)	Mean
Ge(1) (0)	2·875	2·814	2·847		2·784	2·910		2·880		2·852
Ga(1) (*m*)	3·007	2·943	3·008		2·881	3·033		3·025		2·983
Ga(2) (0)	2·792	3·071		3·121	3·062		2·837		2·990	2·979
Ge(2) (*m*)	2·697	2·900		2·967	2·938		2·768		2·843	2·852

Table 6. *Tetrahedral bond distances* (Å) *and angles* (°) *for* $BaGa_2Ge_2O_8$

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

Ge(1) (0) –O(1) (0)	1·763 (8)	Ga(1) (*m*)–O(1) (*m*)	1·838 (8)	Ga(2) (0)–O(1) (0)	1·808 (8)	Ge(2) (*m*)–O(1) (*m*)	1·745 (8)
–O(2) (0)	1·756 (8)	–O(2) (*m*)	1·810 (8)	–O(2) (0)	1·842 (8)	–O(2) (*m*)	1·776 (8)
–O(3) (0)	1·751 (8)	–O(3) (*m*)	1·815 (8)	–O(3) (0)	1·811 (8)	–O(3) (*m*)	1·754 (8)
–O(4)	1·731 (8)	–O(4)	1·792 (9)	–O(5)	1·838 (9)	–O(5)	1·748 (8)

(*b*) Bond angles at tetrahedral sites (e.s.d. ≤0·4)

	O(1)–O(2)	O(1)–O(3)	O(1)–O(4)	O(1)–O(5)	O(2)–O(3)	O(2)–O(4)	O(2)–O(5)	O(3)–O(4)	O(3)–O(5)	Mean
Ge(1) (0)	110·2	107·2	111·0		104·5	112·5		111·0		109·4
Ga(1) (*m*)	109·4	107·4	112·7		102·4	113·0		111·3		109·4
Ga(2) (0)	100·8	115·5		115·3	114·4		101·7		108·2	109·3
Ge(2) (*m*)	101·8	114·4		115·4	113·4		103·0		108·3	109·4

(*c*) Oxygen–oxygen distances in tetrahedra (e.s.d. ≤0·011 Å)

	O(1)–O(2)	O(1)–O(3)	O(1)–O(4)	O(1)–O(5)	O(2)–O(3)	O(2)–O(4)	O(2)–O(5)	O(3)–O(4)	O(3)–O(5)	Mean
Ge(1) (0)	2·886	2·829	2·880		2·773	2·899		2·870		2·856
Ga(1) (*m*)	2 977	2 943	3·021		2·826	3·003		2·978		2·958
Ga(2) (0)	2·812	3·060		3·080	3·072		2·853		2·955	2·972
Ge(2) (*m*)	2·732	2·941		2·951	2·949		2·757		2·837	2·861

the results of Table 4; equally important are the dimensions of the divalent cations and the capability of adaptation of the framework. We shall therefore conclude this section with some considerations on the dimensions of the cavity containing the M cations. The eight-rings (Fig. 1) enlarge passing from $SrGa_2Si_2O_8$ to the two gallogermanates. The longer diagonals, O_2^3–O_2^4, increase from about 9·83 for $SrGa_2Si_2O_8$ to about 10·15 Å for the gallogermanates, and the shorter diagonals, O_2^1–O_2^2, from about 3·47 for $SrGa_2Ge_2O_8$ to about 3·67 Å for $BaGa_2Ge_2O_8$; the two Sr compounds, however, show similar lengths. The distances between the pairs O(1)(0) and O(1)(*m*), O(2)(0) and O(2)(*m*), O(3)(0) and O(3)(*m*), which coordinate the same M cation and which belong to two overlapping eight-rings, do not increase from $SrGa_2Si_2O_8$ to $SrGa_2Ge_2O_8$; on the other hand, a marked increase is shown by the Ba compound. These distances, in fact, define the 'thickness' of that part of the cavity which contains a Sr ion for both compounds (Figs. 1 and 2) and the ⟨Sr–O⟩ values are identical for $SrGa_2Si_2O_8$ and $SrGa_2Ge_2O_8$: 2·621 (2) and 2·625 (2) Å respectively. On the other hand, the O(0)–O(*m*) distances for the pairs of atoms not coordinating the same M cation, *i.e.* those determining the 'thickness' of that part of the cavity not occupied by divalent cations, increase markedly from $SrGa_2Si_2O_8$ to $SrGa_2Ge_2O_8$. The increment of the *c* parameter of the unit cells ($c=8\cdot407$ and 8·570 Å for $SrGa_2Si_2O_8$ and $SrGa_2Ge_2O_8$ respectively) due to the substitution of SiO_4 by GeO_4 groups, is therefore taken up, here, mainly by the dilatation of the empty part of the cavity. An opposite trend is shown by $SrGa_2Ge_2O_8$ and $BaGa_2Ge_2O_8$ which have a tetrahedral framework of the same dimensional type; for $BaGa_2Ge_2O_8$ the distances which show a marked increase are those between the pairs of O atoms coordinating the same M cation. In conclusion, the framework changes its shape mainly by movements, along the normal to the eight-rings, of the atoms of the layers at elevation ≃0·5 with respect to those at elevation ≃0·0 and 1·0.

Bond distances and interbond angles

The tetrahedral bond distances and angles are given in Tables 5, 6, 7 and 8; the distances for the coordination polyhedra around the divalent cations are reported in Table 9.

The pure Ga–O tetrahedral bond length seems to be 1·83 Å (Stewner & Hoppe, 1971; Cotton & Wilkinson, 1972); the ⟨Ge–O⟩ distance is 1·74 Å for the quartz-like modification of GeO_2 (Smith & Isaacs, 1964), but other results indicate a longer length: 1·75–1·76 Å (*e.g.* Peacor, 1968; Fang, Townes & Robinson, 1969). The ⟨Ge–O⟩ values reported in Table 7 do not differ significantly from 1·75 Å; the ⟨Ga–O⟩ values for $SrGa_2Ge_2O_8$ are equal to 1·83 Å within the standard deviations, whilst for $BaGa_2Ge_2O_8$ they are somewhat shorter. In order to verify whether these results might be interpreted in terms of a limited Ga/Ge substitutional disorder, we calculated the bond strengths for the tetrahedral bonds from the function proposed by Brown & Shannon (1973) and their empirical coefficients. The function is of the form $s=s_0\,(R/R_0)^{-N}$, where s_0 is the ideal bond strength associated with a bond of length R_0; the coefficients R_0 and N were deduced by Brown & Shannon, for several cations, by least-squares procedures from the results of many X-ray investigations. An important result, for our purpose, is that the sums of the bond strengths over the T cations must be equal, within 5%, to the valence of the cations if the structural model is topochemically correct; this assumption is valid also when the bond is primarily covalent.

Table 7. *Tetrahedral means and r.m.s. values of the deviations for a tetrahedron* $\epsilon_t(r)$

	$SrGa_2Ge_2O_8$		$BaGa_2Ge_2O_8$	
	Mean	$\epsilon_t(r)$	Mean	$\epsilon_t(r)$
Ge(1) (0)	1·747 (2) Å	0·008 Å	1·750 (4) Å	0·012 Å
Ga(1) (*m*)	1·828 (2)	0·014	1·814 (4)	0·016
Ga(2) (0)	1·830 (2)	0·013	1·825 (4)	0·015
Ge(2) (*m*)	1·749 (2)	0·010	1·756 (4)	0·012

Table 8. *Germanium–oxygen–gallium bond angles* (*e.s.d.* ≤ 0·5°)

	$SrGa_2Ge_2O_8$	$BaGa_2Ge_2O_8$
Ge(1) (0)–O(1) (0)–Ga(2) (0)	122·0°	123·8°
Ge(2) (*m*)–O(1) (*m*)–Ga(1) (*m*)	124·6	125·0
Ge(1) (0)–O(2) (0)–Ga(2) (0)	118·6	122·0
Ge(2) (*m*)–O(2) (*m*)–Ga(1) (*m*)	119·1	123·6
Ge(1) (0)–O(3) (0)–Ga(2) (0)	123·9	127·7
Ge(2) (*m*)–O(3) (*m*)–Ga(1) (*m*)	123·0	127·1
Ge(1) (0)–O(4)——Ga(1) (*m*)	128·7	132·5
Ge(2) (*m*)–O(5)——Ga(2) (0)	124·2	129·5
	Mean 123·0	Mean 126·4

The sums of the bond strengths are reported in Table 10 for the paracelsian modifications of $SrGa_2Si_2O_8$, $SrGa_2Ge_2O_8$ and $BaGa_2Ge_2O_8$. For the first compound we had found: ⟨Si–O⟩ = 1·631 and 1·621 Å, ⟨Ga–O⟩ = 1·826 and 1·832 Å, for the four independent tetrahedra (Calleri & Gazzoni, 1974). From the parameters derived by Brown & Shannon without correcting for the oxygen coordination number, the bond strengths sums are within 5% of the expected values except perhaps for the Ga tetrahedra of $BaGa_2Ge_2O_8$ which show an excess of bond strength, though the Ge tetrahedra do not show a corresponding decrement (Table 10). All the sums take the ideal values, within 3%, if one uses for the calculation of the Ge–O and Si–O strengths the coefficients not corrected for the oxygen coordination and for the Ga–O strengths the coefficients corrected for the oxygen coordination (Table 10). This amounts to saying either that the bond-strength calculations are not accurate enough for determining a limited degree of disorder or that the ideal lengths to be introduced in the Brown & Shannon function are 1·625, 1·822 and 1·750 Å for Si–O, Ga–O and Ge–O, with N equal to 4·5, 5·2 and

5·4 respectively; the ideal bond strength s_0 is obviously unity for Si and Ge, and 0·75 for Ga in tetrahedral coordination.

The sums, over the O atoms, of the bond strengths from the two bonded T cations were calculated with both the corrected and non-corrected parameters and also with corrected parameters for Ga and non-corrected parameters for Ge or Si. The sums never exceed 1·80 except for atoms O(4) which do not coordinate the M cations (Fig. 1). The difference of these sums from 2 gives a measure of the bond strengths from the O atoms to the divalent cations. The sums of these differences are given in the last three rows of Table 10, calculated, respectively, with corrected, non-corrected and mixed parameters. It is clear that the most sensible results are, again, those obtained with corrected parameters for the Ga cations and with non-corrected parameters for the Ge or Si cations.

Even though at the moment we are not able to assign a precise value to the pure Ga–O and Ge–O bond lengths, we may say that the present gallogermanates appear to be, at least, very highly ordered; only the means for the T(*m*) tetrahedra of $BaGa_2Ge_2O_8$ may suggest a slight substitutional disorder (Table 7).

The scatter of the individual T–O bonds around the tetrahedral means [Tables 5(*a*), 6(*a*) and 7] is not very large and is less marked than for the feldspars (Calleri & Gazzoni, 1975*a*). The T–O(4)–T bonds are significantly longer than the rest and this agrees with the fact that the O(4) atoms do not take part in the coordination of the M cations and are, therefore, more strongly bound to the tetrahedral cations; the T–O (4)–T angles are, consequently, larger than the others (Table 8). The distortions of the tetrahedra (Tables 5 and 6) are comparable with those found for $SrGa_2Si_2O_8$ (Calleri & Gazzoni, 1974).

Two quantitative differences between the feldspar and the paracelsian modifications of our synthetic compounds should be noted. The first concerns the coordination of the divalent cations, much tighter for the paracelsian forms, and is considered in the next section. The second concerns the T–O–T angles. Their mean values for the paracelsian form of $SrGa_2Si_2O_8$, $SrGa_2Ge_2O_8$ and $BaGa_2Ge_2O_8$ are respectively: 125·7, 123·0 and 126·4° [Table 8 and the corresponding table in Calleri & Gazzoni (1974)]. The corresponding feldspar modifications are characterized by ⟨T–O–T⟩ values about 10° larger and by a scatter of angular values between 123° and 146°; here all the angles are between 119° and 129°, the only exception being the T–O(4)–T angles. $SrGa_2Ge_2O_8$ shows the smallest value not only for ⟨T–O–T⟩, but for the T–O(2)–T angles as well (≃119°); in this large tetrahedral framework the T–O(2)–T angles need to shrink greatly in order that the O(2) atoms may still exert a screening effect between neighbouring Sr cations (Fig. 1). Despite the fact that a paracelsian framework with Ga and Ge in the tetrahedral sites looks, at first sight, too large for the Sr ion, $SrGa_2Ge_2O_8$ shows only the paracelsian modification (Gazzoni, 1973).

Environment of the divalent cations

The divalent cations have seven nearby O neighbours, within 2·71 Å for the Sr and within 2·81 Å for the Ba compound; for both compounds there are two other O atoms, of type O(2), at a much longer distance, about 3·5 Å (Table 9 and Figs. 2 and 3). If the latter

Table 9. *Environment of strontium and barium (within* 3·5 Å)

Sr–O_1^3 (0)	2·648 (5) Å	Ba–O_1^3 (0)	2·786 (8) Å
O_1^3 (*m*)	2·706 (5)	O_1^3 (*m*)	2·809 (8)
O_2^1 (0)	2·625 (5)	O_2^1 (0)	2·784 (8)
O_2^1 (*m*)	2·589 (5)	O_2^1 (*m*)	2·777 (8)
O_3^1 (0)	2·581 (5)	O_3^1 (0)	2·724 (8)
O_3^1 (*m*)	2·602 (5)	O_3^1 (*m*)	2·727 (8)
O_5^4	2·622 (5)	O_5^4	2·751 (8)
Mean	2·625 (2)	Mean	2·765 (3)
Sr–O(2) (0) (at $1+x,y,1-z$)	3·474 (5)	Ba–O(2) (0) (at $1+x,y,1-z$)	3·499 (8)
Sr–O(2) (*m*) (at $1+x,y,z$)	3·476 (5)	Ba–O(2) (*m*) (at $1+x,y,z$)	3·487 (8)

Table 10. *Sums of the bond strengths s_i, over the* T *cations, calculated using individual parameters not corrected for the oxygen coordination, column* I, *or corrected, column* II; *for the sums over the* M *cations, see text*

	$SrGa_2Ge_2O_8$			$BaGa_2Ge_2O_8$			$SrGa_2Si_2O_8$	
	$\sum s_i$			$\sum s_i$			$\sum s_i$	
	I	II		I	II		I	II
Ge(1) (0)	4·035	3·855	Ge(1) (0)	4·001	3·821	Si(1) (0)	3·942	3·756
Ge(2) (*m*)	4·008	3·830	Ge(2) (*m*)	3·932	3·759	Si(2) (*m*)	4·025	3·828
Ga(1) (*m*)	3·072	2·949	Ga(1) (*m*)	3·192	3·076	Ga(1) (*m*)	3·048	2·970
Ga(2) (0)	3·053	2·930	Ga(2) (0)	3·101	2·980	Ga(2) (0)	3·070	2·926
M	1·699			1·680			2·112	
	2·221			2·105			2·332	
	1·918			1·892			2·006	

atoms were to be included in the coordination sphere, the coordination of O(2) (0) and O(2) (*m*) would be fourfold. The T–O(2) distances, however, are significantly longer than the rest only for the Ge(2)(*m*) tetrahedra of both compounds and not for the other tetrahedra (Tables 5 and 6) [compare hurlbutite, $CaBe_2P_2O_8$, which has a similar structure (Lindbloom, Gibbs & Ribbe, 1974)]. Besides, O(5) exerts a screening effect on these farther O(2) atoms as can be seen from the scale diagram of Fig. 3. Therefore the coordination is sevenfold as for the feldspar modifications, but here no O atom coordinates two M cations and only one atom, O(4), does not participate in the coordination.

The shape of the coordination polyhedron is similar for the three compounds we are considering and may be approximated, as for the feldspars, to a distorted cube with one corner missing and another, O(5), shifted to lie on the bisector of the O(1) (0)–M–O(1) (*m*) angle [*cf.* also Megaw, Kempster & Radoslovich (1962)]. The cube edges are approximately parallel to [110], [$\bar{1}$10] and [001] (Figs. 1 and 2). While in the feldspar forms we have four edges shared between tetrahedra and coordination polyhedron, here we have only two tetrahedral edges, O_1^4–O_2^1 (Fig. 1), which are simultaneously edges of the M polyhedron.

The nearest-neighbour M cations are related by the inversion centre at $(0,\frac{1}{2},1)$ and $(0,\frac{1}{2},\frac{1}{2})$, (Table 4 and Fig. 1); their mutual repulsion is partly shielded by the centrosymmetric pairs of O(2) atoms, which are in a position allowing them to exert a screening effect because of the values of the T–O (2)–T angles that are narrower than the rest (Table 8).

The coordination is more compact for the paracelsian than for the feldspar modifications: $\langle$Sr–O$\rangle$ = 2·684 and 2·621 Å for the feldspar and paracelsian form of $SrGa_2Si_2O_8$ (Calleri & Gazzoni, 1975*a*, 1974); $\langle$Ba–O$\rangle$ = 2·84 and 2·765 Å respectively for $BaGa_2Ge_2O_8$ (results to be published and Table 9); for the paracelsian form of $SrGa_2Ge_2O_8$, $\langle$Sr–O$\rangle$ = 2·625 Å (Table 9) and this compound does not show the feldspar form. However, all the M–O distances of the paracelsian forms are not shorter than the sums of the commonly accepted radii, excepting perhaps Ba–O(3) (0) and Ba–O(3) (*m*) of $BaGa_2Ge_2O_8$ (Table 9). We noted elsewhere (Calleri & Gazzoni, 1975*a* and the references quoted there) that for Sr and Ba in sevenfold coordination the M–O distances are often shorter than the expected values (~2·53 and 2·75 Å respectively) and that probably no particular meaning, from the bonding point of view, can be attached to this effect.

Besides being tighter, the coordination around the M cations is decidedly more regular; the scatter from the mean of the M–O distances is smaller here than for the feldspars by a factor of 3 and the effect is particularly apparent for $BaGa_2Ge_2O_8$ (Table 9).

We have noted that the anisotropy is appreciable for $BaGa_2Ge_2O_8$ and also for the paracelsian form of $SrGa_2Si_2O_8$. The anisotropy of the Ba ion might be accounted for in terms of its large polarizability, but the anisotropy of the T cations and the orientation of their ellipsoids is not easy to explain. Grundy & Ito (1974) found a comparable effect for a non-stoichiometric, disordered, Sr feldspar and attributed the thermal behaviour to substitutional and positional disorder. In our case, however, neither the chemical analyses nor the difference maps suggested an alkali deficiency or positional disorder. The amplitude of the thermal motion and the character of anisotropy are not significantly greater than for the fully ordered anorthite (Wainwright & Starkey, 1971).

Structural features and crystallochemical properties

It has been found experimentally that the expansion of the framework due to the introduction of larger anionic groups causes a progressive contraction of the stability field of the feldspar modification and shifts it towards higher temperatures, whilst the denser paracelsian form, which initially is the modification stable at lower temperatures, becomes, in the end, the sole stable form at atmospheric pressure. On the other hand, the introduction of larger divalent cations opposes this effect (Gazzoni, 1973; Calleri & Gazzoni, 1975*b*, and results to be published). Among the three compounds examined in this article, $SrGa_2Si_2O_8$ and $BaGa_2Ge_2O_8$ are characterized by a paracelsian modification stable practically over the whole field of a temperature *vs.* composition diagram, with the feldspar modification crystallizing at the boundary of the field; $SrGa_2Ge_2O_8$ does not show the feldspar form and its only stable modification is the paracelsian. We suggested, when considering the unit-cell volume variations as a function of the dimensions of the divalent cations (Calleri & Gazzoni, 1975*b*), that the different linkage between adjacent chains of the four-rings makes the paracelsian more flexible than the feldspar framework, in agreement with the deductions of Smith (1968). The relations between flexibility and stability need, however, a closer examination. The paracelsian framework might actually enlarge appreciably by rotation, in opposite senses, of the contiguous chains of four-rings connected by the O(2) atoms, with a simultaneous expansion along *z*. In this way, the eight-membered rings, and the cavity defined by them, could so round themselves as to bring to comparable distances the two pairs of O(2)(0) and O(2)(*m*) atoms belonging to the eight-membered ring (shorter and longer diagonals of the ring, Fig. 1). This dilatation should make room for larger M cations, but, actually, the new cavity does not turn out to be better for accommodating M cations: the nearest-neighbour cations would have lost the shielding effect of the O(2) atoms. Experimentally we find that the tetrahedral groups undergo small tilts only and that the coordination polyhedron keeps a constant shape for the different compounds.

The paracelsian framework with Ga and Si in the tetrahedral sites just fits the Sr ion and that with Ga and Ge just fits the Ba ion. This latter, large, cation seems to have the effect of keeping the framework atoms in positions simulating more closely orthorhombic symmetry. The framework with Ga and Ge is more than large enough for the Sr ion, but we found that the paracelsian is the sole stable form for $SrGa_2Ge_2O_8$. The adaptation of this framework to the Sr ion takes place with an appreciable collapse which manifests itself in a smaller $\langle$T–O–T$\rangle$ value and a greater ellipticity of the four-rings.

Despite the fact that the T–O–T angles for the paracelsian are smaller, by about 10°, than for the feldspar modifications, the three compounds examined in this article are characterized by a paracelsian form stable at room conditions. This result contrasts with the expectations of Takéuchi, Haga & Ito (1973) who tentatively assumed that a decrease of the T–O–T angles is related to the metastability of the modification showing it. Actually we might assign (Gazzoni, 1973) a greater degree of stability to the paracelsian form of $SrGa_2Ge_2O_8$, which has $\langle$T–O–T$\rangle = 123°$, than to that of the other two compounds with $\langle$T–O–T$\rangle \simeq 126°$. The small $\langle$T–O–T$\rangle$ value is therefore characteristic of the paracelsian framework which can probably remain perfectly stable until too small a size for the M cations would require an excessive collapse and too narrow T–O–T angles. It is interesting to note that in $SrGa_2Si_2O_8$ the $O_1^4(0)$–$O_3^2(0)$ distance (2·870 Å) is just longer than the sum of the van der Waals radii; this means that a further collapse of the framework to accommodate smaller cations would be very difficult.

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