

The Structures of the Ordered Synthetic Feldspars $\text{SrGa}_2\text{Si}_2\text{O}_8$, $\text{BaGa}_2\text{Si}_2\text{O}_8$ and $\text{BaGa}_2\text{Ge}_2\text{O}_8$

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The structures of three ordered synthetic feldspars, $\text{SrGa}_2\text{Si}_2\text{O}_8$, $\text{BaGa}_2\text{Si}_2\text{O}_8$ and $\text{BaGa}_2\text{Ge}_2\text{O}_8$, have been refined by conventional X-ray methods. Their common space group is $I2/c$, $Z = 8$ and their lattice parameters, in the above-mentioned order, are: $a = 8.4857$ (8), $b = 13.1412$ (9), $c = 14.4462$ (17) Å, $\beta = 115.459$ (6)°; $a = 8.7262$ (6), $b = 13.2117$ (7), $c = 14.6001$ (11) Å, $\beta = 115.059$ (4)°; $a = 8.8931$ (11), $b = 13.5248$ (12), $c = 14.9076$ (20) Å, $\beta = 114.803$ (9)°. A ninefold coordination model can be applied for the M cations (Sr and Ba). The $\langle M-O \rangle$ distances were found to be 2.796, 2.910 and 2.916 Å. The tetrahedral bond-length distortions and the angular O–T–O distortions are mainly governed by the spatial distribution of edges and corners shared between tetrahedra and M polyhedra. Modifying influences arise from the size of the M cations, the mean T–O bond lengths and the tetrahedral cation combination. The $T1$ tetrahedra are more distorted than the $T2$ tetrahedra with respect to both bond lengths and angles which can be rationalized in terms of edge and corner sharing. Multiple linear-regression analysis of the T–O bond lengths shows no correlation with T–O–T angles, whereas significant correlations exist for the parameters $\langle O-T-O \rangle_3$ and $\Sigma d(M-O)^{-2}$.

Introduction

At present the structures of seven stoichiometric alkaline-earth feldspar compounds have been refined: $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Megaw, Kempster & Radoslovich, 1962; Wainwright & Starkey, 1971), $\text{SrAl}_2\text{Si}_2\text{O}_8$ (Chiari, Calleri, Bruno & Ribbe, 1975), $\text{BaAl}_2\text{Si}_2\text{O}_8$ (Newnham & Megaw, 1960; Griffen & Ribbe, 1976), $\text{SrGa}_2\text{Si}_2\text{O}_8$, $\text{BaGa}_2\text{Si}_2\text{O}_8$ and $\text{BaGa}_2\text{Ge}_2\text{O}_8$ (Calleri & Gazzoni, 1975, 1976) and $\text{SrAl}_2\text{Ge}_2\text{O}_8$ (Phillips, Kroll & Peninghaus, in preparation). This paper presents structural data for the feldspars $\text{SrGa}_2\text{Si}_2\text{O}_8$, $\text{BaGa}_2\text{Si}_2\text{O}_8$ and $\text{BaGa}_2\text{Ge}_2\text{O}_8$ which are abbreviated as SGSF, BGSF and BGGF by use of the initial letters of the alkaline-earth (M) and the tetrahedral (T) cations, and the letter F to denote the feldspar structure type.

These refinements are part of an investigation of compounds having the general chemical formula $M^{1+}T_1^{3+}T_3^{4+}O_8$ and $M^{2+}T_2^{3+}T_2^{4+}O_8$, where M is an alkali or alkaline-earth cation, T^{3+} may be B, Al, Ga or Fe, and T^{4+} may be Si or Ge. In addition to the feldspar, paracelsian, hexacelsian and hollandite modifications of these compounds, two other structure types have been reported. One is an orthorhombic variation of the feldspar structure (space group $Fddd$) reported for $\text{SrAl}_2\text{Ge}_2\text{O}_8$ by Peninghaus & Kroll (1975). The other is a new type of framework reported for $\text{CaAl}_2\text{Si}_2\text{O}_8$ by Takeuchi, Haga & Ito (1973). The

$\text{CaAl}_2\text{Si}_2\text{O}_8$ structure is monoclinic (space group $P2_1/a$); topologically identical orthorhombic frameworks (space group $Pnam$) have been found in $\text{NaAlGe}_3\text{O}_8$ (Kroll, Löns & Peninghaus, 1974) and in $\text{NaGaGe}_3\text{O}_8$ (Nabbe, 1975).

Detailed interpretation of the steric behaviour in these structures requires refinements of high precision and accuracy. Recent results on SGSF, BGSF and BGGF reported by Calleri & Gazzoni (1975, 1976) (hereinafter CG) enable a comparison to be made. The crystals used in their and in our studies are not identical, but were grown by a similar process. There are, however, a number of discrepancies. Whereas the bond-angle data are similar, the differences in bond-length data are greater than expected, which is particularly true for BGGF where the standard deviations associated with CG's data are about four to five times larger than ours. Deviation of the results could originate from differences in the real structure of the crystals and/or differences in the process of data collection and handling. A comparison of the results cannot reveal the sources of the observed deviations, but can only classify the results as being consistent or inconsistent with previously published data.

Experimental details and refinement

The feldspars treated in this study represent the stable high-temperature polymorphs of the respective chemical compositions. Suitable single crystals were grown from the melt.

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The lattice parameters (Table 1) have been determined by means of a Guinier–Jagodzinski powder camera employing monochromatized Cu K α radiation ($\lambda = 1.54051 \text{ \AA}$). The powder samples were taken from the same charges as the single crystals. ‘Specpure’ Si previously calibrated against the Parrish (1960) silicon ($a_0 = 5.43054 \text{ \AA}$ at 25°C) served as internal standard. 51 lines for SGSF, 58 lines for BGSF, and 50 lines for BGGF could be indexed unambiguously. The lattice parameters were refined with the least-squares program *LCLSQ* of Burnham (1962). Systematic extinctions on precession photographs indicate the common space group to be *Ic* (No. 9) or *I2/c* (No. 15). The centrosymmetric space group was preferred so as to be consistent with all previous feldspar refinements.

Intensity data were collected on a Picker FACS-1 automated four-circle diffractometer with a scintillation counter employing Nb-filtered Mo K α radiation and using a θ – 2θ scan (for details see Table 2). Corrections

for background, Lorentz–polarization effects and absorption were applied. All reflexions with $|F_o|$ less than four times the standard deviation in $|F_o|$ (Stout & Jensen, 1968) were considered to be unobserved and were not included in the refinements.* The atomic coordinates of celsian (Newnham & Megaw, 1960) served as starting data. Atomic scattering factors for neutral atoms (Doyle & Turner, 1968) were employed and corrections for anomalous dispersion were applied with the coefficients of Cromer (1965). Correction for extinction effects was made (Stout & Jensen, 1968). The weighting scheme was chosen so that the variation of $w(\Delta F)^2$ was independent of the magnitude of $|F_o|$ as was suggested by Cruickshank (1965).* Tables 2–7 list *R* factors, atomic and thermal parameters, interatomic distances and angles, and site populations.

M-cation coordination

In many feldspars it is difficult to determine the coordination number of the *M* cation because the *M*–O distances increase gradually without any well-defined break. One indirect crystal–chemical approach to the problem is to utilize the fact that individual *T*–O bond lengths depend in part on the coordination number of

Table 1. *Lattice parameters*

Estimated standard errors in Tables 1–7 are given in parentheses and refer to the last decimal place.

	SGSF	BGSF	BGGF
<i>a</i> (Å)	8.4857 (8)	8.7262 (6)	8.8931 (11)
<i>b</i> (Å)	13.1412 (9)	13.2117 (7)	13.5248 (12)
<i>c</i> (Å)	14.4462 (17)	14.6001 (11)	14.9076 (20)
β (°)	115.459 (6)	115.059 (4)	114.803 (9)
<i>V</i> (Å ³)	1454.5 (4)	1524.8 (2)	1627.7 (5)
<i>D_x</i> (g cm ⁻³)	3.756	4.016	4.488

* Lists of structure factors, anisotropic temperature factors and the coefficients of the weighting scheme have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32993 (66 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Experimental details*

a and *b* refer to reflexions of type *a* ($h + k = \text{even}, l = \text{even}$) and type *b* ($h + k = \text{odd}, l = \text{odd}$).

	SGSF	BGSF	BGGF
(a) Data collection			
Scan speed (°2 θ min ⁻¹)	0.5	1.0	1.0 <i>a</i> 0.5 <i>b</i>
Scan width (°2 θ) (without α_1 – α_2 separation)	1.2	1.2	1.2
Total background counting time (s)	80	40	40 <i>a</i> 80 <i>b</i>
Range of data collection (sin θ/λ)	0.10–0.76	0.22–0.81	0.22–0.70
Number of scale factors	2	1	2
Number of non-zero reflexions	970 <i>a</i> 716 <i>b</i> 1686	1595 <i>a</i> 1090 <i>b</i> 2685	1318 <i>a</i> 911 <i>b</i> 2229
(b) Crystal shape, size and linear absorption coefficient			
Shape	Tetragonal prism	Sphere	Oblate ellipsoid of revolution
Size (mm)	0.05 × 0.14 × 0.14	0.153 (7)	0.154 (5)/0.180 (9)
μ (Mo K α) (cm ⁻¹)	157.8	129.2	195.4
(c) <i>R</i> factors (%)			
$R = \sum F_o - F_c / \sum F_o $	5.2	2.9	3.4
$wR = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	4.8	3.0	3.3

Table 3. Atomic coordinates ($\times 10^4$) and isotropic temperature factors

	x	y	z	B (\AA^2)
SGSF				
Sr	2671 (1)	-33 (1)	664 (1)	1.33 (3)
T1(0) (Si)	59 (3)	1731 (2)	1056 (3)	0.71 (7)
T1(z) (Ga)	0 (1)	1791 (1)	6189 (1)	0.65 (3)
T2(0) (Ga)	6943 (1)	1230 (1)	1703 (1)	0.62 (3)
T2(z) (Si)	6794 (5)	1106 (4)	6708 (2)	0.79 (6)
OA(1)	57 (8)	1256 (4)	1 (4)	1.13 (13)
OA(2)	5850 (5)	1 (4)	1431 (4)	0.88 (12)
OB(0)	8303 (8)	1230 (5)	1033 (4)	1.25 (13)
OB(z)	7982 (7)	1237 (5)	6091 (5)	1.34 (13)
OC(0)	67 (8)	2944 (5)	1151 (5)	1.64 (15)
OC(z)	118 (8)	3158 (5)	6308 (5)	1.37 (13)
OD(0)	1872 (8)	1255 (5)	1925 (5)	1.53 (14)
OD(z)	2005 (7)	1162 (5)	7058 (5)	1.30 (13)
BGSF				
Ba	2805 (0)	3 (0)	652 (0)	0.97 (1)
T1(0) (Si)	84 (1)	1806 (1)	1060 (1)	0.52 (4)
T1(z) (Ga)	47 (1)	1843 (0)	6189 (0)	0.60 (2)
T2(0) (Ga)	7072 (1)	1255 (0)	1737 (0)	0.57 (2)
T2(z) (Si)	6943 (1)	1128 (1)	6737 (1)	0.49 (4)
OA(1)	42 (4)	1341 (2)	1 (2)	0.82 (6)
OA(2)	6127 (4)	-2 (3)	1439 (3)	1.11 (7)
OB(0)	8383 (4)	1321 (3)	1066 (3)	1.24 (8)
OB(z)	8071 (4)	1338 (3)	6117 (3)	1.35 (9)
OC(0)	131 (4)	3021 (2)	1151 (3)	1.24 (8)
OC(z)	238 (4)	3192 (2)	6341 (2)	1.00 (7)
OD(0)	1846 (4)	1325 (3)	1903 (2)	1.27 (8)
OD(z)	1963 (4)	1187 (3)	7052 (2)	1.25 (8)
BGGF				
Ba	2758 (0)	4 (0)	670 (0)	0.87 (1)
T1(0) (Ge)	31 (1)	1800 (1)	1085 (2)	0.52 (1)
T1(z) (Ga)	11 (1)	1820 (1)	6151 (2)	0.54 (1)
T2(0) (Ga)	6985 (3)	1219 (2)	1738 (0)	0.48 (1)
T2(z) (Ge)	6916 (2)	1157 (2)	6734 (0)	0.48 (1)
OA(1)	17 (4)	1295 (3)	-3 (2)	0.60 (8)
OA(2)	5990 (5)	9 (2)	1469 (3)	1.04 (10)
OB(0)	8217 (6)	1274 (3)	1035 (3)	1.16 (9)
OB(z)	8077 (7)	1286 (3)	6047 (3)	1.17 (9)
OC(0)	71 (5)	3072 (3)	1207 (4)	1.11 (8)
OC(z)	100 (5)	3142 (3)	6293 (4)	1.13 (8)
OD(0)	1885 (5)	1287 (4)	1938 (3)	1.17 (9)
OD(z)	1917 (5)	1229 (3)	6987 (3)	1.23 (9)

the O atom. Megaw *et al.* (1962) noted that in anorthite the T -O bond lengths tend to increase with increasing coordination number.

Phillips, Ribbe & Gibbs (1973) tested a number of Ca coordination models in anorthite based on multiple regression analyses in which individual T -O bond lengths were assumed to be the dependent variables and a number of structural parameters (one of which gauged the influence of the M cation) were treated as independent variables. Although such a statistical approach may not yield a unique coordination number, it is helpful in reaching a decision.

Table 4. Tetrahedral bond lengths (\AA)

	SGSF	BGSF	BGGF
T1(0)-OA(1)	1.646 (8)	1.650 (3)	1.755 (4)
-OB(0)	1.616 (6)	1.619 (3)	1.736 (4)
-OC(0)	1.601 (6)	1.609 (4)	1.728 (4)
-OD(0)	1.636 (7)	1.637 (4)	1.748 (4)
$\langle T1(0)-O \rangle$	1.625 (Si)	1.629 (Si)	1.742 (Ge)
T1(z)-OA(1)	1.838 (6)	1.831 (3)	1.844 (4)
-OB(z)	1.810 (6)	1.810 (3)	1.811 (4)
-OC(z)	1.803 (6)	1.795 (3)	1.798 (4)
-OD(z)	1.822 (6)	1.830 (3)	1.815 (4)
$\langle T1(z)-O \rangle$	1.818 (Ga)	1.817 (Ga)	1.817 (Ga)
T2(0)-OA(2)	1.819 (6)	1.823 (4)	1.824 (4)
-OB(0)	1.798 (6)	1.796 (3)	1.807 (4)
-OC(0)	1.804 (6)	1.814 (3)	1.820 (4)
-OD(0)	1.796 (6)	1.804 (3)	1.803 (4)
$\langle T2(0)-O \rangle$	1.804 (Ga)	1.809 (Ga)	1.814 (Ga)
T2(z)-OA(2)	1.626 (8)	1.627 (4)	1.746 (4)
-OB(z)	1.617 (6)	1.618 (4)	1.742 (4)
-OC(z)	1.608 (6)	1.621 (3)	1.746 (4)
-OD(z)	1.631 (6)	1.617 (4)	1.750 (4)
$\langle T2(z)-O \rangle$	1.621 (Si)	1.621 (Si)	1.746 (Ge)

If the M -O distances in SGSF, BGSF and BGGF are arranged in increasing order, there is a large natural break for each structure between the ninth [OC(0)] and tenth [OA(2)] O atoms (Table 6). It is then necessary to decide whether or not the OC atoms are bonded to the M cation. Regression analyses of individual T -O bond lengths *versus* the weighted coordination number, $\Sigma d(M-O)^{-2}$, show that a ninefold coordination model in two of three cases yields slightly larger correlations than does a sevenfold coordination model (Table 10). The following discussion is based on a ninefold coordination, although such a choice is somewhat questionable in irregular structures like feldspars.

Order-disorder

The tetrahedral site occupancies (Table 7) indicate that both SGSF and BGSF are slightly disordered; however, the large errors arising from the similar scattering curves of Ga and Ge preclude such determination for BGGF, which is considered to be completely ordered. With the given occupancies assumed to be correct, the mean T -O bond lengths for pure Si- and Ga-containing tetrahedra were calculated. These 'corrected values', the observed mean distances and those determined by CG (1975) are given in Table 7.

Although CG did not perform site refinements, comparison of the respective mean T -O bond lengths in the two SGSF structures indicates that their crystal is fully ordered and that the slight disorder indicated in our crystal is probably real. The similarity of the 'corrected' mean bond lengths for BGSF and SGSF suggests that the substitution of Ba for Sr has very little

Table 5. Tetrahedral O...O distances (Å) and O-T-O angles (°)

	SGSF		BGSF		BGGF	
	O...O distances	O-T-O angles	O...O distances	O-T-O angles	O...O distances	O-T-O angles
T1(0) tetrahedron						
OA(1)-OB(0)	2.519 (8)	101.1 (3)	2.533 (5)	101.6 (2)	2.652 (5)	98.9 (2)
-OC(0)	2.770 (9)	117.1 (3)	2.763 (4)	116.0 (2)	2.992 (6)	118.4 (2)
-OD(0)	2.534 (8)	101.1 (4)	2.547 (4)	101.6 (2)	2.665 (5)	99.0 (2)
OB(0)-OC(0)	2.669 (9)	112.1 (4)	2.687 (5)	112.7 (2)	2.888 (6)	113.0 (2)
-OD(0)	2.735 (9)	114.5 (4)	2.738 (5)	114.4 (2)	2.961 (7)	116.4 (2)
OC(0)-OD(0)	2.656 (9)	110.3 (4)	2.659 (5)	110.0 (2)	2.853 (7)	110.3 (2)
Mean	2.647	109.4	2.655	109.4	2.835	109.3
T1(z) tetrahedron						
OA(1)-OB(z)	2.741 (8)	97.4 (3)	2.767 (5)	98.9 (2)	2.740 (5)	97.1 (2)
-OC(z)	3.098 (8)	116.7 (3)	3.079 (4)	116.2 (1)	3.127 (7)	118.3 (2)
-OD(z)	2.729 (8)	96.5 (3)	2.765 (5)	98.1 (1)	2.729 (5)	96.5 (2)
OB(z)-OC(z)	3.043 (9)	114.8 (3)	3.026 (5)	114.1 (2)	3.020 (7)	113.6 (2)
-OD(z)	3.085 (8)	116.3 (3)	3.085 (5)	115.8 (2)	3.101 (7)	117.6 (2)
OC(z)-OD(z)	3.021 (9)	112.9 (3)	3.006 (5)	112.1 (2)	2.996 (7)	112.0 (2)
Mean	2.953	109.1	2.955	109.2	2.952	109.2
T2(0) tetrahedron						
OA(2)-OB(0)	2.881 (7)	105.6 (3)	2.853 (5)	104.1 (2)	2.889 (6)	105.4 (2)
-OC(0)	2.768 (9)	99.6 (2)	2.735 (5)	97.5 (1)	2.701 (5)	95.6 (2)
-OD(0)	2.853 (8)	104.3 (3)	2.904 (6)	106.4 (2)	2.905 (6)	106.4 (2)
OB(0)-OC(0)	3.025 (8)	114.3 (3)	3.021 (5)	113.6 (2)	3.046 (7)	114.2 (2)
-OD(0)	3.017 (9)	114.2 (3)	3.056 (5)	116.2 (2)	3.061 (7)	116.0 (2)
OC(0)-OD(0)	3.061 (9)	116.5 (3)	3.071 (5)	116.1 (2)	3.074 (7)	116.1 (2)
Mean	2.934	109.1	2.940	109.0	2.946	109.0
T2(z) tetrahedron						
OA(2)-OB(z)	2.632 (8)	108.5 (3)	2.625 (5)	108.0 (2)	2.808 (6)	107.3 (2)
-OC(z)	2.489 (9)	100.6 (4)	2.494 (5)	100.3 (2)	2.626 (5)	97.5 (2)
-OD(z)	2.646 (8)	108.6 (4)	2.640 (5)	108.9 (2)	2.823 (6)	107.7 (2)
OB(z)-OC(z)	2.701 (8)	113.7 (4)	2.700 (5)	112.9 (2)	2.925 (6)	114.0 (2)
-OD(z)	2.672 (9)	110.7 (4)	2.694 (5)	112.7 (2)	2.930 (7)	114.1 (2)
OC(z)-OD(z)	2.717 (9)	114.0 (3)	2.700 (5)	113.0 (2)	2.938 (7)	114.4 (2)
Mean	2.643	109.4	2.635	109.3	2.842	109.2

Table 6. M-O distances (Å) and T-O-T angles (°)

M = Sr, Ba	SGSF	BGSF	BGGF
M-OA(1)	2.623 (6)	2.811 (3)	2.819 (4)
OA(1)	2.637 (6)	2.868 (3)	2.847 (4)
OA(2)	2.437 (4)	2.627 (3)	2.609 (4)
OB(0)	2.724 (6)	2.868 (4)	2.890 (4)
OB(z)	2.883 (7)	2.949 (4)	2.917 (4)
OC(0)	3.306 (7)	3.197 (3)	3.204 (4)
OC(z)	3.028 (7)	3.071 (3)	3.150 (4)
OD(0)	2.776 (7)	2.895 (4)	2.902 (4)
OD(z)	2.749 (6)	2.908 (4)	2.903 (4)
OA(2)	3.741 (5)	3.551 (4)	3.793 (5)
⟨M ^{IX} -O⟩	2.796	2.910	2.916
T-OA(1)-T	135.2 (3)	136.9 (2)	134.5 (2)
T-OA(2)-T	126.2 (4)	131.8 (2)	128.4 (2)
T-OB(0)-T	142.1 (4)	144.9 (2)	140.4 (2)
T-OB(z)-T	142.5 (4)	145.2 (2)	139.9 (2)
T-OC(0)-T	127.4 (4)	123.5 (2)	123.0 (2)
T-OC(z)-T	129.6 (4)	128.1 (2)	124.9 (2)
T-OD(0)-T	138.6 (4)	137.3 (2)	137.7 (2)
T-OD(z)-T	137.2 (4)	136.0 (2)	136.8 (2)
⟨T-O-T⟩	134.9	135.5	133.2

effect on mean T-O distances. CG (1975) argue that the fact that the mean Si-O bond length is larger and the mean Ga-O bond length is smaller in their BGSF than in their SGSF does not necessarily imply that their BGSF is partially disordered. They point out that certain environmental factors such as the M cation and the T-O-T linkages may also affect mean T-O bond lengths. However, as noted above, it appears that the chemical identity of the M cation (Ba or Sr) has little if any influence on the mean T-O bond lengths. Furthermore, the predominant linkage in both structures is of the type Ga-O-Si; therefore linkage can also be ruled out as a possible factor.

In support of their argument against disorder in their BGSF, CG also point out that both the mean Si-O and Ga-O bond lengths in the paracelsian SrGa₂Si₂O₈ are somewhat larger than in the corresponding feldspar. Kroll & Phillips (1976) suggested that paracelsians generally have slightly larger mean T-O bond lengths, due to bonding relations arising from basic differences in the two structure types. Their arguments do not

Table 7. Site occupancies and mean tetrahedral bond lengths (Å)

Data denoted by CG are taken from Calleri & Gazzoni (1975).

	$T1(0)$	$T1(z)$	$T2(0)$	$T2(z)$
SGSF Ga	0.048 (14)	0.976 (21)	0.945 (14)	0.030 (14)
Si	0.952 (14)	0.024 (21)	0.055 (14)	0.097 (14)
BGSF Ga	0.043 (4)	0.978 (6)	0.960 (4)	0.020 (4)
Si	0.957 (4)	0.022 (6)	0.040 (4)	0.980 (4)
BGGF Ga	-0.03 (12)	1.00 (18)	0.99 (12)	0.03 (11)
Ge	1.03 (12)	0.00 (18)	0.01 (12)	0.97 (11)

	$\langle T1(0)-O \rangle$	$\langle T1(z)-O \rangle$	$\langle T2(0)-O \rangle$	$\langle T2(z)-O \rangle$
SGSF	1.625	1.818	1.804	1.621
SGSF (corrected)	1.615	1.823	1.815	1.615
SGSF (CG)	1.611	1.822	1.820	1.617
BGSF	1.629	1.817	1.809	1.621
BGSF (corrected)	1.620	1.821	1.817	1.617
BGSF (CG)	1.634	1.807	1.803	1.634

account for the differences between the two isostructural $I2/c$ feldspars of CG. If it is assumed that our BGSF site-occupancy data are correct and that tetrahedral size varies linearly within a limited range of Ga/Si substitution, then the BGSF crystal of CG is appreciably disordered with as many as 7 to 8% of the Si sites occupied by Ga and *vice versa*.

O—T—O angles and tetrahedral angular distortion

The individual O—T—O angles (Table 5) in the $T1$ tetrahedra show a wider range of variation than do those in the $T2$ tetrahedra. Each $T1$ tetrahedron shares two edges ($OA \cdots OB$ and $OA \cdots OD$) with the M polyhedra. These edges are the shortest in the $T1$ tetrahedra, and the O—T—O angles the smallest. Thus, the other four angles widen, and the mean O—T—O angle is close to the ideal value of 109.47° . There is also an adjustment in individual O \cdots O distances such that the mean O \cdots O distance is characteristic for the T cation species. Only one edge is common to the M polyhedron and the $T2$ tetrahedron, and this edge also is the shortest in the $T2$ tetrahedron.

Pauling's (1929) rules state that edge sharing results in edge shortening so as to reduce cation—cation repulsion. In addition, M —O bonding is also expected to influence tetrahedral angular distortion. An M —O bond weakens the neighbouring T—O bond which may then cause the three O—T—O angles involved to become narrower (Gibbs, Louisnathan, Ribbe & Phillips, 1974). Therefore, besides constraining geometrical conditions noted by Megaw (1974), M —T repulsion and M —O bonding are assumed to be the major sources of variation in O—T—O angles and O \cdots O distances. These two influences can be related to the intratetrahedral angular distortion by counting

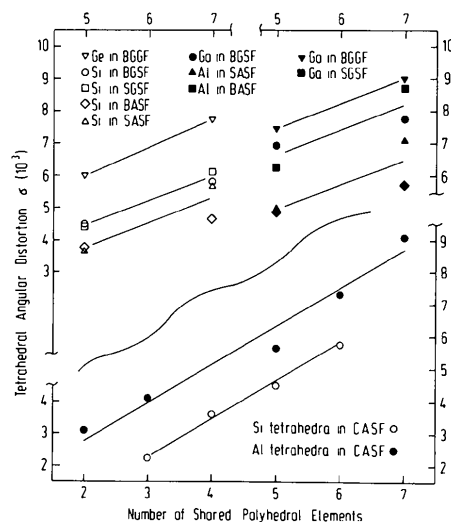


Fig. 1. Tetrahedral angular distortion parameter σ , where $\sigma = \{\sum_{i=1}^6 |(\text{O}-\text{T}-\text{O})_i - \langle \text{O}-\text{T}-\text{O} \rangle|^2/6\}^{1/2}$, plotted versus the number of polyhedral elements (edges plus corners) shared between a tetrahedron and its surrounding M polyhedra.

the edges and corners shared between a tetrahedron and the surrounding M -cation polyhedra (Ribbe, Phillips & Gibbs, 1974). Fig. 1 is a plot of the distortion parameter $\sigma(\text{O}-\text{T}-\text{O}) = \{\sum_{i=1}^6 |(\text{O}-\text{T}-\text{O})_i - \langle \text{O}-\text{T}-\text{O} \rangle|^2/6\}^{1/2}$ vs the sum of shared polyhedral elements for SGSF, BGSF and BGGF. The distortion data for anorthite, CASF (Ribbe *et al.*, 1974), SASF (Chiari *et al.*, 1975) and BASF (Griffen & Ribbe, 1976) are included for comparison.

A ninefold coordination for M in all structures, except for anorthite, means that the $OA(2) \cdots OC$ edges are shared edges. In the case of anorthite, four of the OC atoms involved in the eight non-equivalent $OA(2) \cdots OC$ edges are considered to be bonded (Phillips, Ribbe & Gibbs, 1973). Three of the remaining four OC atoms are too distant from Ca (more than 3.55 Å). The eighth edge [$OA(2000) \cdots OC(mzi0)$] is questionable; however, it has also been excluded in order to be consistent with the previous study of Ribbe *et al.* (1974).

Comparing compounds with the same framework chemistry — such as CASF, SASF, BASF or SGSF, BGSF — with respect to their mean distortion index, it is seen that the Sr compounds are more distorted than the Ba and Ca compounds. The O environment of Ba is more regular than that of Sr, thereby reducing the distortion. Although Ca has the most irregular environment, CASF is less distorted than SASF, because there are less shared polyhedral elements (n) in CASF. The ratio $n(\text{CASF}):n(\text{SASF}) = 4.5:5.5 = 0.82$ is close to the ratio of the distortions $\sigma(\text{SASF}):\sigma(\text{CASF}) = 4.8:5.4 = 0.89$.

If we look at different framework chemistries, we find that the distortion index of a particular T -cation

species appears to be related to the *T*-cation combination in which it occurs: Si tetrahedra are more distorted in the presence of Ga than in the presence of Al, and Ga tetrahedra are more distorted when they occur with Ge than when they occur with Si.

Tetrahedral *T*–O bond-length distortions

A strong direct relation exists between the coordination number of the O atoms and the individual *T*–O bond lengths to these O atoms (Table 8). It was first established for anorthite by Megaw *et al.* (1962), and has since been found in other feldspars including SASF (Chiari *et al.*, 1975). From this relation one would expect the *T*–OA(1) and *T*–OA(2) bonds to be long, because OA(1) is four-coordinated and OA(2), though three-coordinated, is involved in the very short *M*–OA(2) distance. Conversely, the *T*–OC bonds should be short, because the *M*–OC distances are long. This predicted behaviour is observed in all six *T*1 tetrahedra, but not for all of the *T*2 tetrahedra, possibly due to other structural influences.

The data given in Table 4 indicate that there is much more variation in bond length in the *T*1 than in the *T*2 tetrahedra. In the *T*1 tetrahedra the OA atoms are four-coordinated and OB, OC and OD are three-coordinated, whereas in the *T*2 tetrahedra all O atoms are three-coordinated. The larger *T*–O distance variation in *T*1, therefore, reflects its less uniform O coordination. The O–*T*–O angles in the *T*1 tetrahedra

Table 8. Mean *T*–O distances involving three- and four-coordinated oxygen atoms (Å)

CN(O)	⟨Ga–O⟩	⟨Ge–O⟩	⟨Si–O⟩
3	1.809	1.742	1.620
4	1.838	1.755	1.648

Table 9. Tetrahedral bond-length distortion (σ), $\sigma^2(T-O) = \sum_{i=1}^4 [(T-O)_i - \langle T-O \rangle]^2/4$ (Å)

The data for hurlbutite (CaBe₂P₂O₈) are taken from Lindbloom, Gibbs & Ribbe (1974), for SASF from Chiari *et al.* (1975), for BASF from Griffen & Ribbe (1976), for SGSP (SrGa₂Si₂O₈-paracelsian) and SGGP (SrGa₂Ge₂O₈-paracelsian) from Phillips *et al.* (1975). The data given in parentheses are derived from the refinements of Calleri & Gazzoni (1975).

Feldspars	SASF	BASF	SGSF	BGSF	BGGF
$\sigma(T1) \times 10^3$	13.9	12.7	15.4 (18.6)	15.2 (22.9)	13.6 (26.8)
$\sigma(T2) \times 10^3$	8.0	10.5	8.9 (11.9)	7.1 (16.5)	5.8 (14.3)
Paracelsians			Hurlbutite	SGSP	SGGP
$\sigma(T1) \times 10^3$			10.2	8.4	11.1
$\sigma(T2) \times 10^3$			14.1	12.6	11.9

are also more distorted than in the *T*2 tetrahedra (compare Tables 4 and 5). In contrast, in paracelsians the *T*1 tetrahedra have the larger angular, but the smaller *T*–O distortions [see Table 7 of Phillips, Kroll, Pentinghaus & Ribbe (1975) and Table 9 in this paper]. Whereas the number of shared polyhedral elements in paracelsians is larger for the *T*1 than the *T*2 tetrahedra, the *M*-coordination of the *T*1 O atoms is more regular than that of *T*2. The paracelsians, therefore, illustrate how O–*T*–O angles and *T*–O distances differently reflect the *M*-cation environment.

The distortion parameters $\sigma(T-O) = \{\sum_{i=1}^4 [(T-O)_i - \langle T-O \rangle]^2/4\}^{1/2}$ (Table 9) show little variation in SASF (Chiari *et al.*, 1975), BASF (Griffen & Ribbe, 1976) and SGSF, BGSF, BGGF (this paper). However, the values for SGSF, BGSF and BGGF, calculated from CG's (1975, 1976) data and given in parentheses, fall considerably outside this range.

Multiple regression analysis of *T*–O bond lengths

Phillips, Ribbe & Gibbs (1973) showed that in anorthite *T*–O bond lengths are correlated with the coordination number of O atoms – treated as $\Sigma d(M-O)^{-2}$ – and the *T*–O–*T* angles. The parameter $\langle O-T-O \rangle_3$ (the mean of the three angles common to a *T*–O bond) was not included in their final analysis, as it did not contribute significantly to the sum of squares due to regression when run in the presence of the coordination parameter. These three variables were used in a modified form in the regression analysis of the bond-length data of SASF (Chiari *et al.*, 1975), BASF (Griffen & Ribbe, 1976), SGSF, BGSF and BGGF. In order to minimize the effects of the different chemistry of the *M* cations and of partial disorder on *T*–O distances, we used the differences of the individual values of the variables from their respective tetrahedral means, such that:

$$\Delta T-O = T-O - \langle T-O \rangle$$

$$\Delta T-O-T = T-O-T - \langle T-O-T \rangle$$

$$\Delta \Sigma d(M-O)^{-2} = \Sigma d(M-O)^{-2} - \langle \Sigma d(M-O)^{-2} \rangle$$

$$\Delta \langle O-T-O \rangle_3 = \langle O-T-O \rangle_3 - \langle \langle O-T-O \rangle_3 \rangle$$

$\Delta T-O$ was considered as the dependent variable; however, this does not necessarily imply any cause-and-effect relation (Phillips, Ribbe & Gibbs, 1973). A multiple regression analysis on the Si-containing tetrahedra of anorthite indicated that the delta parameters used in this study yield correlations very similar to those found by Phillips, Ribbe & Gibbs (1973) using absolute parameters. The data from the *I*/*c* feldspars were then subdivided into three groups; multiple regression analyses performed on each group yielded the correlation coefficients quoted in Table 10.

Significant correlations (with $|r|$ greater than 0.60) have been found between *T*–O and *T*–O–*T* in

Table 10. Correlation coefficients $|r|$ (%) obtained in a multiple regression analysis in which $\Delta T-O$ was treated as a dependent variable

	Independent variables chosen in the regression analysis of $\Delta T-O$ data					
	$\Delta T-O-T$	$\Delta \Sigma d(M-O)^{-2}$	$\Delta \langle O-T-O \rangle_3$	$\Delta T-O-T + \Delta \Sigma d(M-O)^{-2}$	$\Delta T-O-T + \Delta \langle O-T-O \rangle_3$	$\Delta \Sigma d(M-O)^{-2} + \langle O-T-O \rangle_3$
Si tetrahedra in anorthite	63	93	75	96	87	93
Si tetrahedra in SASF, BASF, SGSF, BGSF	4	78	74	78	74	82
Al and Ge tetrahedra in SASF, BASF, BGGF	5	71	68	71	69	76
Ga tetrahedra in SGSF, BGSF, BGGF	18	73	90	77	90	91

anorthite (Phillips, Ribbe & Gibbs, 1973), the sodic plagioclases (Phillips & Ribbe, 1973a) and the monoclinic K-rich feldspars (Phillips & Ribbe, 1973b). This correlation is also high in the paracelsians $\text{SrGa}_2\text{Si}_2\text{O}_8$ and $\text{SrGa}_2\text{Ge}_2\text{O}_8$ (Phillips *et al.*, 1975) and in the feldspars $\text{NaAlGe}_3\text{O}_8$ and $\text{NaGaGe}_3\text{O}_8$ (Kroll, Nabbe & Peninghaus, 1975). In sharp contrast to these structures, it appears that in the $I2/c$ feldspars this correlation is not developed.

In the case of the Si and, though less clearly, the Al and Ge tetrahedra, the $\langle O-T-O \rangle_3$ variable could be rejected because of its low $|r|$ value (Student's t -statistic) when it was run in the presence of $\Sigma d(M-O)^{-2}$, which is in accordance with the results of Phillips, Ribbe & Gibbs (1973). The opposite behaviour was found for the Ga tetrahedra. This observation is supported by our unpublished analyses of the two paracelsians and two albites mentioned above. For the smaller Si tetrahedra the major influencing factor is $\Sigma d(M-O)^{-2}$, for the larger Ga tetrahedra it is $\Delta \langle O-T-O \rangle_3$.

Lastly, combinations of the three variables were regressed; no significant improvements were found because of the low correlation between $\Delta T-O$ and $\Delta T-O-T$ and the high correlation between $\Delta \Sigma d(M-O)^{-2}$ and $\Delta \langle O-T-O \rangle_3$.

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