

Fig. 3. Unit cell projected along $\langle 001 \rangle$; approximate z coordinates and the angles α and β are indicated for one BiO_4 polyhedron.

c and d (indicated in Fig. 3) are somewhat longer than the equatorial bonds to a and b . Whereas β , angle $c\text{--Bi--}d = 172.1(3)^\circ$, is identical to that indicated by the single-crystal X-ray diffraction measurements, $172(2)^\circ$, the equatorial angle, $\alpha = a\text{--Bi--}b = 82.4(2)^\circ$, is very much lower than that previously reported, $115(2)^\circ$. Aurivillius & Malmros (1972) compared a range of Sb^{3+} and Bi^{3+} compounds for which $78 < \alpha < 96^\circ$ and $143 < \beta < 172^\circ$. Whereas the X-ray structure is incompatible with these observations, the present results are consistent, and comply with the general observation that long equatorial bonds

Table 4. Selected bond distances (\AA) and angles ($^\circ$)

Bi—O1, d	2.463 (7)	O2—Bi—O1, α	82.4 (2)
O2, a	2.096 (4)	O1—Bi—O1, β	172.1 (3)
O1, c	2.253 (7)	O1—Bi—O2	95.2 (2)
O1, b	2.128 (7)	O1—Bi—O1	82.4 (2)
		O2—Bi—O1	85.1 (2)
O1—Bi	2.463 (7)	O1—Bi—O1	89.8 (2)
Bi	2.253 (7)	Bi—O1—Bi	110.3 (2)
Bi	2.128 (7)	Bi—O1—Bi	109.9 (2)
O2—Bi	2.096 (4)	Bi—O1—Bi	135.9 (3)
Bi	2.096 (4)	Bi—O2—Bi	130.6 (3)

and high values for β tend to be associated with low α values, due to changes in electron pair repulsions.

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Chlorosilicate with the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ Structure and its Relationship to Garnet

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Abstract. $\text{Ca}_{12}\text{Al}_{10.6}\text{Si}_{3.4}\text{O}_{32}\text{Cl}_{5.4}$, $M_r = 1565.88$, cubic, $I\bar{4}3d$ (No. 220), $a = 11.981(6) \text{\AA}$, $Z = 2$, $D_x = 3.023 \text{ Mg m}^{-3}$, $V = 1719.8 \text{\AA}^3$, $\text{Mo K}\alpha$, $\lambda = 0.71069 \text{\AA}$, $\mu = 2.706 \text{ mm}^{-1}$, $F(000) = 1546.4$. Single crystals have been prepared and characterized by electron microprobe and X-ray crystal structure analysis; $R = 0.056$ for 225 unique reflections. The structure is closely related to that of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (C_{12}A_7 in oxide notation) but with Cl substituted for some of the oxide of the type structure and Si replacing some Al to provide charge balance for Cl present in excess of the stoichiometric

requirement. The structure exhibits many similarities to that of garnet.

Introduction. Several compounds of the type $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{X}$ have been reported; $\text{X} = \text{O}^{2-}$: Bartle (1969*b*), Bussem & Eitel (1936), Jeevaratnam, Dent Glasser & Glasser (1962) and Hentschel (1964); $\text{X} = 2(\text{OH}^-)$: Bartl (1969*a*); $\text{X} = 2(\text{F}^-)$: Williams (1973); $\text{X} = 2(\text{O}_2^-)$ (superoxide): Hosono & Abe (1987). The substitution of OH^- , F^- , Cl^- for O^{2-} has hitherto been believed to be limited to a maximum of four monovalent anions per

unit cell, with continuous solid solution between the end members. The presence of F stabilizes the structure, increases the melting point with respect to that of Ca₁₂Al₁₄O₃₃ and enhances its stability with respect to other calcium aluminates in cement systems (Klemm, Jawed & Holub, 1979; Smart & Roy, 1979).

The compound described here is also an example of this structure type but is remarkable in that Cl is present to an extent that necessitates extensive substitution of Al by Si to maintain charge balance.

Experimental. Crystals were grown by heating CaO, SiO₂ and Al₂O₃ in the presence of excess CaCl₂ at 1123 K for 72 h in open crucibles. Slow evaporation of the excess CaCl₂ causes partial isothermal crystallization to occur. Crystals were extracted under the petrographic microscope. X-ray diffraction data were obtained from a suitable small crystal (*ca* 0.05 mm edge) on a Nicolet P3 four-circle diffractometer with Mo K α radiation ($\lambda = 0.71069$ Å) and graphite monochromator. The cubic unit-cell dimension was determined as 11.981 (6) Å using the 008 and 444 reflections at 27.4 and 23.7°2 θ . Data were collected using the $\theta/2\theta$ method for 2 θ in the range 0–60° for the body-centred set of reflections with $h \leq k \leq l$, hkl all positive and $l < 17$. Pre-scan intensities (*I*_p) were used to select 2 θ scan rates in the range 5.33 to 58.6° min⁻¹, the limiting values corresponding to *I*_p < 150 and *I*_p > 2500 respectively. The 2 θ scan width varied from 2.4 to 2.8° depending on 2 θ for the reflection. The resulting data contained 225 unique reflections of which ten were classed as unobserved [$I < 3\sigma(I)$]. These were converted to structure amplitudes in the usual way. The intensities of the 008 and 444 reflections monitored at intervals of 50 measurements showed no significant variation and no absorption correction was applied.

Initial atomic parameters were taken from Williams (1973) omitting Ca(2), interchanging Al(1) and Al(2), replacing F by Cl and giving all atoms full occupancy. Three cycles of block-diagonal least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with all atoms vibrating anisotropically and unit weights gave $R = 0.0584$. A difference map then showed no feature in excess of ± 0.7 e Å⁻³ and therefore there is no evidence of atomic sites other than those used in the calculations. Analytical electron microscopy of selected single crystals gave Ca:Al:Si:Cl in numbers of atoms, with estimated errors in parentheses, as 1:0.74 (15):0.23 (12):0.38 (8). Representing the unit-cell content as Ca₂₄Al_{28-x}Si_xCl_{4+x}, the value of *x* was calculated from the observed Al:Si ratio, which was assumed to be the most reliable component of the analysis due to the possible presence of extraneous CaCl₂, to give the value 6.8 (14). Thus the cell contains 10.8 Cl and the Cl occupancy is 0.9. Further refinement adopting the revised value for the Cl occupancy and treating all tetrahedral cations as Al

Table 1. Atomic parameters with e.s.d.'s applicable to the least significant digits in parentheses

	Number of atoms and Wyckoff notation	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>B</i> _{eq} * (Å ² × 100)
O(1)	48e	19997 (23)	28175 (22)	10215 (23)	1.0	62
Ca(1)	24d	10593 (8)	0	$\frac{1}{2}$	1.0	58
O(2)	16c	31506 (47)	31506 (48)	31506 (48)	1.0	125
Al(1)	16c	23290 (14)	23290 (14)	23290 (14)	1.0	29
Al(2)	12a	$\frac{1}{2}$	0	$\frac{1}{2}$	1.0	37
Cl(1)	12b	$\frac{1}{2}$	0	$\frac{1}{2}$	0.900 (6)	180

* Equivalent *B*_{iso} calculated as $4a^2(B_{11} + B_{22} + B_{33})$ where the correction for anisotropic thermal vibration is of the form

$$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{12}hk + B_{13}hl)].$$

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.'s applicable to the least significant digits in parentheses

Tetrahedra			
Al(1)—O(1)	1.718 (3) × 3	O(1)—Al(1)—O(1)	100.3 (2) × 3
—O(2)	1.705 (6)	—O(2)	117.5 (2) × 3
Al(2)—O(1)	1.762 (3) × 4	O(1)—Al(2)—O(1)	101.3 (1) × 2
			113.7 (1) × 4
O(1)—Al(1)	1.718 (3)	Al(1)—O(1)—Al(2)	140.5 (2)
—Al(2)	1.762 (3)	—Ca(1)	99.0 (1)
—Ca(1)	2.426 (3)	—Ca(1')	96.0 (1)
—Ca(1')	2.509 (3)	Al(2)—O(1)—Ca(1)	116.6 (1)
		—Ca(1')	96.5 (1)
		Ca(1)—O(1)—Ca(1')	96.5 (1)
O(2)—Al(1)	1.705 (6)	Ca(1)—O(1)—Al(1)	117.6 (3) × 3
—Ca(1)	2.399 (6) × 3	Ca(1)—O(1)—Ca(1')	100.2 (2) × 3
Ca coordination; the significance of the O designations is explained in the Discussion			
Ca(1)—O(1e)	2.426 (3) × 2	O(1e)—Ca(1)—O(1a)	64.6 (1) × 2
—O(1a)	2.509 (3) × 2	—O(1'e)	177.9 (1)
—O(2e)	2.399 (6) × 2	—O(1'a)	117.4 (1) × 2
—Cl(1)	2.767 (1)	—Cl(1)	88.9 (1) × 2
O(1a)—Ca(1)—O(1'a)	65.8 (1)	—O(2e)	79.6 (2) × 2
—Cl(1)	147.1 (1) × 2	—O(2'e)	99.9 (2) × 2
—O(2e)	78.0 (2) × 2	Cl(1)—Ca(1)—O(2e)	78.2 (1) × 2
—O(2'e)	123.4 (2) × 2	O(2e)—Ca(1)—O(2'e)	156.4 (2)

reduced R ($= wR$) to the final value of 0.056 with $S = 31.47$ and $(\Delta/\sigma)_{\max} = 0.13$ for the parameters given in Table 1.* Selected bond lengths and angles are given in Table 2. All calculations were carried out on the Honeywell 66/80 computer of the Computing Centre of the University of Aberdeen using the NRC programs of Ahmed, Hall, Pippy & Huber (1966) and, for the preparation of Fig. 1, STRUPL082 (Fischer, 1982). Scattering factors for neutral Al, Si, O and Cl and Ca²⁺ were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The structure contains a complex framework consisting of two distinct types of Al tetrahedron in the ratio of 4:3. A portion of the structure is illustrated in projection (Fig. 1a). Al(1) is coordinated

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles and powder diffraction intensity data calculated for the final parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44584 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

by $3 \times O(1)$ and $1 \times O(2)$. Al(2) is surrounded by $4 \times O(1)$. O(1) always bridges between Al(1) and Al(2) but O(2) is connected directly to a single Al(1). The shared O(1) connect alternating Al(1) and Al(2) tetrahedra into approximately boat-shaped eight-membered rings. Sharing the remaining O(1) serves to fuse the rings into a complete, rather open, three-dimensional structure in an elegant but rather complex manner shown in Fig. 2. Linear units Ca(1)—Cl(1)—Ca(1) lie on twofold axes parallel to the unit-cell edges in the interstices of the aluminate framework in such a way as to allow Ca to achieve 7-coordination by contacts with $4 \times O(1)$ and $2 \times O(2)$ exactly as described by Williams (1973). The Ca environment can be viewed as a variant of octahedral coordination with Ca, $2 \times O(1)$ and $2 \times O(2)$ in the equatorial plane [O(1e) and O(2e) in Fig. 1a and Table 2] and Cl at one apex and two more O(1), related by the twofold axis passing through Ca and Cl, at the other [O(1a) in Fig. 1a and Table 2]. Including Ca—O contacts both O(1) and O(2) are surrounded by a roughly tetrahedral arrangement of Ca and Al.

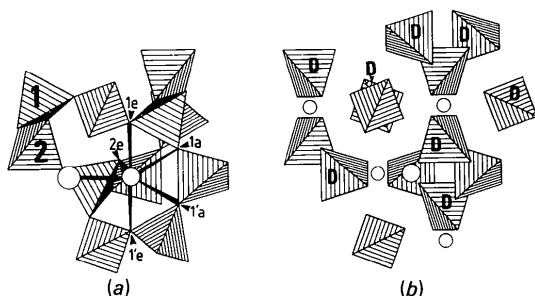


Fig. 1. (001) projections comparing the structures of (a) $\text{Ca}_{12}\text{Al}_{10.6}\text{Si}_{3.4}\text{Cl}_{5.4}$ and (b) garnet [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$]. The circles in order of increasing radius are Al [(b) only], Ca and Cl [(a) only]. Only one representative Ca is shown in each case and only one Cl is present in (a). The tetrahedra marked 'D' in (b) are absent from (a) and their sites are available for occupancy by Cl. Only those Al are shown in (b) which form tetrahedra in (a). In (a) the representation of the zeolite-like aluminate framework is limited to a cluster of three eight-membered rings of alternating Al(1) and Al(2) tetrahedra of which typical representatives are identified by number. O at the corners of the Al tetrahedra involved in the coordination of Ca are labelled as explained in the Discussion.

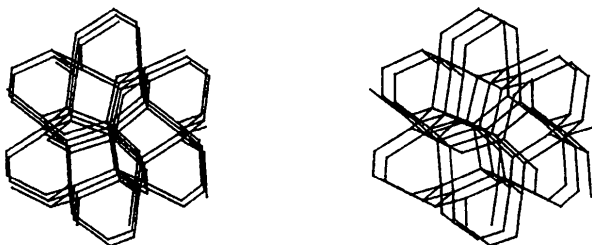


Fig. 2. Stereoscopic view of the aluminate framework of $\text{Ca}_{12}\text{Al}_{10.6}\text{Si}_{3.4}\text{Cl}_{5.4}$ viewed along [111]. The lines connect Al of adjacent tetrahedra and their midpoints approximate the O(1) sites. Ca, Cl and O(2) are not shown.

As implied in connection with the refinement of the structure (above) the results of the structural analysis can only be reconciled with the results of the analytical electron microscope analysis by postulating partial substitution of Al by Si ($\text{Al}_{0.76}\text{Si}_{0.24}$). This is necessary owing to the presence of Cl in excess of the stoichiometric amount which, while the analytical electron microscope results are subject to rather large standard deviations, is confirmed by the Cl occupancy factor adopted in the structure refinement. Al and Si sites are disordered; similar disorder of Si and Al over tetrahedral sites has been noted before in the structure of alinite, $\text{Ca}_{11}\text{Si}_3\text{AlO}_{18}\text{Cl}$ ($\text{Ca}_{11}\text{Si}_4\text{O}_{18}\text{Cl}$), by Ilyukhin, Nevsky, Bickbau & Howie (1977). The present case differs from that of alinite in that there are two tetrahedral sites rather than one, both of which are predominantly occupied by Al. Noting the significantly shorter Al(1)—O(1) distances compared with Al(2)—O(1), refinement was attempted for a model in which all Si was assumed to be in the Al(1) sites. This had no significant effect on any of the structural parameters or the *R* factor. Thus it is not possible to confirm that the variation in Al—O(1) distances is related to the distribution of Si in the Al sites.

Another feature of the phase described here is the striking similarity (allowing for difference in the unit-cell dimensions) of its observed powder diffraction pattern to that of grossularite garnet, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$. This implies a general similarity in the distribution of electron density within the unit cells of these materials but the detailed structures require the chemical significance of that electron density to be very different. Table 3 and Fig. 1 show the relationship between the distribution of atoms in the two structures. The two structure types are readily distinguished by the presence of $0kl$ reflections with *k* (and *l*) odd in single-crystal data for compounds of the C_{12}A_7 structure type. Such reflections are systematically absent for the garnet structure. Even in C_{12}A_7 -type compounds these reflections are generally rather weak and so will not contribute appreciably to the intensity of the X-ray powder diffraction pattern. In the powder pattern calculated from the results of the crystal structure analysis most reflections of this type which do occur are coincident in spacing with other, more general, reflections which do not distinguish between the two structures: the weak 035 reflection is an exception. Therefore it is virtually impossible to assign an unknown compound to one or other of these structures reliably by consideration of X-ray powder diffraction data alone.

This calcium aluminate structure type permits novel chemical reactions involving oxygen to be achieved, amongst which are the ability to stabilize superoxide ion to very high temperatures and to participate in rapid and reversible zeolite water exchanges at temperatures up to ~ 1570 K at low water vapour pressures (Singh &

Table 3. *Distribution of atoms in the garnet and C₁₂A₇ structures (see also Fig. 1)*

Fractional coordinates of representative atoms are also given.

Garnet [Ca ₃ Al ₂ (SiO ₄) ₃]*		C ₁₂ A ₇ (Ca ₁₂ Al ₁₄ O ₃₂ X)
1a3d		143d
O 96h 0.2043, 0.2882, 0.0978	(a) →	O(1) 48e 0.1997, 0.2818, 0.1022
	(c) →	O(2) 16c x, x, x; x = 0.3151
Si 24d ½, 0, ¼	(a) →	Al(2) 12a ½, 0, ¼
	(b) →	X (= Cl) 12b ½, 0, ¼
Al 16a ½, ½, ½	(c) →	Al(1) 16c x, x, x; x = 0.2329
Ca 24c ½, 0, ¼	(d) →	Ca(1) 24d 0.1059, 0, ¼

(a) Half of the SiO₄ tetrahedra of the garnet structure are retained in C₁₂A₇, as Al(2)O₄ tetrahedra, avoiding any pairs of SiO₄ related by a centre of symmetry.

(b) Those sites from which SiO₄ have been omitted are available for occupancy by the X atoms of C₁₂A₇, e.g. Cl in this case.

(c) Al of garnet is retained in C₁₂A₇, but its coordination is reduced from octahedral to tetrahedral by replacing triplets of garnet O omitted as indicated in (a) above by a single O(2).

(d) Ca of garnet is retained in C₁₂A₇, but again as a result of the omission of SiO₄ as in (a) above its coordination by oxygen is reduced from 8 (cubic) to the distorted sixfold coordination described by Williams (1973). Occupancy of the 'empty' SiO₄ site by X (here Cl) as in (b) above will then restore some of the symmetry of the Ca coordination again exactly as described by Williams (1973).

* Data from Wyckoff (1968).

Glasser, 1987). These properties combine with high thermal stability; Ca₁₂Al₁₄O₃₃ melts at ~1670 K. However, the structure type has hitherto appeared to be confined to Ca, Al and O, with only limited OH, F and Cl inclusion. The present study shows that further chemical tailoring is possible, leading to the synthesis of materials with potentially useful properties.

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Crystal Structure of KLiSO₄ at 200 K: a Neutron Diffraction Study

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Abstract. $M_r = 142.10$, trigonal, $P31c$, $a = 5.129$, $c = 8.639$ Å, $V = 196.82$ Å³, $Z = 2$, $D_x = 2.397$ g cm⁻³, $\lambda(\text{neutron}) = 1.176$ Å, $\mu_c = 0.74$ cm⁻¹, $T = 200$ K. Refinement for the ordered structure with 593 reflections with $(\sin\theta)/\lambda \leq 0.57$ Å⁻¹ gave $R(F^2) = 0.055$. The study has revealed merohedral twinning of

the crystal about (110), with twin components in nearly equal proportion, and large thermal vibration for the oxygens. Displacing the oxygens into three disordered positions gave a somewhat better R factor.

Introduction. The crystal structure of KLiSO₄ at room temperature was determined by Bradley (1925). It crystallizes in space group $P6_3$ ($F1$ phase). In recent years much work has been done to study the behaviour

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