

## Refinement of the Structure of a Framework Aluminate

BY L. S. DENT GLASSER, A. P. HENDERSON\* AND R. A. HOWIE

Department of Chemistry, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland

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### Abstract

Reinterpretation of previous structural data [Nevskii, Glasser, Ilyukhin & Belov (1979). *Kristallografiya*, **24**, 161–166] shows that the compound of empirical composition  $5\text{SrO} \cdot 4\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  is rhombohedral,  $R\bar{3}$ ,  $a = 17.91$  (2),  $c = 7.16$  (1) Å. The final  $R$  value is 0.064 for 1163 reflections. The structure has a framework of aluminate tetrahedra sharing all corners. Sr atoms and hydroxyl groups are located within cavities in the framework, the latter, and some of the former, being statistically distributed over more than one site. The structural formula (for one primitive rhombohedral cell) is  $\text{Sr}_{7.5}[\text{AlO}_2]_{12}(\text{OH})_3$ . The structure is compared with those of other framework aluminates, silicates and aluminosilicates.

### Introduction

In the course of a systematic investigation of the system  $\text{SrO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  (Henderson, 1975), colourless birefringent crystals were obtained from mixtures with mole ratio  $3\text{SrO}:\text{Al}_2\text{O}_3$  by hydrothermal treatment at about 773 K and low pressure (less than 14 MPa). Powder data showed that the product was similar to that prepared by Carlson (1955) by hydrothermal decomposition of  $\text{Sr}_3[\text{Al}(\text{OH})_6]_2$ , for which he suggested the empirical composition  $5\text{SrO} \cdot 4\text{Al}_2\text{O}_3$ . Henderson's analyses suggested the formula  $4\text{SrO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2-4\text{H}_2\text{O}$ , the water content appearing somewhat variable. Single-crystal data showed the crystals to be rhombohedral,  $R\bar{3}$  or  $R\bar{3}$ ; crystal data are given in Table 1.

\* Now A. P. Russell. Present address: Macmillan Education Ltd, Houndmills, Basingstoke, Hampshire RG21 2XS, England.

Table 1. Crystal data for  $5\text{SrO} \cdot 4\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$

From single crystals	From powder data
$a = 17.91$ (2) Å	$a = 17.935$ (5) Å
$c = 7.16$ (1)	$c = 7.169$ (3)
$d_{x\text{-ray}} = 3.55 \text{ Mg m}^{-3}$	$d_{x\text{-ray}} = 3.53 \text{ Mg m}^{-3}$
$Z = 4.5$ [or $Z = 1.5$ , contents $\text{Sr}_{7.5}[\text{AlO}_2]_{12}(\text{OH})_3$ , for primitive rhombohedral cell. $a = 10.612$ Å, $\alpha = 115.096^\circ$ ]	
$d_{\text{meas}} = 3.85 \text{ Mg m}^{-3}$ (by water displacement), $3.48 \text{ Mg m}^{-3}$ (calculated from refractive index)	

Single-crystal intensity data were measured on a Syntex P1 four-circle diffractometer (Mo  $K\alpha$  radiation,  $\sin \theta/\lambda \leq 0.75 \text{ \AA}^{-1}$ ) at Moscow University, and an approximate solution of the structure was subsequently published (Nevskii, Glasser, Ilyukhin & Belov, 1979). This had several unsatisfactory features: the formula suggested was  $6\text{SrAl}_2\text{O}_4 \cdot \text{SrO}$ , which does not agree well with either Carlson's or Henderson's analyses; the Al–O bond lengths varied from 1.66 to 1.85 Å; and the space group assumed was  $P\bar{3}$ , which does not agree with Henderson's original determination. A re-examination of the structure therefore seemed worthwhile.

### Refinement of the structure

The coordinates given by Nevskii *et al.* (1979) are very nearly in accordance with a rhombohedral lattice, and careful examination of the photographic evidence gave no support for the primitive space group. Examination of the data obtained in Moscow showed that, of the 1438 planes listed, only 275 extremely weak ones did not have  $-h + k + l = 3n$ ; these could well be an artefact resulting from the use of Mo  $K\alpha$  radiation to study a compound rich in strontium. Our own experience with this combination is that unless great care is taken, the high overall background and correspondingly poor counting statistics lead to spurious reflections being recorded.

Accordingly, these reflections were excluded, and a refinement was begun in  $R\bar{3}$  using the remaining 1163 planes. Calculations were performed with programs supplied by F. R. Ahmed of the National Research Council of Canada, and modified for use on an ICL 4/50 computer by Mr J. S. Knowles and RAH of this University. Initial coordinates for the  $\text{AlO}_2$  framework and the Sr in the general position were adapted from Nevskii *et al.* After apparent convergence, an electron density map confirmed the presence of additional scattering matter on the threefold axis found by Nevskii *et al.*, and suggested that additional O atoms were partially occupying a set of general positions. It appeared also that the structure had a centre of symmetry; the refinement was therefore continued in  $R\bar{3}$ .

The sites on the threefold axes appeared to be partially occupied by Sr atoms, rather than Sr and O as suggested by Nevskii *et al.* After introduction of an anisotropic temperature factor for Sr(1), the final *R* value was 0.064, very slightly higher than that quoted by Nevskii *et al.* (0.06) but based on only ten independent atoms (Table 2) as opposed to 54 in the original paper. A difference map calculated at this stage showed no significant features.\*

Bond lengths calculated from these coordinates (Table 3) were satisfactory. In particular, the variation

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36239 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic parameters for 5SrO·4Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O*

Figures in parentheses give the e.s.d. corresponding to the least significant digit.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> (Å <sup>2</sup> )	Occupancy (if ≠ 1)
Sr(1)	0.47996 (5)	0.55777 (5)	0.75777 (1)	(=0.865)*	
Sr(2)	0	0	0.8012 (4)	0.69 (3)	$\frac{1}{4}$
Sr(3)	0	0	0.3170 (8)	0.89 (7)	$\frac{1}{4}$
Al(1)	0.2798 (2)	0.2608 (2)	0.2835 (4)	0.44 (3)	
Al(2)	0.1957 (2)	0.0777 (2)	0.4638 (3)	0.42 (3)	
O(1)	0.2518 (4)	0.1509 (4)	0.2850 (8)	0.77 (8)	
O(2)	0.2004 (4)	0.2739 (4)	0.3984 (8)	0.64 (8)	
O(3)	0.2720 (4)	0.2848 (4)	0.0472 (9)	0.88 (9)	
O(4)	0.1445 (5)	0.1178 (5)	0.613 (1)	1.5 (1)	
O(5)	0.1075 (10)	0.0023 (10)	0.979 (2)	1.5 (2)	

\* Anisotropic temperature factor for Sr(1) in the form  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$  with coefficients ( $\times 10^4$ ):

<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
11.8 (3)	8.8 (3)	41.5 (10)	10.3 (10)	15.6 (10)	14.0 (5)

The corresponding *B*<sub>iso</sub> is computed as  $\frac{1}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab \cos \gamma B_{12} + ac \cos \beta B_{13} + bc \cos \alpha B_{23})$ .

Table 3. *Bond lengths (Å) and angles (°)*

Al(1)—O(1)	1.772 (9)	Al(2)—O(1)	1.746 (7)
O(2)	1.757 (8)	O(2)	1.745 (7)
O(3)	1.735 (8)	O(4)	1.771 (10)
O(3')	1.768 (7)	O(4')	1.779 (9)
O(1)—Al(1)—O(1)	110.3 (3)	O(1)—Al(2)—O(2)	105.9 (3)
O(3)	108.0 (4)	O(4)	114.7 (4)
O(3')	105.3 (4)	O(4')	111.0 (4)
O(2)—Al(1)—O(3)	113.8 (4)	O(2)—Al(2)—O(4)	110.9 (4)
O(3')	104.4 (3)	O(4')	105.3 (4)
O(3)—Al(1)—O(3')	114.9 (4)	O(4)—Al(2)—O(4')	108.7 (4)
Al(1)—O(1)—Al(2)	125.1 (4)	Al(1)—O(3)—Al(1)	126.4 (4)
Al(1)—O(2)—Al(2)	125.0 (4)	Al(2)—O(4)—Al(2)	121.7 (5)
Sr(1)—O(1)	2.695 (6)	Sr(2)—O(4)	2.737 (9) × 3
O(1')	2.779 (7)	O(5)	2.47 (2) × 3
O(2)	2.604 (6)		
O(2')	2.665 (7)	Sr(3)—O(4)	2.436 (8) × 3
O(3)	2.716 (8)	O(5)	2.85 (2) × 3
O(3')	2.542 (7)		
O(4)	2.770 (8)		
or			
	O(5)	2.550 (18)	
	O(5')	2.666 (17)	

in Al—O distances was much diminished: all now lay between 1.73 and 1.78 Å. Assuming that O(5) is a hydroxyl ion (as required by charge-balance considerations) each primitive rhombohedral cell contains Sr<sub>7.5</sub>[Al<sub>12</sub>O<sub>24</sub>](OH)<sub>3</sub> (the centred trigonal cell given in Table 1 contains three times as much). This corresponds to an oxide ratio 5SrO·4Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O, which agrees reasonably well with both Carlson's (1955) and Henderson's (1975) formulae.

## Description of the structure

The final structure (Fig. 1) has an AlO<sub>2</sub> framework essentially similar to that described by Nevskii *et al.* (1979) but more symmetrical. It is built from rings of

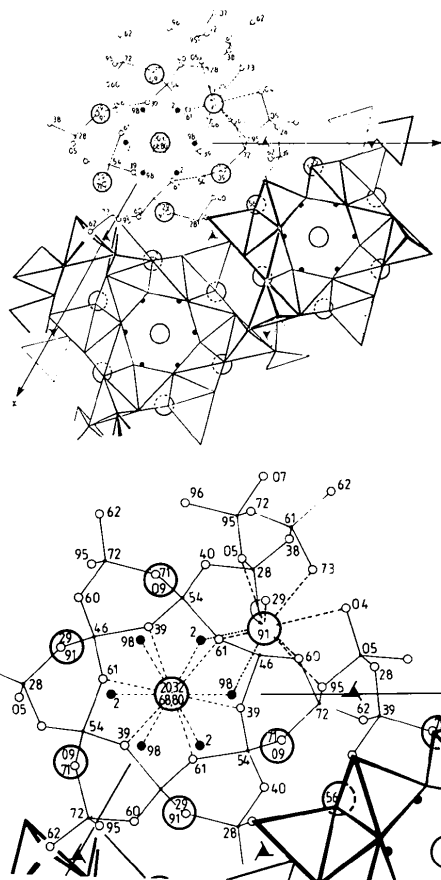


Fig. 1. The structure of 5SrO·4Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O projected along *z*; only part of the unit cell is shown. Large open circles represent Sr, small open circles O, small filled circles OH; Al atoms are represented by points; oxygen tetrahedra about Al are also shown. An enlargement of part of the diagram showing heights in *c*/100 is also given. Some of the screw axes are indicated. Coordination about Sr(1) near the top of the diagram is shown by heavy, dashed lines; shorter dashes indicate contacts to the disordered O(5) atoms. One O atom, at height 29, is displaced to make the coordination clearer. Light dashed lines indicate coordination about the disordered Sr(2) and Sr(3); this is given in more detail in Fig. 2.

three and six tetrahedra enclosing cavities whose centres lie at  $0,0,0$ ,  $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$  and  $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$  (*i.e.* at the origin of each primitive rhombohedral cell). The Sr(1) atoms lie in positions similar to those described in the earlier paper. The principal difference between the two structures is in the arrangement of the remainder of the cavity contents. The Sr and O, with occupancies of 0.5, originally thought to lie on the threefold axes, are replaced in the refined structure by Sr(2) and Sr(3) with occupancies of  $\frac{1}{2}$  and  $\frac{1}{4}$  respectively. A group of three hydroxyl ions, distributed over six equivalent sites, completes the coordination of the Sr atoms, and provides charge balance. The somewhat peculiar coordination of Sr(2) and Sr(3) is shown in Fig. 2; it is best discussed in terms of local charge balance.

Within any one cavity, one of the two possible Sr(2) sites must be wholly occupied: let us suppose it to be the lower one in Fig. 2. The three hydroxyl ions must then occupy the positions more remote from Sr(2): the others are too close (2.29 Å). The probability that any cavity also contains an Sr(3) atom is 0.5 [there are two Sr(3) sites each with an occupancy of 0.25]. If this particular cavity *does* contain an Sr(3) atom, it must be the upper site that is occupied, since the other is too close to Sr(2). Within any one cavity there is thus considerable local order, as Fig. 2 shows; if one begins with the assumption that the upper Sr(2) site is occupied, the whole arrangement inverts.

The alternation of distances to be seen in Fig. 2 can be rationalized, by considering the electrostatic valence requirements of the structure. These are summarized in Fig. 3. Since all the Al—O bonds are nearly equal in length, and therefore in strength, a valence of  $\frac{3}{4}$  of a unit can be assigned to each bond. The eight Sr(1)—O

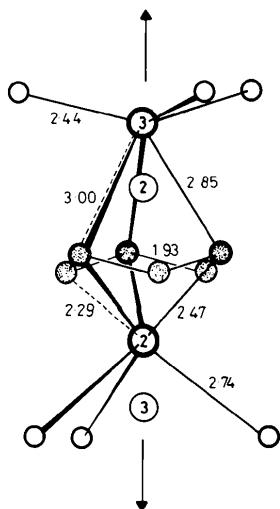


Fig. 2. Coordination about the disordered Sr(2) and Sr(3) atoms for one configuration; unoccupied sites are shown by less heavy lines. Large open circles Sr, small open circles O, small stippled circles OH. (Distances in Å.)

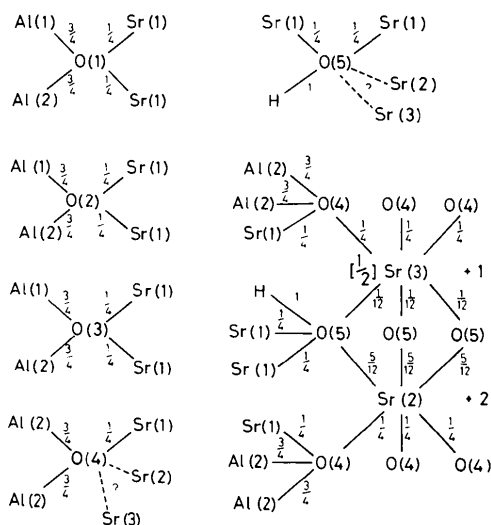


Fig. 3. The electrostatic valence rule applied to  $5\text{SrO} \cdot 4\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . Fractions indicate the order of the bonds beside which they appear.

distances are also all sufficiently near equal to justify the assumption of  $\frac{1}{4}$  of a unit for each Sr(1)—O bond. On this basis, as Fig. 3 shows, the valence balance at O(1), O(2) and O(3) is quite straightforward. The situation at O(4) and O(5), both of which make contact with the disordered Sr(2) and Sr(3) atoms, is more complex. At the bottom right of Fig. 3 we show the *average* situation, over many unit cells, for the configuration shown in Fig. 2; this assumes a charge of +1 for Sr(3) because it is present, on average, in half the cavities (see previous paragraph). In this average structure, the valence assigned to the Sr(2)—O(5) and Sr(3)—O(4) contacts is greater than that for Sr(2)—O(4) and Sr(3)—O(5) respectively, in agreement with the observed bond distances. The ill-defined coordination of O(4) and O(5) is reflected in their relatively high temperature factors (Table 2).

In reality, of course, half-atoms do not occur: in any given cavity either Sr(3) is present or else it is not. In either case, satisfactory assignments of bond valences can no longer be made. The discrepancies — surpluses or deficiencies of charge — are presumably spread out through the structure as a whole, so perhaps the use of an 'average' balance is not unreasonable.

### Comparison with other structures

The most interesting feature of  $5\text{SrO} \cdot 4\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  is undoubtedly the framework, which is quite different from any other so far described, and it is particularly instructive to compare it with those found in silicates and aluminosilicates. An unusual feature is the occurrence of rings of three tetrahedra. Although they are relatively uncommon in silicates, such rings are found

as isolated units, for example in pseudo-wollastonite,  $\alpha$ - $\text{CaSiO}_3$  (Hilmer, 1962), high-pressure  $\text{CaSiO}_3$  (Trojer, 1969), benitoite,  $\text{BaTiSi}_3\text{O}_9$  (Fischer, 1969), walstromite,  $\text{Ca}_2\text{BaSi}_3\text{O}_9$  (Glasser & Dent Glasser, 1961), margarosanite,  $\text{PbCa}_2\text{Si}_3\text{O}_9$  (Freed & Peacor, 1969), wadeite,  $\text{K}_2\text{ZrSi}_3\text{O}_9$  (Henshaw, 1955; Blinov, Shumyatskaya, Voronkov, Ilyukhin & Belov, 1977), and in various synthetic compounds such as low  $\text{BaSiO}_3$  (Funk, 1958),  $\text{SrSiO}_3$  (Liebau, 1960) and  $\text{BaSnSi}_3\text{O}_9$  (Choisnet, Deschanvres & Ranveau, 1972): their formation appears to be favoured by the presence of large cations such as Ba, K or Pb. The only example of their occurrence as part of a sheet or framework structure appears to be in the  $(\text{SiAl})_{18}\text{O}_{42}$  sheet of zussmanite (Lopez-Vieira & Zussman, 1969).

A possible explanation for the rarity of such rings in crystalline silicates is that even the most favourable configuration results in rather short Si—Si distances compared with the favourable value found in rings of four tetrahedra (O'Keeffe & Hyde, 1978). A compilation of Si—O—Si angles by Glidewell (1977) shows that in rings of three tetrahedra the observed angle is consistently less than that calculated using a 'hard atom' model. O'Keeffe & Hyde (1978) considered that the most favourable angle for Al—O—Al should be similar to that for Si—O—Si; however, data for condensed aluminates are scarce compared with silicates. On a crude electrostatic model, it would not be surprising to find that Al...Al repulsion was less important than Si...Si repulsions, and that in consequence configurations can be found in aluminates that do not occur in silicates. It is interesting to note that, in the case of zussmanite, the average Si—O distance in the tetrahedra forming the  $\text{Si}_3\text{O}_9$  ring is 1.65 Å, compared with 1.61 Å in the rest of the sheet. This is perhaps due to Si...Si repulsion in the ring, but would also be consistent with an increased amount of Al substitution; it must, however, be added that the valence-bond analysis given by the authors lends no support to this idea.

Framework aluminates analogous to framework silicates are, however, known. The 'stuffed tridymite' structures such as  $\text{BaAl}_2\text{O}_4$  (Wallmark & Westgren, 1937; Nowacki, 1942; Perrotta & Smith, 1968) and  $\text{CaAl}_2\text{O}_4$  (Dougill, 1957) are based on tridymite-like  $\text{AlO}_2$  frameworks with cations in the interstices. Frameworks are also found in the sodalite analogues  $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (Ahmed, Dent Glasser & King, 1973),  $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (Henderson, 1975) and  $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  (Ponomarev, Kheiker & Belov, 1970).

The present structure, and all those listed in the previous paragraph (as well as many others), contain  $\text{AlO}_4$  tetrahedra sharing corners. It is frequently

claimed, with particular reference to aluminosilicate frameworks, that this never happens: this is the 'aluminium avoidance rule', or 'Loewenstein's rule' (Loewenstein, 1954). While it certainly seems reasonable that in an  $(\text{Al,Si})\text{O}_2$  framework the most favourable situation energetically would be that in which the Al and Si were more or less evenly distributed throughout the framework, there is plainly nothing inherently impossible in two Al-containing tetrahedra being linked. Indeed, Loewenstein himself pointed out that  $\text{KAlO}_2$  (Barth, 1935) is an exception to the rule. In the light of our earlier remarks concerning repulsion between adjacent Si atoms, it is tempting to suggest that the effect is indeed rather one of 'silicon avoidance'; in any case it should be regarded as a tendency rather than a rule.

#### References

- AHMED, A. H. M., DENT GLASSER, L. S. & KING, M. G. (1973). *Acta Cryst.* **B29**, 1166–1167.  
 BARTH, T. F. W. (1935). *J. Chem. Phys.* **3**, 323–325.  
 BLINOV, V. A., SHUMYATSKAYA, N. G., VORONKOV, A. A., ILYUKHIN, V. V. & BELOV, N. V. (1977). *Kristallografiya*, **22**, 59–65.  
 CARLSON, E. T. (1955). *J. Res. Natl Bur. Stand.* **54**, 329–334.  
 CHOISNET, J., DESCHANVRES, A. & RANVEAU, B. (1972). *J. Solid State Chem.* **4**, 209–218.  
 DOUGILL, M. W. (1957). *Nature (London)*, **180**, 292–293.  
 FISCHER, K. (1969). *Z. Kristallogr.* **129**, 222–243.  
 FREED, R. L. & PEACOR, D. R. (1969). *Z. Kristallogr.* **128**, 213–228.  
 FUNK, H. (1958). *Z. Anorg. Allg. Chem.* **296**, 46–62.  
 GLASSER, F. P. & DENT GLASSER, L. S. (1961). *Z. Kristallogr.* **116**, 263–265.  
 GLIDEWELL, C. (1977). *Inorg. Chim. Acta*, **25**, 77–90.  
 HENDERSON, A. P. (1975). PhD Thesis, Univ. of Aberdeen.  
 HENSHAW, D. M. (1955). *Mineral. Mag.* **30**, 585–595.  
 HILMER, W. (1962). *Kristallografiya*, **7**, 704–708.  
 LIEBAU, F. (1960). *Neues Jahrb. Mineral. Abh.* **94**, 1209–1222.  
 LOEWENSTEIN, W. (1954). *Am. Mineral.* **39**, 92–96.  
 LOPEZ-VIEIRA, A. & ZUSSMAN, J. (1969). *Mineral. Mag.* **37**, 49–59.  
 NEVSKII, N. N., GLASSER, L. D., ILYUKHIN, V. V. & BELOV, N. V. (1979). *Kristallografiya*, **24**, 161–166.  
 NOWACKI, W. (1942). *Naturwissenschaften*, **30**, 471–472.  
 O'KEEFFE, M. & HYDE, B. G. (1978). *Acta Cryst.* **B34**, 27–32.  
 PERROTTA, A. J. & SMITH, J. V. (1968). *Bull. Soc. Fr. Minéral. Cristallogr.* **91**, 85–87.  
 PONOMAREV, V. I., KHEIKER, D. M. & BELOV, N. V. (1970). *Kristallografiya*, **15**, 918–921.  
 TROJER, F. J. (1969). *Z. Kristallogr.* **130**, 185–206.  
 WALLMARK, S. & WESTGREN, A. (1937). *Ark. Kemi Mineral. Geol.* **12B**, 1–4.