

# High-pressure $\text{Ca}_4\text{Al}_6\text{O}_{13}$ : An example of a calcium aluminate with three different types of coordination polyhedra for aluminum

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## ABSTRACT

The crystal structure of tetracalcium trialuminate ( $\text{Ca}_4\text{Al}_6\text{O}_{13}$ ), synthesized at 1250 °C and 2.5 GPa, has been determined from single-crystal X-ray data by direct methods [space group *Pcan*,  $Z = 8$ ,  $a = 5.3002(2)$  Å,  $b = 17.7610(5)$ ,  $c = 21.0887(9)$  Å] and refined to  $R1 = 6.42\%$ . The unit cell parameters of  $\text{Ca}_4\text{Al}_6\text{O}_{13}$  exhibit a relationship to those of perovskite:  $a \approx \sqrt{2} a_{\text{pv}}$ ,  $b \approx 5 a_{\text{pv}}$ , and  $c \approx 4 \sqrt{2} a_{\text{pv}}$ . The diffraction data showed the typical features of a pseudotranslational symmetry: all reflections ( $hkl$ ) with  $l$  equal  $4n$  ( $n$  is an integer) had significantly higher intensity than the reflections with  $l \neq 4n$ . Furthermore, diffuse streaks parallel to  $b^*$  were observed. The new compound exhibits  $\text{Al}^{3+}$  in three different kinds of coordination polyhedra: octahedra, tetrahedra, and trigonal bipyramids. One of the two main building units is slightly corrugated sheets of perovskite-type corner sharing  $\text{AlO}_6$  octahedra perpendicular to  $[010]$ . The octahedral sheets are connected by layers containing tetrahedral zweier single chains. Within these layers the tetrahedral chains are linked by two different kinds of rods containing distorted trigonal bipyramids sharing common corners and edges, respectively. The tetrahedral chains and the bipyramidal rods are parallel to  $[100]$ . Charge compensation is achieved by the Ca ions, which are coordinated by 9 or 10 oxygen cations.

## INTRODUCTION

The system  $\text{CaO-Al}_2\text{O}_3$  has been the subject of many phase equilibrium studies. This interest is mainly due to the fact that calcium aluminum oxides are of special importance as constituents of Portland cements and calcium aluminate cements (Taylor 1997). A summary of the structures of known calcium aluminate compounds is given in Table 1. The number of observed phases depends strongly on the  $P_{\text{H}_2\text{O}}$  and the  $f_{\text{O}_2}$  of the furnace atmosphere. For conditions in air of ordinary humidity, the following five compounds have been found: Tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ),  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ , monocalcium aluminate ( $\text{CaAl}_2\text{O}_4$ ), calcium dialuminate ( $\text{CaAl}_2\text{O}_7$ ) and calcium hexaluminate ( $\text{CaAl}_{12}\text{O}_{19}$ ). Synthesis in the absence of water results in the formation of an additional compound, pentacalcium trialuminate ( $\text{Ca}_5\text{Al}_3\text{O}_{14}$ ). Furthermore, a sodalite-type phase of composition  $\text{Ca}_4\text{Al}_6\text{O}_{13}$  can be prepared by thermal decomposition of  $\text{Ca}_4\text{Al}_6\text{O}_{13} \cdot 3\text{H}_2\text{O}$ . We recently reported the crystal structure of a brownmillerite compound with composition  $\text{Ca}_2\text{Al}_2\text{O}_5$  synthesized at 1250 °C and 2.5 GPa. Here we present the crystal structure of a new high-pressure polymorph of  $\text{Ca}_4\text{Al}_6\text{O}_{13}$ , whose structure is completely different from the above mentioned sodalite-type phase.

## EXPERIMENTAL DETAILS

### Sample preparation

The starting material was prepared by solid state reactions, using  $\text{CaCO}_3$  (Merck, 99%) and  $\text{Al}_2\text{O}_3$  (Aldrich, 99.8%) as reagents. The mixed powders were pressed into pellets and sintered at 1250 °C for 24 h in air. Grinding and firing were repeated twice. The sintered precursor material was re-ground and used for high-pressure experiments performed at the Bayerisches Geoinstitut. The experiments were carried out in a 1/2 inch piston cylinder apparatus using talc-pyrex cells with a tapered graphite heater. The samples were encapsulated in 1 cm long and 5 mm diameter welded Pt capsules. The experiments were performed at 2.5 GPa and 1250 °C for 48 hours. Pressure was calibrated against the quartz–coesite and kyanite–sillimanite transitions, as well as the melting point of diopside. A friction correction of 18% was applied to the nominal pressure on the basis of these calibration data. Temperature was measured with a  $\text{Pt}_{90}\text{Rh}_{10}$ –Pt thermocouple and controlled with a Eurotherm 818 controller. Temperatures are considered accurate within  $\pm 10$  °C with a temperature gradient of about 5 °C from the top to the middle of the capsule (Shaw and Fliervoet, unpublished data). The experiments were carried out using the hot-piston out technique. The samples were quenched isobarically by turning off the power of the furnace while maintaining pressure within 0.02 GPa of the run pressure. Quench rates were of the order of 75 °C per second.

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### Single-crystal data measurement

Preliminary investigations included polarization microscopy and X-ray diffraction camera techniques. The photographs indicated orthorhombic Laue symmetry ( $a = 5.3 \text{ \AA}$ ,  $b = 17.8 \text{ \AA}$ ,  $c = 21.2 \text{ \AA}$ ). However, most of the crystals showed a superposition of the sharp Bragg peaks by weak continuous diffuse streaks parallel to  $b^*$ . Furthermore, the photographs revealed the typical intensity distribution of a superstructure: reflections with  $l = 4n$  ( $n$  is an integer) had significantly higher intensity than those with  $l \neq 4n$ . The evaluation of the systematic extinction rules resulted in the space group  $Pcan$  (no. 60). Experimental details pertaining to data collection from the single-crystal are given in Table 2. This sample with good optical quality showed only extremely weak diffuse scattering effects. The morphology of the crystal was described by six external faces and a face absorption correction was applied. Data reduction included Lorentz and polarization corrections.

### Structure solution and refinement

The structure was solved by direct methods with the program SIR92 (Altomare et al. 1992) using a multisolution process. The pseudotranslational symmetry detected in the preliminary investigations was included as a priori information during the normalization of the structure factors. The phase set with the maximum combined figure of merit resulted in an E-map, the most intense peaks of which could be interpreted as a partial structure containing the calcium, aluminum, and some of the oxygen atoms. The structure was completed by difference Fourier calculations providing the starting parameters for the least squares refinements performed with the program SHELXL-93 (Sheldrick 1993). Neutral-atom scattering factors and anomalous-dispersion corrections were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). The calculations using isotropic temperature factors converged to  $R1 = 6.42\%$  for 93 parameters and 1933 independent reflections with  $I > 2 \sigma(I)$ , Table 2. The introduction of anisotropic displacement parameters improved the residual index  $R1$  only slightly ( $R1 = 5.05\%$ ) and resulted in a non-positive definite temperature factor of the oxygen site O13. A re-examination of the diffraction data, the absorption correction and the resulting bond distances and angles did not reveal any indications that a wrong space group symmetry had been chosen nor did we detect any evidence for a systematic error during the data reduction. We attribute the problems with the thermal motion of the oxygen O13 to an unfavorable ratio of parameters to observed reflections. To model the anisotropic thermal motion of each atom the total number of parameters is increased to 211 and the over-determination is reduced to  $1933/211 \approx 9$ , or to a factor 6, if the reflections with  $I > 3 \sigma(I)$  are considered. The final atomic coordinates of the calculations with isotropic temperature factors as well as the bond distances are given in Table 3 and Table 4, respectively.

### DESCRIPTION OF THE STRUCTURE

Two main building units exist in the Al-O network of the structure (Fig. 1) perpendicular to  $[010]$ : (1) Perovskite-type layers of corner connected Al-O octahedra and (2) layers of different corner sharing rods of polyhedra where aluminum

TABLE 1. Compounds in the system  $\text{CaO-Al}_2\text{O}_3$

Space group	Composition	Al-coordination	Reference
$P\bar{a}3$	$\text{Ca}_3\text{Al}_2\text{O}_6$	tet	Mondal and Jeffery (1975)
$I2mb$	$\text{Ca}_2\text{Al}_2\text{O}_5$	tet, oct	Kahlenberg et al. (2000)
$I\bar{4}3d$	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	tet	Bartl and Scheller (1970)
$Cmc2_1$	$\text{Ca}_5\text{Al}_5\text{O}_{14}$	tet	Vincent and Jeffery (1978)
$I\bar{4}3m$	$\text{Ca}_4\text{Al}_6\text{O}_{13}$	tet	Ponomarev et al. (1971)
$Pcan$	$\text{Ca}_4\text{Al}_6\text{O}_{13}$	tet, bipr*, oct	This work
$P2_1/n$	$\text{CaAl}_2\text{O}_4$	tet	Hörkner and Müller-Buschbaum 1976
$C2/c$	$\text{CaAl}_4\text{O}_7$	tet	Goodwin and Lindop 1970
$P6_3/mmc$	$\text{CaAl}_{12}\text{O}_{19}$	tet/bipr/oct	Kato and Saalfeld 1968

\* Bipyramidal.

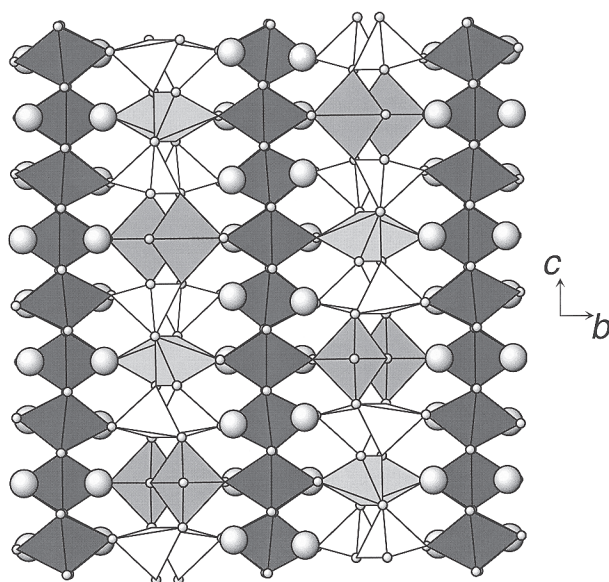
TABLE 2. Summarized CCD data collection and refinement parameters

$a$ (Å)	5.3002(2)
$b$ (Å)	17.7610(5)
$c$ (Å)	21.0887(9)
$V$ (Å <sup>3</sup> )	1985.2(1)
Space group	$Pcan$
$Z$	8
Formula	$\text{Ca}_4\text{Al}_6\text{O}_{13}$
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	3.548
$\mu$ (cm <sup>-1</sup> )	28.03
Crystal shape	Fragment of a plate
Crystal dimensions	$20 \times 90 \times 120 \text{ }\mu\text{m}^3$
Diffractometer	Nonius Kappa-CCD
Monochromator	Graphite
X-ray radiation	Sealed tube $\text{MoK}\alpha$ (0.71073 Å)
X-ray power	50 kV, 30 mA
$\Theta$ -range	$2.0 - 30.0^\circ$
Reflection range	$ h  \leq 7; -23 \leq k \leq 22; -29 \leq l \leq 22$
No. of frames	186
Data collection time per frame	63 seconds
Rotation width	$1.3^\circ$
Measured reflections	16266
Unique reflections in $m m m$	2909
Observed reflections [ $I > 2 \sigma(I)$ ]	1933
$R_{\text{int}}$ for $m m m$	0.065
Max./min. transmission	0.908 / 0.720
Parameters used in the refinement	93
$R1$ [ $F_o > 4 \sigma(F_o)$ ]	0.064
$wR2$ [ $F_o > 4 \sigma(F_o)$ ]	0.132
Weighting parameter $a, b$	0.06, 81.73
Goodness of Fit	1.12
Final $\Delta\rho_{\text{min}}$ (e/Å <sup>3</sup> )	1.2
Final $\Delta\rho_{\text{max}}$ (e/Å <sup>3</sup> )	-1.3

Notes:  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ ;  $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ ;  $P = [2F_c^2 + \max(F_o^2, 0)] / 3$ .

adopts a fivefold coordination. Whereas two (Al3 and Al4) of the four different Al sites of the second building unit are coordinated in form of distorted trigonal bipyramids, the remaining two sites Al6 and Al7 show a distinct  $[4+1]$  coordination geometry. The inner four oxygen ligands form distorted tetrahedra and therefore, these two sites will be described as "tetrahedral" positions.

Projection of a single octahedral sheet parallel to  $[010]$  shows that the layers are corrugated (Fig. 2a). However, the degree of undulation is not very pronounced (cf. Fig. 2b). The Al-O bond distances within the octahedra about Al1, Al2, and Al5 vary between 1.85 Å and 2.1 Å. The distances between Al1 and Al2, respectively, and the two oxygen atoms bridging each octahedron with the "tetrahedral" chains of the second unit are considerably longer (about 2.1 Å) than the bonds to the four oxygen atoms within the octahedral layer. These two



**FIGURE 1.** Projection of the crystal structure of  $\text{Ca}_4\text{Al}_6\text{O}_{13}$  parallel to  $[100]$  with  $\text{AlO}_6$ -octahedra (dark gray),  $\text{AlO}_4$ -tetrahedra (white) and  $\text{AlO}_5$ -bipyramids (medium gray). Small and large spheres represent oxygen ligands of the polyhedra and Ca cations, respectively.

octahedra are primarily distorted along the crystallographic  $b$ -axis, perpendicular to the layers. The third octahedron about Al5 does not show the two distinct groups of four shorter and two longer bond distances observed for Al1 and Al2. However, in common with Al1 and Al2, the two longest bonds for this octahedron connect the octahedral layer with polyhedra (distorted trigonal bipyramids) of the second main building unit. Adjacent octahedral layers are shifted about  $a/2$  against each other. Therefore, in a projection perpendicular to the sheets the vertices of octahedra belonging to neighboring perovskite layers do not project upon each other, a structural feature which is not observed in perovskite, but is seen in the octahedral layers of the  $\text{K}_2\text{NiF}_4$  structural type.

A single intermediate layer connecting the octahedral sheets is shown in Figure 3 in a projection parallel to  $[010]$ . The layer can be built up from three different linear structural elements running along  $[100]$ : zweier single chains of  $\text{AlO}_4$ -tetrahedra, rods of corner sharing trigonal bipyramids (type 1) and rods of edge sharing trigonal bipyramids (type 2).

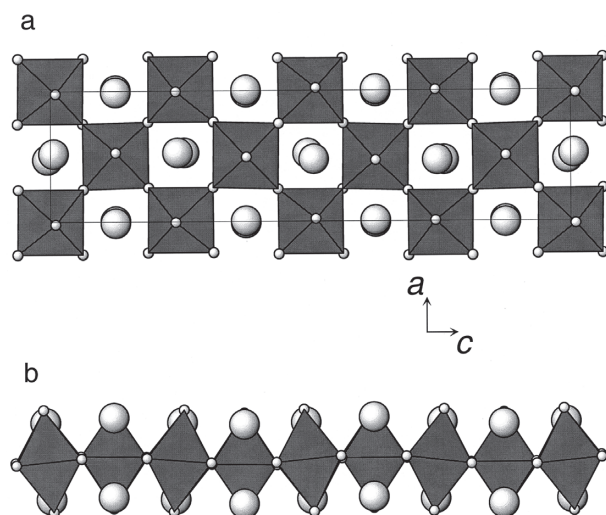
The tetrahedra about Al6 and Al7 show a considerable spread in both bond lengths and bond angles. One short Al-O (about 1.74 Å) and three longer bonds (about 1.80 Å) can be distinguished. The short bond links the tetrahedral chains to the octahedral layers, whereas the other three bonds connect the chains to the rods of types 1 and 2. The O-Al-O angles in the tetrahedra vary between  $94^\circ$  and  $124^\circ$ , indicating a significant amount of distortion. Tetrahedral chains with their vertices pointing to each other are connected by rods of type 2. Chains having a reversed orientation of the vertices are linked by type 1 rods (cf. Fig. 3). Additional linkage to the rods of type 1 results from the fifth O13 atom, about 2.5 Å away from Al6 and Al7, respectively. The calculation of the bond valences for Al6 and Al7 using the data of Brown and Altermatt (1985) reveal, that

**TABLE 3.** Fractional atomic coordinates and isotropic temperature factors

	$x$	$y$	$z$	$U_{\text{iso}}$
Al1	0	0	$\frac{1}{2}$	0.006(1)
Al2	0.9846(6)	0	$\frac{1}{4}$	0.005(1)
Al3	0.5635(4)	-0.2034(1)	0.3754(1)	0.005(1)
Al4	0.0023(4)	-0.2834(1)	0.6248(2)	0.004(1)
Al5	0.0040(4)	-0.4904(1)	0.6252(2)	0.006(1)
Al6	0.8920(5)	-0.2070(1)	0.2573(1)	0.008(1)
Al7	0.8986(5)	-0.2068(1)	0.4927(1)	0.008(1)
Ca1	0.9933(3)	0.0983(1)	0.3750(1)	0.011(1)
Ca2	0.0095(3)	-0.0826(1)	0.3753(1)	0.005(1)
Ca3	0.4780(3)	-0.0871(1)	0.4943(1)	0.007(1)
Ca4	0.4707(3)	-0.0872(1)	0.2562(1)	0.007(1)
O1	0.7515(10)	0.0045(3)	0.4371(3)	0.006(1)
O2	0.8203(12)	-0.2245(3)	0.1760(3)	0.013(1)
O3	0.7383(10)	0.0055(3)	0.3118(3)	0.007(1)
O4	0.8277(12)	-0.2227(3)	0.5747(3)	0.012(1)
O5	0.2361(10)	0.0085(3)	0.3128(3)	0.005(1)
O6	0.0692(11)	-0.2867(3)	0.2829(3)	0.007(1)
O7	0.2484(10)	0.0096(3)	0.4382(3)	0.005(1)
O8	0.4698(10)	-0.1083(3)	0.3751(3)	0.007(1)
O9	0.5745(11)	-0.2123(3)	0.4676(3)	0.008(1)
O10	0.0044(9)	-0.1154(3)	0.2596(3)	0.006(1)
O11	0.0200(10)	-0.1160(4)	0.4905(3)	0.008(1)
O12	0.9957(11)	-0.3815(3)	0.6241(4)	0.015(1)
O13	0.8991(12)	-0.2099(4)	0.3759(3)	0.017(1)

**TABLE 4.** Selected bond distances (Å)

Al1	O7	1.861(5) ×2	Al2	O3	1.848(6) ×2
Al1	O1	1.871(5) ×2	Al2	O5	1.885(6) ×2
Al1	O11	2.073(5) ×2	Al2	O10	2.062(6) ×2
Al3	O8	1.760(6)	Al4	O12	1.743(7)
Al3	O13	1.770(7)	Al4	O4	1.771(7)
Al3	O13	1.783(7)	Al4	O2	1.773(7)
Al3	O9	1.951(6)	Al4	O4	2.025(7)
Al3	O6	1.960(6)	Al4	O2	2.026(7)
Al5	O3	1.849(6)	Al6	O10	1.733(7)
Al5	O7	1.872(6)	Al6	O6	1.783(6)
Al5	O1	1.889(6)	Al6	O2	1.783(6)
Al5	O5	1.900(6)	Al6	O6	1.797(6)
Al5	O12	1.935(7)	Al6	O13	2.501(8)
Al5	O8	2.099(6)			
Al7	O11	1.736(7)			
Al7	O4	1.792(7)			
Al7	O9	1.793(6)			
Al7	O9	1.800(6)			
Al7	O13	2.465(8)			
Ca1	O5	2.434(6)	Ca2	O13	2.335(6)
Ca1	O7	2.466(6)	Ca2	O5	2.407(6)
Ca1	O1	2.476(6)	Ca2	O1	2.442(6)
Ca1	O3	2.513(6)	Ca2	O7	2.458(6)
Ca1	O12	2.617(6)	Ca2	O8	2.482(6)
Ca1	O4	2.628(6)	Ca2	O11	2.501(7)
Ca1	O2	2.650(6)	Ca2	O10	2.508(7)
Ca1	O12	2.732(6)	Ca2	O3	2.511(6)
Ca1	O11	2.855(7)	Ca2	O8	2.897(6)
Ca1	O10	2.856(7)			
Ca3	O9	2.351(6)	Ca4	O6	2.368(6)
Ca3	O1	2.393(6)	Ca4	O5	2.369(6)
Ca3	O7	2.415(6)	Ca4	O5	2.420(6)
Ca3	O7	2.454(6)	Ca4	O3	2.470(6)
Ca3	O11	2.483(6)	Ca4	O3	2.484(6)
Ca3	O1	2.490(6)	Ca4	O10	2.523(5)
Ca3	O8	2.542(7)	Ca4	O8	2.536(8)
Ca3	O12	2.796(9)	Ca4	O12	2.845(9)
Ca3	O11	2.919(6)	Ca4	O10	2.874(5)



**FIGURE 2.** View of a single layer of corner sharing  $\text{AlO}_6$ -octahedra. (a) Projection parallel to  $[010]$ . (b) Projection parallel to  $[100]$ .

the contribution of O13 to the total sum of about 2.97 v.u. and 2.94 v.u., respectively, is only very small (about 0.10 v.u. in both cases)

The single bipyramids about Al3 (type 1 rods) and Al4 (type 2 rods) both adopt an elongated form with three shorter equatorial and two longer terminal Al-O distances (Fig. 4). However, they differ with respect to the orientation of their longest axis. In the Al3-bipyramid this direction is approximately parallel to  $[001]$ . The longest axis of the bipyramids about Al4 are located within planes parallel to  $(101)$ , making an angle of  $\pm 25^\circ$  with  $[100]$ .

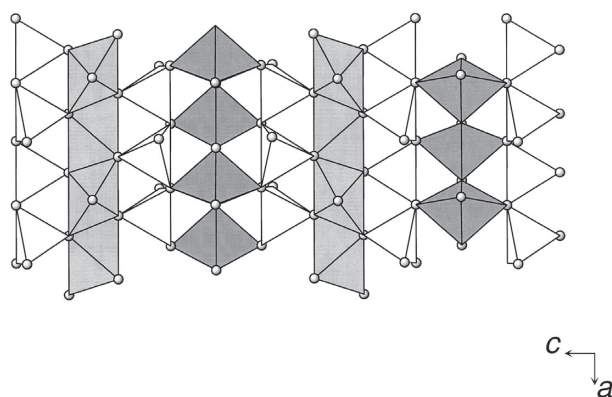
The calcium cations in the structure of  $\text{Ca}_4\text{Al}_6\text{O}_{13}$  are coordinated by nine (Ca2, Ca3, Ca4) or ten (Ca1) O-atoms up to 3.0 Å. From Figure 5, the coordination polyhedra can be described as distorted mon capped tetragonal antiprisms and distorted bicapped cubes, respectively.

The bond valences for all cations give reasonable values. The variation is between 2.88 and 3.05 v.u. for the crystallographic non equivalent  $\text{Al}^{3+}$ —and between 1.83 and 2.09 v.u. for the  $\text{Ca}^{2+}$ —cations.

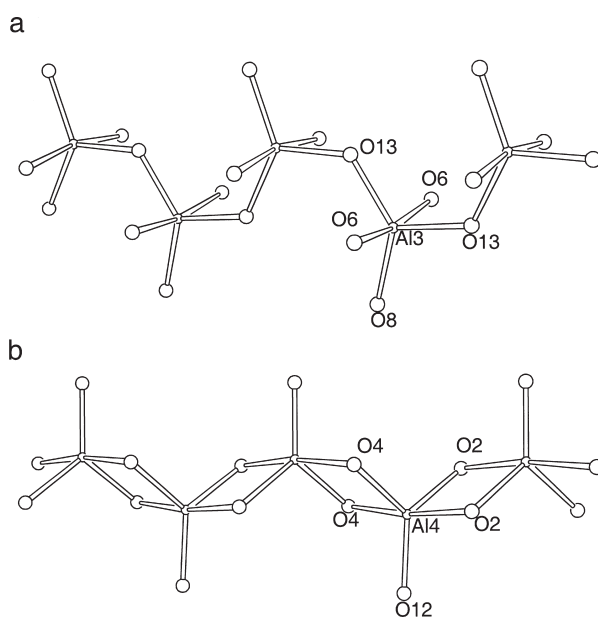
## DISCUSSION

### Pseudosymmetry

Interestingly, the structure reveals a distinct pseudo-translational symmetry, which can be easily identified by inspection of Figure 2a. The atoms building up the octahedral sheets are mapped onto themselves after a translation period of about  $1/4c$ . The same pseudo-translation vector relates the positions of the calcium cations located near the apices of the octahedra. Therefore, a considerable amount of electron density  $\rho(\mathbf{r})$  satisfies the condition  $\rho(\mathbf{r}) \approx \rho(\mathbf{r} + 1/4c)$  and this structural feature accounts for the different intensities of the reflections belonging to the class  $l = 4n$  (defining the substructure) and the superstructure reflections with  $l \neq 4n$ , as mentioned above. The pseudo-translational symmetry of the octahedral slabs can also



**FIGURE 3.** Projection parallel to  $[010]$  of a single intermediate layer containing tetrahedral zweier single chains (white) as well as rods of corner-sharing (type 1) and edge-sharing (type 2) bipyramids.



**FIGURE 4.** Side view of the two different kinds of bipyramidal rods. (a) Rods of type 1. (b) Rods of type 2.

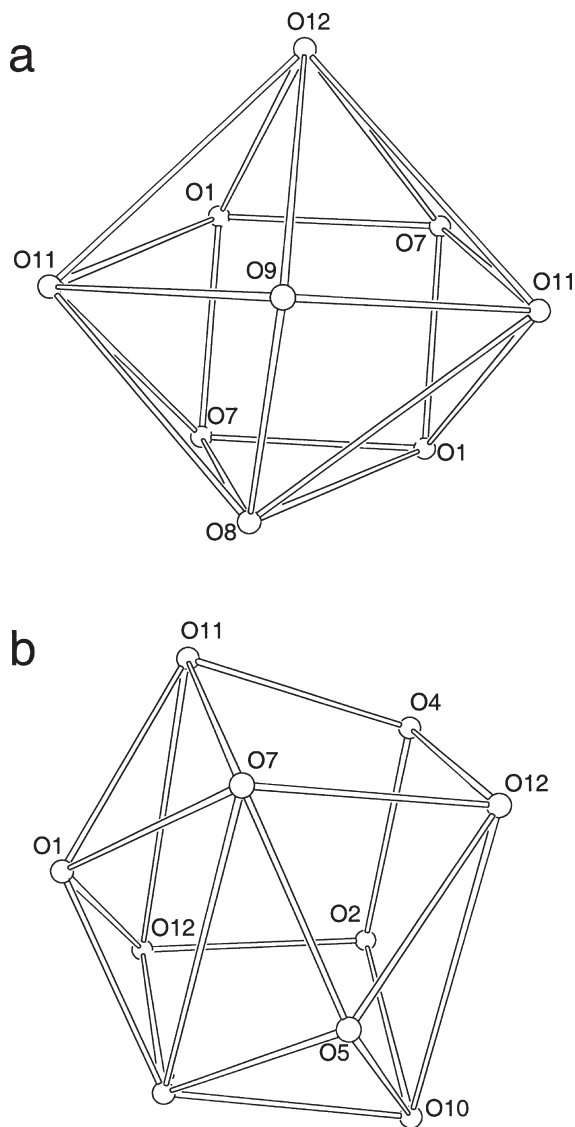
induce stacking faults perpendicular to  $[010]$ , which may explain the diffuse scattering effects observed parallel to  $b^*$ , perpendicular to the octahedral layers.

### Comparison with related structures

Within the group of calcium aluminates Al-O coordination numbers higher than four are an exception, Table 1. Apart from the present work, simultaneously occurring tetrahedral, octahedral and bipyramidal coordination for aluminum has been observed only in  $\text{CaAl}_{12}\text{O}_{19}$  (Kato and Saalfeld 1968). However, its crystal structure has no perovskite-type structural elements, but is closely related to those of corundum and  $\beta\text{-Al}_2\text{O}_3$ .

The combination of alternating layers of corner connected  $\text{AlO}_6$  octahedra and sheets of zweier single chains of  $\text{AlO}_4$  tet-





**FIGURE 5.** Coordination polyhedra about the calcium cations. (a) Distorted monocapped tetragonal antiprisms. (b) Distorted bicapped cubes.

rahedra as building elements has only recently been reported for  $\text{Ca}_2\text{Al}_2\text{O}_5$  (Kahlenberg et al. 2000). This compound belongs to the brownmillerite type structure family and can be considered as a defect perovskite where the oxygen vacancies are ordered along alternate  $[110]$  rows of the cubic perovskite structure. In  $\text{Ca}_2\text{Al}_2\text{O}_5$  as well as in high pressure  $\text{Ca}_4\text{Al}_6\text{O}_{13}$  the tetrahedra within the zweier single chains exhibit a distinct amount of distortion, especially with regard to the scatter in the O-Al-O angles.

In contrast to  $\text{Ca}_4\text{Al}_6\text{O}_{13}$ , where adjacent octahedral layers exhibit a shift parallel to the layer plane, a relative translation of the octahedral sheets is not observed in  $\text{Ca}_2\text{Al}_2\text{O}_5$ .

The high-pressure polymorph of tetracalcium trialuminate shows a degree of structural relationship to two other compounds of composition  $\text{A}_4\text{B}_6\text{O}_{13}$ :  $\text{Ba}_4\text{In}_6\text{O}_{13}$  (Yoshiasa et al. 1992) and  $\text{Sr}_4\text{Fe}_6\text{O}_{13}$  (Yoshiasa et al. 1986). Both materials are isotypic and crystallize in the orthorhombic space group  $Iba2$  with four formula units per unit cell. As in the case of  $\text{Ca}_4\text{Al}_6\text{O}_{13}$  the cell parameters can be related to those of perovskite:  $a = 2\sqrt{2}a_{\text{Pv}}$ ,  $b = 5a_{\text{Pv}}$ , and  $c = \sqrt{2}a_{\text{Pv}}$ . The basic building units are similar to those observed in  $\text{Ca}_4\text{Al}_6\text{O}_{13}$  with layers of corner-sharing octahedra and intermediate layers, where the B-cations adopt fivefold coordination polyhedra and similar problems due to many weak superstructure reflections were encountered during the structure refinement. Furthermore, neighboring octahedral layers are also shifted about one half of the short lattice constant ( $a = 5 \text{ \AA}$ ).

However, the comparison of the intermediate layers reveals definite differences. The In-O and Fe-O polyhedra are strongly distorted square pyramids sharing common edges, rather than trigonal bipyramids. Tetrahedral building elements are completely absent.

In summary, the high-pressure form of  $\text{Ca}_4\text{Al}_6\text{O}_{13}$  shows relationships to other known crystal structures, but up to now no similar coordination schemes have been found.

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