

Crystal synthesis and structure refinement of high-pressure ScAlO_3 perovskite

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Summary. Single crystals of ScAlO_3 perovskite have been synthesized at 3.5 GPa pressure using lithium fluoride as a high-temperature solvent. The crystal structure has been refined by the least-squares method using 498 three-dimensional reflections to a final R value of 0.028. Unit-cell dimensions at ambient conditions (1 bar, 20°C) are $a = 4.9355(3)$, $b = 5.2313(3)$, $c = 7.2007(5)$ Å, with space group $Pbnm$. The structure differs slightly from the powder refinement, resulting in less distortion of the aluminium octahedron. The space-group confirmation and the more regular octahedron are used as evidence in support of a centrosymmetric structure for the lower-mantle phase MgSiO_3 perovskite.

Introduction

MgSiO_3 perovskite was first synthesized by Liu (1974), who demonstrated that pyrope garnet disproportionated into a distorted perovskite phase plus corundum at pressures above 30.0 GPa in a laser-heated diamond anvil press. More recently, Liu (1975, 1976a) Ito (1977), Ito and Matsui (1978) and Yagi et al. (1978) have shown that MgSiO_3 pyroxene transforms to the distorted-perovskite structure at pressures greater than 25.0 GPa. Forsterite has also been found to transform to this modification above 25.0 GPa pressure (Liu, 1975, 1976b; Ito, 1977). Thus it appears certain that the distorted-perovskite structure is adopted by the major minerals within the earth's lower mantle.

Reid and Ringwood (1975) first proposed that MgSiO_3 pyroxene would transform to the distorted-perovskite structure on the basis of information obtained from a powder X-ray analysis of the high-pressure analogue compound ScAlO_3 . In this structure the B(Al) atoms occupy a site surrounded by six oxygen atoms in a distorted octahedral arrangement. Refinement of the crystal structure from powder patterns is made difficult by the large number of variable atomic parameters. This results in large errors

for the positional parameters and therefore bond lengths and angles. Furthermore, the powder data cannot distinguish the space groups *Pbnm* (centric) from *Pbn2₁* (non-centric), hence the true symmetry remains unresolved.

As shown in the experiments mentioned above, ScAlO₃ may be an excellent analogue structure for the important mantle phase, MgSiO₃ perovskite. However, detailed confirmation of the ScAlO₃ structure by single-crystal X-ray analysis remained to be carried out. It was therefore decided to grow sizeable crystals of this phase and refine its atomic structure by single-crystal X-ray analysis.

Experimental

High-pressure crystal synthesis

The crystals used in this study were synthesized under high temperature and pressure using the piston-cylinder apparatus described by Boyd and England (1960). The ScAlO₃ starting material was the same powder used by Reid and Ringwood (1975). Eighty weight percent of A.R. grade, lithium fluoride (flux) was thoroughly ground and mixed with twenty weight percent ScAlO₃ powder and sealed in a platinum capsule. At 3.5 GPa pressure, temperature was raised to 1250°C, held for 1 h and then lowered slowly at 2.5°C/min to 900°C. The charge was then quenched and pressure released. After removing the LiF by dissolving in dilute hydrochloric acid, many euhedral crystals of the perovskite phase remained, ranging from 10–200 μm in dimension. The most prominent forms are {110} and {001}. The crystals characteristically lack cleavage, parting or observable defects. Some crystals, however, were slightly pink in colour.

Crystal-structure analysis

Unit-cell dimensions were obtained by least-squares refinement of the setting angles of twelve carefully centered reflections having 2θ values between 60 and 80° (MoKα₁ radiation λ = 0.70926 Å). They are given in Table 1, together with other crystal data.

Table 1. Crystal data for ScAlO₃ perovskite

Orthorhombic, <i>Pbnm</i>		
<i>a</i> = 4.9355(3) Å	<i>b</i> = 5.2313(3) Å	<i>c</i> = 7.2007(5) Å
<i>V</i> = 185.91(4) Å ³	<i>Z</i> = 4	
<i>D</i> = 4.31 g cm ⁻³		

A nearly cubic crystal 0.1 mm in length bounded by {001} and {110} faces was selected for data collection. Preliminary investigations to check for crystal singularity, orientation and space group extinctions were made of the $h0l$, $h1l$, $0kl$ and $hk0$ layers using precession and Weissenberg X-ray photographic techniques. The Friedel pairs hkl and $\bar{h}\bar{k}\bar{l}$ were carefully examined for inequality such as might originate from anomalous dispersion, but no significant difference was found. Consequently the centric space group was taken as correct. The intensity data were collected on a Philips PW 1100/20 automatic 4-circle diffractometer using MoK α_1 radiation ($\lambda = 0.70926 \text{ \AA}$) reflected from a graphite-crystal monochromator. Five hundred and seventy-seven symmetrically independent reflections were measured within the range $1.5^\circ < \theta < 40^\circ$. The $\omega - 2\theta$ scan technique was used, at a scan speed of $1.2^\circ \text{ min}^{-1}$ and with an asymmetric scan range from $(\theta_{x_i} - 0.4)^\circ$ to $(\theta_{x_i} + 0.4 + \Delta)^\circ$, where Δ is the allowance for angular separation between MoK α_1 , and MoK α_2 components for the reflection concerned. Stationary background counts each of 20 s duration were measured at both limits of the scan range. Three standard reflections collected every 2 h showed little instability during the course of data collection. Intensities were corrected for Lorentz and polarization effects. No absorption correction was made.

The data were then sorted to an efficient order for subsequent computer programs. At the same time, reflections for which $F/\sigma F < 3.0$ were discarded as being unobserved. A total of 498 unique reflections were available for subsequent structural analysis.

Structural refinement

Atomic scattering factors for neutral atoms, together with corrections for the real and imaginary parts of anomalous scattering (f' , f'') used in the structure refinement were taken from Ibers and Hamilton (1974).

The refinement was carried out using the full-matrix least-squares program SFLS which minimizes the function $\sum w (|F_o| - k |F_c|)^2$ where k is an overall scale factor, and w is the weight of an observation (taken as unity in the initial stages and later assumed the form $w(hkl) = 1/\sigma_2$ where $\sigma_2 = [\sigma_1^2 + 0.25 \{0.05 (F_o)\}^2]^{1/2}$).

Initial atomic co-ordinates from Reid and Ringwood (1975) were used in the refinement. The discrepancy factor R (where $R = \sum ||F_o| - k |F_c|| / \sum |F_o|$) at convergence was 0.028. The standard deviation of an observation of unit weight was 1.04. No correlation between parameters was observed. The final positional and thermal parameters, obtained at the completion of refinement are given in Table 2. A table of F_o and F_c values has been deposited at the publishers. Bond angles and lengths from this study are given in Table 3.

Table 2. Final atomic and thermal parameters for ScAlO₃ perovskite. The e.s.d's., in parentheses, are expressed in units of the last digit

Atom site	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}
Sc 4 <i>c</i>	0.9793(1)	0.0701(1)	$\frac{1}{4}$	0.0029(1)	0.0029(1)
Al 4 <i>b</i>	0.0	$\frac{1}{2}$	0.0	0.0022(2)	0.0028(2)
O(1) 4 <i>c</i>	0.1196(3)	0.4551(3)	$\frac{1}{4}$	0.0034(4)	0.0036(4)
O(2) 8 <i>d</i>	0.6906(2)	0.3061(2)	0.0611(1)	0.0029(3)	0.0032(3)
	β_{33}	β_{12}	β_{13}	β_{23}	Bcq
Sc 4 <i>c</i>	0.0022(1)	-0.00025(7)	0.0	0.0	0.35
Al 4 <i>b</i>	0.0018(1)	-0.00003(12)	0.00009(10)	0.00009(10)	0.29
O(1) 4 <i>c</i>	0.0014(2)	-0.0009(3)	0.0	0.0	0.34
O(2) 8 <i>d</i>	0.0023(1)	-0.0004(2)	0.0003(2)	-0.0004(2)	0.37

The following constraints are required from the symmetry for atoms on special position 4*c*: $\beta_{13} = \beta_{23} = 0.0$

The 1975 ANUCRYS System of crystallographic programmes, as implemented on the UNIVAC 1108 at A.N.U. by P.O. Whimp and D. Taylor, was used throughout the structure solution.

Discussion

Crystal growth

The results presented above indicate that lithium fluoride may be used as a flux for the growth of large ScAlO₃ perovskite crystals. The slight pink colouration of some crystals is probably due to trace amounts of a transition metal incorporated into the structure. Macroscopic inclusions of the flux in the crystals were absent. Cell dimensions of the flux-grown crystal used in this study agree within error for those given by Reid and Ringwood (1975), confirming the absence of any flux substitution.

Description of the structure

The structure of ScAlO₃ is of the distorted orthorhombic-perovskite type (Megaw, 1973; Marezio et al., 1970) consisting of a 3-dimensional framework of corner-joined AlO₆ octahedra with the Sc atoms lying in the spaces between them (Fig. 1). The structure is distorted from the ideal cubic modification (outlined within the unit cell in Fig. 1) by displacements of the

Table 3. Interatomic distances and bond angles in ScAlO₃ perovskite. The e.s.d's., in parentheses, are expressed in units of the last digit

<i>Polyhedron</i>			
Sc–O(1)	2.068(1) Å		
Sc–O(1)	2.129(2)		
Sc–O(2)	2 × 2.112(1)		
Sc–O(2)	2 × 2.325(1)		
Sc–O(2)	2 × 2.555(1)		
Mean of 8	2.273		
Sc–O(1)	3.017(1)		
Sc–O(1)	3.291(2)		
Sc–O(2)	2 × 3.398(1)		
Mean of 12	2.607		
O(2)–O(2)	2.681(05)		
O(2)–O(2)	2.685(08)		
O(2)–O(2)	2.719(2)		
<i>Octahedron</i>			
Al–O(2)	2 × 1.885(1)		
Al–O(2)	2 × 1.909(1)		
Al–O(1)	2 × 1.909(05)		
O(1)–O(2)	2.634(2)		
O(1)–O(2)	2.647(1)	O(2)–Al–O(2)	89.89(2)°
O(1)–O(2)	2.731(1)	O(2)–Al–O(1)	87.93(5)
O(1)–O(2)	2.750(2)	O(2)–Al–O(1)	87.81(5)
<i>Cation-cation</i>			
Sc–Al	2.882(03)		
	2.995(03)		
Al–Al	3.596(02)		

Sc and oxygen atoms. Al atoms are situated on centres of symmetry on special position $4b$, and are centrally placed within the distorted octahedron. Oxygen atoms lie at two different distances from the Al atoms with an average Al–O distance of 1.901 Å, the difference between the two lengths being 0.024(2) Å. These bond lengths differ from those obtained by Reid and Ringwood (1975). They found the oxygens to lie at three different distances from aluminium, producing a greater distortion of the octahedron. The distortion of the octahedron measured by Al–O bond lengths and O–Al–O angles however, is fairly small in comparison to the Sc–O polyhedra.

The most prominent change of the structure from that of ideal perovskite is the tilting of the octahedron. This causes large distortions of the Sc–O

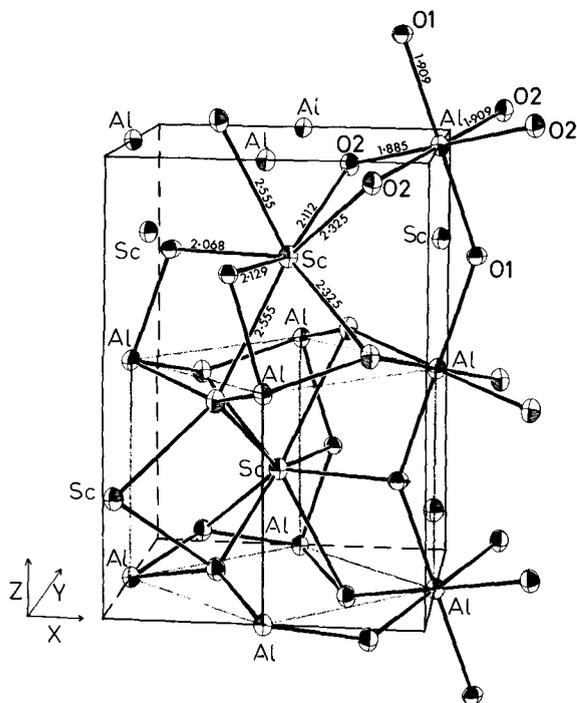


Fig. 1. Drawing of ScAlO_3 perovskite showing 70% probability vibrational ellipsoids. The cubic subcell is out-lined within the larger orthorhombic unit cell. The program ORTEP (Johnson, 1965) was used to provide this figure

polyhedron from the ideal structure, in which Sc would be surrounded by 12 oxygen atoms at a distance of about 2.54 Å, based on the cubic subcell of 3.59 Å. The Sc atom has been displaced from its ideal position by 0.1 Å in the *X* direction and 0.37 Å in the *Y* direction. A range of bond lengths from 2.068 to 3.398 Å as well as a range of bond angles results. The average of the first six near-neighbour oxygen atoms is 2.179 Å and of the first eight is 2.273 Å. The large range of bond distances for the polyhedral site makes the A cation coordination number difficult to resolve.

Reid and Ringwood (1975), concluded that scandium was in eight-fold coordination with oxygen by comparison with results obtained from the rare-earth orthoferrite perovskite (Marezio et al., 1970) the rare type Sc_2O_3 and powder X-ray data of $\text{Sc}_2\text{Si}_2\text{O}_7$. In ScAlO_3 perovskite the 9th bonding oxygen distance is 0.75 Å longer than the sum of their ionic radii, the 12th bonding oxygen being 1.13 Å longer, using the value for Sc in 8 coordination (Shannon and Prewitt, 1969). Therefore, the effective coordination of Sc is best considered as being in eight-fold coordination with oxygen.

Values of the isotropic thermal motions (B) for each atom are smaller than for compounds formed at the earth's surface. Low thermal parameters were obtained from the stishovite refinement (Sinclair and Ringwood, 1978) also grown under high pressure, and were thought to be due to the close packing of Si and O atoms. The situation in ScAlO₃ is similar for the volume is the smallest so far observed in a perovskite compound (after MgSiO₃).

Implications for MgSiO₃ perovskite

The diffraction symmetry of the high-pressure perovskite polymorph of MgSiO₃, like ScAlO₃ perovskite, is identical for both $Pbnm$ (centric) and $Pbn2_1$ (non-centric) space groups. Although the true space group of MgSiO₃ perovskite may not become known until large single crystals have been produced, some inferences can be made from close analogue structures. The two types of perovskites that satisfy the above space-group extinctions can be represented by the structures of ScAlO₃ ($Pbnm$) and CdTiO₃ ($Pbn2_1$). The CdTiO₃ structure differs from the centrosymmetric structure primarily by the displacement of the B cation from the central position within the oxygen octahedron.

If the B cation is non-central, then the non-centric polar perovskite phase may undergo a ferroelectric transition. A transition of this kind occurring in MgSiO₃ perovskite (assuming $Pbn2_1$ symmetry) could have important implications for explaining certain physical properties such as the anomalous electrical conductivity and acoustic discontinuities that occur at depths where this phase is stable (Schloessin and Timco, 1977; Timco and Schloessin, 1978 and Litov and Anderson, 1978). Thus it is necessary to establish the correct space group for this important lower-mantle phase.

On the basis of the space-group information derived from the ScAlO₃ structural analysis, MgSiO₃ perovskite is expected to crystallize in the centrosymmetric space group and consequently lacks B -cation displacements. Furthermore, the new results for ScAlO₃ perovskite show that the AlO₆⁹⁻ octahedra are more regular. This gives added support for the central position of the B cation and so centrosymmetry of the overall structure. Centrally located Si is already known to exist in the CaSiO₃ cubic perovskite synthesized by Liu and Ringwood (1975), therefore the centric space group seems the most probable choice for the perovskite modification of MgSiO₃ synthesized at high pressure.

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