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Structure of Nickel Aluminosilicate (Phase V): A High-Pressure Phase Related to Spinel

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Abstract. $Ni_3Al_2SiO_8$ (phase V), orthorhombic, *Pmma*, $a = 5{\cdot}665$ (1), $b = 8{\cdot}590$ (1), $c = 8{\cdot}097$ (2) Å, $Z = 3$, $D_x = 4{\cdot}907$ Mg m^{-3}. The crystals are products quenched from $8{\cdot}6 \times 10^3$ MPa and 1533 K, and are the highest-pressure phase of the $NiAl_2O_4$–Ni_2SiO_4 system known at present. The structure was solved by the Patterson method and refined to an R of 0·059 for 1358 unique reflections from diffractometer data with $|F_o| \geq 3\sigma(F_o)$. The structure is based on a cubic close packing of O atoms and is closely related to phase IV of the $NiAl_2O_4$–Ni_2SiO_4 system, which is an extended spinel and modified-spinel structure. Both isolated TO_4 and coupled T_2O_7 tetrahedra exist and the $TO_4:T_2O_7$ ratio is 1 : 1.

Introduction. Phase V is the highest-pressure form known of five phases which have been observed in studies of the $NiAl_2O_4$–Ni_2SiO_4 system (Ma, 1974; Akaogi, Akimoto, Takahashi, Horiuchi & Morimoto, 1978). The structures of phases I, II, III and IV were reported by Ma, Sahl & Tillmanns (1975), Ma & Tillmanns (1975), Ma & Sahl (1975) and Horioka, Takahashi, Morimoto, Horiuchi, Akaogi & Akimoto (1981), respectively. All phases in this system have spinel-related structures and were classified into 'spinelloids' (Horiuchi, Horioka & Morimoto, 1980). Phase relations of these structures at about 1400 K have been investigated by Horioka, Horiuchi, Akaogi & Akimoto (1981).

The crystals of phase V used in this study were prepared by the following method. An intimate mixture of synthetic Ni_2SiO_4 (olivine) and $NiAl_2O_4$ (spinel) in the ratio 1 : 1 was used as the starting material. The mixture was inserted into a cylindrical platinum heater which was placed in a pyrophyllite tetrahedron of edge 14 mm. High-pressure and high-temperature experiments were carried out at $8{\cdot}6 \times 10^3$ MPa and 1533 K with a tetrahedral press with anvils of edge 9 mm. The run-time was 10 min. The crystals of phase V were transparent green with dimensions of *ca* 20–40 μm. The single crystal used for the X-ray photographic experiments and intensity measurements was about 0·03 × 0·03 × 0·04 mm. Cell dimensions were determined by the least-squares method using 20 high-angle reflections (Mo $K\alpha_1$ and α_2) measured on a four-circle diffractometer.

Photographs indicated *mmm* Laue symmetry; systematic absences were $hk0$, $h = 2n + 1$. These result in the possible space groups *Pmma*, $P2_1ma$ and *Pm2a*. The space group *Pmma*, which has a center of symmetry, was assumed for the structure analysis and confirmed to be correct from the final results.

The composition of the specimen was confirmed to be in good agreement with the starting bulk composition, $Ni_3Al_2SiO_8$, by means of an analytical electron microscope (Hitachi-12SE). Kyanite (Al_2SiO_5) was used as a standard. The ratio of the characteristic X-ray intensities of Al to Si is 1·74 for the specimen, whereas it is 1·60 for kyanite.

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Mo $K\alpha$ radiation monochromatized by pyrolytic graphite was used to collect the intensities. The intensities of 1538 unique reflections within the range of $0° < 2\theta \leq 100°$ were obtained using a four-circle diffractometer (Rigaku AFC-3) employing the θ–2θ scan technique. Of the reflections measured, 1358 with low standard deviations $[|F_o| \geq 3\sigma(F_o)]$ were used for the structure determination and refinement, while 241 with $|F_o| < 3\sigma(F_o)$ were treated as unobserved and excluded from the refinement. Conventional polarization and Lorentz corrections were carried out during the data collection. No absorption correction was made ($\mu = 11{\cdot}22$ mm^{-1} and $\mu r \simeq 0{\cdot}4$ for Mo $K\alpha$).

The structure was solved by the Patterson method. The atomic parameters, temperature factors and cation distribution in each site were refined by least squares; they are listed in Table 1. The final R value for 1358 reflections $[|F_o| \geq 3\sigma(F_o)]$ is 0·059. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974) for all atoms. The interatomic distances and angles are shown in Table 2.* Computations of the Patterson and Fourier syntheses, least-squares refinements, and interatomic distances and angles were carried out using the programs *3DFR* (Y. Iitaka & T. Matsusaki, private communication), *RFINE* 2 (Finger, 1972), and *UMBADTEA* (Finger, 1968), respectively, at the Computation Center of Osaka University and at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Table 1. *Positional and thermal parameters with their estimated standard deviations in parentheses*

Cation distributions in sites are given by cNi + $(1-c)$Al for M and cNi + $(0{\cdot}5-c)$Al + 0·5Si for T. $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	Multiplicity	c (occupancies)	x	y	z	B_{eq} (Å^2)
O(1)	0·5		0·4943 (32)	0	0·2500 (10)	1·2
O(2)	0·5		$\frac{1}{4}$	0·1737 (10)	−0·0018 (10)	0·7
O(3)	0·5		$\frac{1}{4}$	0·1690 (13)	0·5010 (12)	1·0
O(4)	1·0		0·5001 (12)	0·3265 (9)	0·2497 (7)	0·7
O(5)	0·25		$\frac{1}{4}$	$\frac{1}{2}$	0·0241 (13)	0·5
O(6)	0·25		$\frac{1}{4}$	$\frac{1}{2}$	0·5209 (13)	0·8
T(1)	0·25	0·07 (2)	$\frac{1}{4}$	0	0·3768 (5)	0·7
T(2)	0·5	0·03 (1)	$\frac{1}{4}$	0·3256 (3)	0·1317 (3)	0·4
M(1)	0·5	0·65 (2)	$\frac{3}{4}$	0·1655 (3)	0·2501 (2)	0·3
M(2)	0·25	0·80 (2)	$\frac{1}{2}$	0	0	0·3
M(3)	0·5	0·70 (1)	$\frac{1}{2}$	0·3332 (2)	$\frac{1}{2}$	0·4
M(4)	0·25	0·86 (3)	$\frac{3}{4}$	$\frac{1}{2}$	0·2240 (2)	0·3

Discussion. A projection on (100) of the structure of phase V is shown in Fig. 1. The structure is based on a slightly distorted cubic close packing of O atoms. The stacking layers are parallel to (032), (0$\bar{3}$2), (101) and (10$\bar{1}$). There are four crystallographically independent cations (M) which are octahedrally coordinated by O atoms, where M(2) and M(3) are located at $x = 0$ and $\frac{1}{2}$, M(1) and M(4) at $x = \frac{3}{4}$. The M(2) and M(3) octahedra form two different types of columns running parallel to the a axis. The M(2) octahedra form a single column, while M(3) columns share edges with crystallographically equivalent M(3) columns to form double columns. M(1) and M(4) form a single column

Table 2. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

Symmetry code

None or (i)	x, y, z		(iv)	$\frac{1}{2}+x$, y, $-z$
(ii)	$-x$, y, $-z$		(v)	x, $-y$, z
(iii)	$\frac{1}{2}-x$, y, z			

		Distance	O–M–O angle
M(1)–O(1)	2×	2·03 (1)	
–O(2)		2·012 (9)	
–O(3)		2·02 (1)	
–O(4)	2×	1·979 (7)	
O(1)–O(1^{iii})		2·89 (4)	90·1 (7)
–O(2^{iv})	2×	2·89 (1)	91·4 (3)
–O(4^{i})	2×	2·805 (8)	88·9 (4)
–O(3^{iv})	2×	2·875 (1)	90·7 (3)
O(2)–O(4^{ii})	2×	2·78 (1)	88·5 (3)
O(3)–O(4^{ii})	2×	2·81 (1)	89·5 (3)
O(4)–O(4^{iii})		2·83 (1)	91·2 (4)
M(4)–O(4)	4×	2·064 (7)	
–O(5)		2·01 (1)	
–O(6)		2·06 (1)	
O(4)–O(4^{iii})	2×	2·83 (1)	86·4 (4)
–O(4^{v})	2×	2·98 (2)	92·5 (4)
–O(5^{iv})	4×	3·02 (1)	95·8 (2)
–O(6^{iv})	4×	2·77 (1)	84·2 (2)

		Distance	O–M–O angle
M(2)–O(1)	2×	2·024 (8)	
–O(2)	4×	2·056 (7)	
O(1)–O(2^{i})	4×	2·88 (1)	89·8 (4)
–O(2^{iv})	4×	2·89 (1)	90·2 (4)
O(2)–O(2^{iv})	2×	2·828 (5)	86·9 (4)
–O(2^{v})	2×	2·99 (2)	93·1 (4)
T(2)–O(2)		1·694 (9)	
–O(4)	2×	1·707 (7)	
–O(5)		1·734 (6)	
O(2)–O(4^{i})	2×	2·81 (1)	111·1 (3)
–O(5^{i})		2·810 (9)	110·2 (4)
O(4)–O(4^{iii})		2·83 (1)	111·9 (4)
–O(5^{i})	2×	2·750 (9)	106·1 (3)

		Distance	O–M–O angle
M(3)–O(3)	2×	1·997 (8)	
–O(4)	2×	2·028 (6)	
–O(6)	2×	2·020 (2)	
O(3)–O(3^{iv})		2·828 (5)	90·1 (5)
–O(4^{i})	2×	2·82 (1)	89·1 (3)
–O(4^{ii})	2×	2·81 (1)	88·6 (3)
–O(6^{i})	2×	2·85 (1)	90·3 (2)
O(4)–O(6^{i})	2×	3·01 (1)	96·0 (4)
–O(6^{iv})	2×	2·77 (1)	86·3 (4)
O(6)–O(6^{iv})		2·85 (3)	89·6 (1)
T(1)–O(1)	2×	1·72 (2)	
–O(3)	2×	1·77 (1)	
O(1)–O(1^{iii})		2·76 (4)	106·7 (9)
–O(3^{i})	4×	2·85 (1)	109·9 (3)
O(3)–O(3^{v})		2·82 (1)	110·6 (7)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35754 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

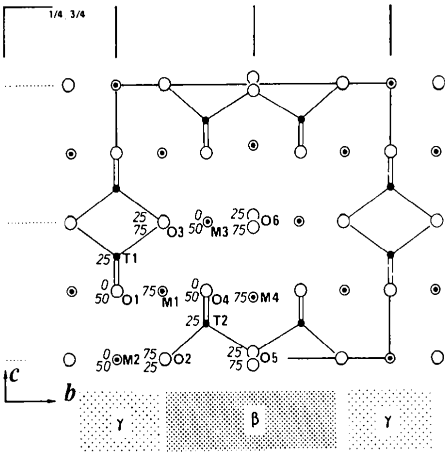

Fig. 1. Crystal structure of phase V projected on (100). The spinel-type (γ) and modified-spinel-type (β) bands are also illustrated.

of octahedra running parallel to the b axis, connected to both the $M(2)$ single column and $M(3)$ double columns by sharing edges.

There are two other crystallographically independent cations (T atoms) in the structure, which are tetrahedrally coordinated by O atoms; they are on the mirror planes at $x = \frac{1}{4}$ and $\frac{3}{4}$ parallel to (100). The $T(2)O_4$ tetrahedron shares corners with an adjacent crystallographically equivalent $T(2)O_4$ tetrahedron to form a T_2O_7 group, while the $T(1)O_4$ tetrahedra are isolated. Neither shared edges nor faces occur between tetrahedra and octahedra in the structure of phase V – only shared corners are present.

The $T(2)_2O_7$ groups and $M(3)$ double columns form a band parallel to (010). This band can be considered as a structural part of a modified-spinel-type (β-phase) structure. On the other hand, the isolated $T(1)O_4$ and $M(2)$ single column make another band which can be considered as a part of the spinel-type (γ-phase) structure. Thus, the structure of phase V can be described as alternating spinel-type and modified-spinel-type bands. These features are shown in Fig. 1. The alternation of the two bands is also observed in the structure of phase IV (Horioka *et al.*, 1981).

In the case where the cation distributions are completely disordered, the M and T sites should be occupied by $\frac{3}{4}$Ni + $\frac{1}{4}$Al and $\frac{1}{2}$Si + $\frac{1}{2}$Al, respectively, if Si atoms are assumed to occupy only tetrahedral sites. However, a higher concentration of Ni atoms in $M(2)$ and $M(4)$ than in $M(1)$ and $M(3)$ has been observed from the results of the least-squares refinements of the site occupancies. The mean M—O distances in the MO_6 octahedra reflect the distributions of Ni and Al atoms: $M(2)$—O, 2·045 (0·80Ni + 0·20Al) and $M(4)$—O, 2·055 Å (0·86Ni + 0·14Al), in which Ni atoms are concentrated, are greater than $M(1)$—O, 2·006 (0·65Ni + 0·35Al) and $M(3)$—O, 2·015 Å (0·70Ni + 0·30Al).

The mean T—O distances in the $T(1)O_4$ and $T(2)O_4$ tetrahedra, 1·744 and 1·711 Å, are larger than the normal Si—O distances in SiO_4 tetrahedra. Since the proportions of Ni in the $T(1)$ and $T(2)$ sites are small (from the results of least-squares refinements of the cation distributions), the large mean T—O distances in this structure are considered to be mainly due to the concentration of Al in each site. The differences in the T—O distances suggest that $T(1)$ is occupied by the atoms with $Al/(Si + Al) > 0{\cdot}5$, and $T(2)$ by those with $Al/(Si + Al) < 0{\cdot}5$. The cation distributions in the structure of phase V show that the $NiAl_2O_4$ component concentrates in the spinel-type parts, while the Ni_2SiO_4 concentrates in the modified-spinel-type parts. Similar cation distributions are found in the structure of phase IV (Horioka *et al.*, 1981).

The structures of phases IV and V are constructed from TO_4 and T_2O_7 groups accompanied by octahedra in single and double columns. The ratios of TO_4 to T_2O_7 in the structures are 1 : 2 in phase IV and 1 : 1 in phase V. Only isolated TO_4 groups are found in the spinel-type structures, while only coupled T_2O_7 groups occur in the modified-spinel-type structures. Therefore, the structures of both phases IV and V can be considered to be intermediate between the spinel type and modified-spinel type.

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