

Nickel Aluminosilicate, Phase III

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Abstract. $\text{Ni}_{12.5}\text{Al}_{7.0}\text{Si}_{14.5}\text{O}_{32}$, orthorhombic, *Imma*, $a = 5.6646(4)$, $b = 11.455(2)$, $c = 8.1007(7)$, $Z = 1$, $D_x = 4.93 \text{ g cm}^{-3}$. Crystals are a quench product from 27.6 kbar and 1650°C. The structure was refined by a combination of least-squares calculations and Fourier synthesis to a final $R = 0.039$ for 207 observed reflexions. Phase III is isostructural with $\beta\text{-Co}_2\text{SiO}_4$. The structure is based on cubic close-packing of O atoms and contains double octahedral columns running parallel to **a** cross-linked by single octahedral columns running parallel to **b**. The tetrahedra are linked in T_2O_7 groups. Slight ordering of Ni and Al may occur in octahedral sites.

Introduction. Phase III is one of three nickel aluminosilicate phases first described by Ma (1972) in connexion with a phase-equilibrium study of the system $\text{SiO}_2\text{-NiO-NiAl}_2\text{O}_4$. Crystals used in this study were grown by Ma from a multiphase assemblage of bulk composition $11\text{NiO} \cdot 2\text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ with a piston-cylinder type pressure apparatus. Precession photographs show Laue symmetry *mmm* and lead to the space group *Imma* if centrosymmetry is assumed. Electron microprobe analysis on the same crystals yields: NiO = 61.07, $\text{Al}_2\text{O}_3 = 16.55$, $\text{SiO}_2 = 21.42$ mol.%; total = 99.04 mol.%. The analysis represents a composition near the join $\text{NiAl}_2\text{O}_4\text{-Ni}_2\text{SiO}_4$. It was normalized to 100% and projected onto the join to give the formula used in the present refinement. Full accounts of crystal growth and microprobe analysis have been given (Ma, 1972).

A crystal, approximately $0.03 \times 0.04 \times 0.05$ mm, was chosen for data collection on an automatic Hilger and Watt four-circle diffractometer (graphite monochromator, scintillation counter). Cell dimensions were obtained by a least-squares fit to the settings of 12 high-angle reflexions (Mo $K\alpha_1$ radiation). Multiple sets of integrated intensities were collected to a 2θ limit of 61° by the θ - 2θ step-scan technique. Two standard reflexions were monitored after every 100 reflexion measurements.

A local version of the data-reduction program *DATAPH* (a Brookhaven crystallographic program)

was used to correct intensities for Lorentz and polarization factors and for absorption ($\mu = 115.8 \text{ cm}^{-1}$ for Mo $K\alpha$ radiation). For the latter (Coppens, Leisero-witz & Rabinovich, 1965) the crystal was approximated by six boundary planes. The transmission factors were in the range 0.59–0.70. Standard deviations of intensities were calculated in the usual manner. No extinction correction was applied.

The equivalent reflexions were averaged giving 460 independent reflexions, of which 253 with $I < 1.3\sigma(I)$ were treated as unobserved and excluded from the refinement.

The refinement was carried out by full-matrix least-squares calculations with a local version of *ORFLS* (Busing, Martin & Levy, 1962). The initial atomic coordinates were those of $\beta\text{-Co}_2\text{SiO}_4$ (Morimoto, Tokonami, Watanabe & Koto, 1974). Complete disordering was assumed initially for the distribution of Ni and Al in octahedral sites. An R of 0.087 was obtained after initial scaling with isotropic temperature factors fixed at $B = 0.8$ for O atoms and 0.4 \AA^2 for cations. Three additional cycles varying scale factor, atomic coordinates and temperature factors reduced R to 0.040 but produced a considerable spread among temperature factors for octahedral sites [$M(1) = 0.3(2)$, $M(2) = 0.0(1)$, and $M(3) = 0.6(1) \text{ \AA}^2$] suggesting possible cation ordering. A Fourier synthesis was calculated with the program *SFS* (Neukäter & Biedl, unpublished). The peak height produced for $M(2)$ sites was approximately 10–20% higher than those for $M(1)$ and $M(3)$ sites. Further least-squares refinement assuming Ni slightly enriched in $M(2)$ while depleted in $M(3)$ sites converged to the final $R = 0.039$ and $R_w = 0.038$ for 207 observed reflexions.*

The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w was defined as $1/\sigma^2(F_o)$. Scattering factors for O^- ,

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31044 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates, temperature factors and the proposed cation distribution with standard deviations

		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
M(1)	3.2Ni + 0.8Al	0.0	0.0	0.0	0.4 (2)
M(2)	3.6Ni + 0.4Al	0.0	0.25	0.9758 (7)	0.3 (1)
M(3)	5.7Ni + 2.3Al	0.25	0.1246 (3)	0.25	0.35 (5)
T	3.5Al + 4.5Si	0.0	0.1202 (7)	0.6186 (6)	0.33 (7)
O(1)		0.0	0.25	0.220 (4)	1.4 (7)
O(2)		0.0	0.25	0.722 (4)	1.6 (7)
O(3)		0.0	0.9997 (9)	0.253 (3)	1.3 (7)
O(4)		0.252 (1)	0.127 (3)	0.9982 (9)	0.5 (2)

Al²⁺, Si⁴⁺ and Ni²⁺ were taken from *International Tables for X-ray Crystallography* (1968).

The final atomic coordinates, temperature factors and the proposed cation distribution are listed in Table 1. The bond lengths and angles with estimated standard deviations were calculated with the program *SADIAN* (Baur & Wenniger, unpublished) and are listed in Table 2.

Discussion. Phase III has the same space group as β -Co₂SiO₄ and similar cell dimensions. The success of the refinement proves that these two compounds are isostructural. Fig. 1 shows a projection on (100). The structure is based on a distorted cubic close-packing of O atoms with layers stacked parallel to (021). There are three crystallographically independent octahedrally coordinated (M) cation sites. M(3) atoms occur at heights $x=0.25$ and 0.75 and form octahedral columns running parallel to **a**. The M(3) octahedral column shares edges with an adjacent symmetrically equivalent M(3) column to form double columns. Likewise, the tetrahedra share corners with adjacent tetrahedra to form T₂O₇ groups. The double columns of M(3) octahedra are cross-linked by single columns

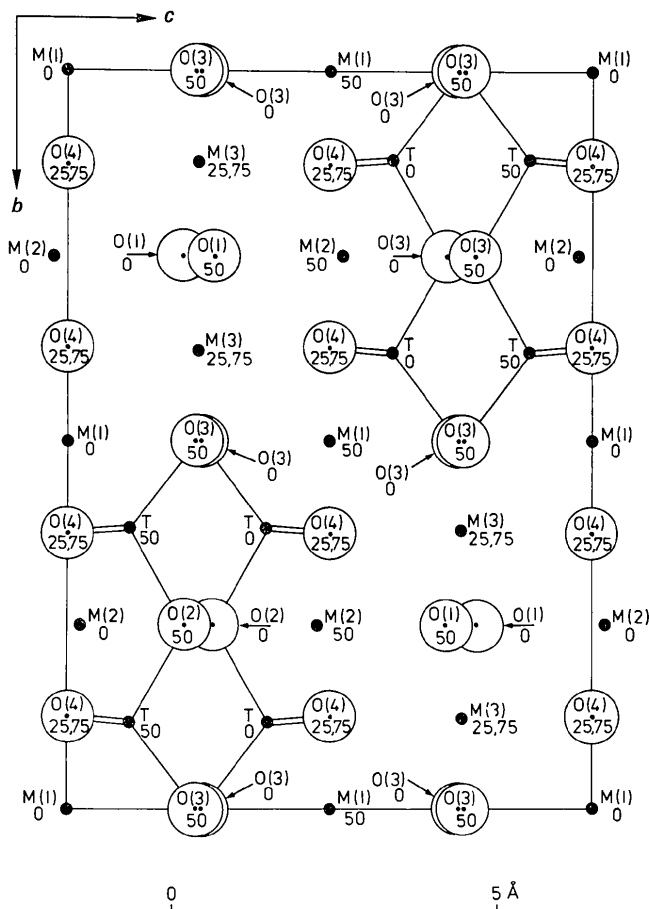


Fig. 1. Projection of the crystal structure of phase III on (100). Heights of atoms are shown by x coordinates ($\times 100$).

Table 2. Bond lengths (\AA) and angles ($^\circ$) with standard deviations

M(1)–O(4)	4 \times	2.04 (2)		
M(1)–O(3)	2 \times	2.05 (2)		
O(4)–O(4)	2 \times	2.86 (1)	O(4)–M(1)–O(4)	2 \times 89.2 (0.9)
O(4)–O(4)	2 \times	2.90 (4)	O(4)–M(1)–O(4)	2 \times 90.8 (0.9)
O(4)–O(3)	4 \times	2.88 (2)	O(4)–M(1)–O(3)	4 \times 89.5 (0.3)
O(4)–O(3)	4 \times	2.90 (2)	O(4)–M(1)–O(3)	4 \times 90.5 (0.3)
M(2)–O(1)	1 \times	1.98 (3)		
M(2)–O(4)	4 \times	2.02 (2)		
M(2)–O(2)	1 \times	2.06 (3)		
O(1)–O(4)	4 \times	2.70 (3)	O(1)–M(2)–O(4)	4 \times 84.8 (0.3)
O(4)–O(4)	2 \times	2.83 (4)	O(4)–M(2)–O(4)	2 \times 88.9 (0.9)
O(4)–O(4)	2 \times	2.86 (1)	O(4)–M(2)–O(4)	2 \times 90.1 (0.9)
O(4)–O(2)	4 \times	3.01 (3)	O(4)–M(2)–O(2)	4 \times 95.2 (0.3)
M(3)–O(3)	2 \times	2.01 (1)		
M(3)–O(1)	2 \times	2.03 (1)		
M(3)–O(4)	2 \times	2.04 (1)		
O(3)–O(3)	1 \times	2.83 (1)	O(3)–M(3)–O(3)	1 \times 89.4 (0.3)
O(3)–O(1)	2 \times	2.88 (1)	O(3)–M(3)–O(1)	2 \times 90.8 (0.2)
O(3)–O(4)	2 \times	2.85 (2)	O(3)–M(3)–O(4)	2 \times 89.4 (0.9)
O(3)–O(4)	2 \times	2.90 (2)	O(3)–M(3)–O(4)	2 \times 91.5 (0.9)
O(1)–O(1)	1 \times	2.87 (1)	O(1)–M(3)–O(1)	1 \times 90.0 (0.2)
O(1)–O(4)	2 \times	2.70 (3)	O(1)–M(3)–O(4)	2 \times 83.0 (1.0)
O(1)–O(4)	2 \times	3.03 (3)	O(1)–M(3)–O(4)	2 \times 96.2 (1.0)
T—O(4)	2 \times	1.69 (1)		
T—O(2)	1 \times	1.71 (2)		
T—O(3)	1 \times	1.72 (2)		
O(4)–O(4)	1 \times	2.81 (1)	O(4)–T–O(4)	1 \times 111.9 (0.4)
O(4)–O(2)	2 \times	2.68 (3)	O(4)–T–O(2)	2 \times 103.7 (1.1)
O(4)–O(3)	2 \times	2.83 (2)	O(4)–T–O(3)	2 \times 111.8 (1.0)
O(2)–O(3)	1 \times	2.87 (1)	O(2)–T–O(3)	1 \times 113.5 (1.2)

of M(1) and M(2) octahedra which run parallel to **b**.

The proposed distribution of Ni and Al corresponds approximately to a metal composition of 80% Ni + 20% Al in M(1), 90% Ni + 10% Al in M(2) and 70% Ni + 30% Al in M(3). The average metal–oxygen distances of octahedral sites [M(1)–O 2.04(2), M(2)–O 2.02(2), M(3)–O 2.03(1) \AA] compare well with literature values for the range of compositions involved. The average T–O length, 1.70(2) \AA , also corresponds well to the proposed Al/Si content of the tetrahedral site. The proposed slight ordering of Ni and Al was, however, derived by trial-and-error and thus involves a large uncertainty.

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