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Indexed X-ray diffraction data for the sialon X-phase

The structure and composition of the X-phase of the sialon system have been subjects of controversy [1–4]. Recently, conclusive electron diffraction data proved that the structure is triclinic, with $a = 0.856$ nm, $b = 0.985$ nm, $c = 0.969$ nm, $\alpha = 70^\circ$, $\beta = 81^\circ$, $\gamma = 81^\circ$. This cell could also be "reduced" to: $a = 1.194$ nm, $b = 0.9685$ nm, $c = 0.8542$ nm, $\alpha = 99.2^\circ$, $\beta = 90^\circ$, $\gamma = 124.3^\circ$, with no increase, however, in the symmetry of the structure [5]. The composition, determined with the aid of experiments at various high temperatures [2] and through tie-line determinations [6], lies close to $Si_{12}Al_{18}O_{39}N_8$ [6], $Si_3Al_6O_{12}N_2$ [7] or $Si_2Al_3O_7N$ [8].

Since large enough single crystals of the phase are not available, the structure determination must be based on X-ray powder diffraction data, which, in this complicated multi-component structure, are far from being sufficient. The complexity is further increased by the difficulty in obtaining the pure phase and by the extremely finely spaced planar defects in the structure, which can give rise to intensity variations.

In view of our present knowledge of the structure, it was observed [5] that the existing X-ray powder diffraction data, as reported in several publications, included reflections which do not belong to the structure, and, more often, lacked many of the important reflections which do belong to the X-ray diffractogram. We present here a fully indexed powder data with the observed relative intensities, which can serve for detecting the X-phase and its relative amount in multi-phase samples.

The mixed powder samples, with compositions shown in Table I, were hot-pressed at 1740 to 1760° C under 30 MPa for 120 min. The final samples were estimated to contain at least 95% of the X-phase and less than 2% of other crystalline phases.

The samples were examined as-hot-pressed (as-polished bulk polycrystals) in an X-ray diffractometer with a LiF monochromator, and in powdered form in a monochromated Guinier camera, with Cu*Kα* radiation in both cases. The relative intensities were determined visually.

Table II lists the indexed observed diffraction lines with their observed intensities. The low symmetry and the relatively large unit cell give rise to numerous reflections; 145 planes with lattice

TABLE I The starting material

Sample	Composition (wt %)			
	Si_3N_4	SiO_2	Al_2O_3	AlN
A–1	17.7	31.7	50.6	–
A–2	–	54.5	24.7	20.8

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TABLE II Indexed X-ray powder diffraction lines for the X-phase

h k l	Interplanar spacing *d* (Å)		Observed intensity
	Observed	Calculated	
$1\bar{1}0$	9.036	9.038	vvw
010	7.847	7.849	ms
101	5.89 (broad)	5.878	vw
$2\bar{1}0$	5.591	5.596	ms
$2\bar{1}1$	4.676	4.661	vw
$1\bar{2}1$	4.46 (broad)	4.452	mw
$20\bar{1}, 002$	4.213	4.231, 4.190	vw
$1\bar{1}2$	3.976	3.979	mw
020	3.920	3.925	mw
111	3.866	3.867	vvw
$1\bar{2}\bar{1}$	3.821	3.828	vvw
$1\bar{1}\bar{2}, 3\bar{1}0$	3.640	3.646, 3.644	vs
$3\bar{2}0$	3.611	3.615	vs
$1\bar{2}2$	3.448	3.445	vvw
$2\bar{1}2$	3.366	3.360	mw
210	3.244	3.240	vw
$2\bar{3}1$	3.164	3.150	vvw
120	3.039	3.037	m
$3\bar{3}0, 1\bar{3}0$	3.008	3.013, 3.009	ms
$4\bar{2}0, 003$	2.798	2.798, 2.793	s
$3\bar{3}\bar{1}$	2.742	2.737	vvw
$0\bar{3}1$	2.648	2.648	vw
$030, 30\bar{2}$	2.615	2.617, 2.615	ms–s
$2\bar{1}3, 2\bar{1}\bar{3}$	2.499	2.501, 2.499	s
$31\bar{1}, 310$	2.428	2.425, 2.424	w
$212, 220, 3\bar{4}1$	2.387	2.388, 2.387, 2.386	m
$21\bar{3}, 400$	2.300	2.303, 2.298	vvw
$203, 12\bar{3}, 1\bar{3}3$	2.274	2.278, 2.278, 2.269	m
$4\bar{4}0$	2.260	2.259	ms
$5\bar{2}0, 3\bar{4}2$(b)	2.220(a)	2.222, 2.217	vw(a)
$130, 3\bar{4}\bar{1}$(b)	2.205	2.207, 2.206	w–mw
$4\bar{1}2, 3\bar{3}3$(b)	2.178	2.180, 2.176	mw
$5\bar{2}1, 0\bar{1}4$	2.132	2.135, 2.130	vw
$5\bar{1}0$	2.070	2.071	w–mw
$21\bar{4}, 4\bar{4}\bar{2}$(b)	1.902	1.902, 1.900	w
$1\bar{3}4, 23\bar{1}$	1.891	1.893, 1.892	w
	6 vvw peaks between 1.853 Å and 1.765 Å		
$4\bar{3}4$(b)	1.694	1.694	w–mw
$4\bar{2}\bar{4}, 6\bar{5}0$(b)	1.672	1.674, 1.673	mw
$04\bar{4}$(b)	1.594 (broad)	1.594	vw–w
$3\bar{2}5, 6\bar{3}\bar{3}$	1.549	1.549	mw
$22\bar{5}, 33\bar{3}$(b)	1.501	1.501, 1.500	w
$6\bar{4}\bar{3}, 31\bar{5}$	1.487	1.486, 1.485	m
$5\bar{1}4$(b)	1.422	1.422	m
006(b)	1.397 (broad)	1.397	w
$5\bar{2}5$(b)	1.323	1.323	mw

(a) Lines weaker than "vw" are omitted from here on.

(b) As too many planes can cause this observed reflection, only partial indexing is given.

TABLE III Strongest diffraction lines of the X-phase

No.	*h k l*	*d* (Å)	I/I_0 (%)
1	$1\bar{1}\bar{2}, 3\bar{1}0$	3.64	40
2	$3\bar{2}0$	3.61	100
3	$4\bar{2}0, 003$	2.80	55
4	$030, 30\bar{2}$	2.62	50
5	$2\bar{1}3, 2\bar{1}\bar{3}$	2.50	65

spacing of 2.26 Å and higher appear in the calculated table, and only 41 of these are accounted for in Table II. Below this spacing only the most important reflections are listed. The strongest lines are listed for convenience in Table III. It should be noted that lines 1 and 2 are frequently recorded as a single line [3, 7].

The refined lattice parameters, calculated to give minimum deviation in $\sin^2\theta$ for the first 29 reflections, are $a = 1.1200 \pm 0.0007$ nm, $b = 0.9785 \pm 0.0005$ nm, $c = 0.8545 \pm 0.0005$ nm, $\alpha = 99.18 \pm 0.06°$, $\beta = 90.11 \pm 0.05°$, $\gamma = 124.26 \pm 0.04°$ and the average deviation* in $\sin^2\theta$ is $R = 1.4 \times 10^{-4}$. The volume of this cell is 0.7461 nm^3.

However, the use of published X-ray data from other laboratories for the refinement does not always lead to parameters which fall within the above tolerance. The reason for this is not obvious; at least in some cases it should be attributed to experimental inaccuracies. Layden's samples [7] were recently studied by Morgan [9]. He refined the lattice parameters with an accuracy similar to ours, with the following result: $a = 1.116$ nm, $b = 0.9656$ nm, $c = 0.8533$ nm, $\alpha = 98.26°$, $\beta = 90°$, $\gamma = 124.32°$. We argue that the unknown homogeneity range of the X-phase is probably large enough to cause such differences between its extreme points. Therefore, the lattice parameters should be given with a lower accuracy than stated above. This will cause only minor variations in the positions of the X-ray reflection results obtained and will explain the differences among the various investigators. The unit cell is therefore defined as: $a = 1.120 \pm 0.004$ nm, $b = 0.9685 \pm 0.003$ nm, $c = 0.9545 \pm 0.003$ nm, $\alpha = 99.2 \pm 0.1°$, $\beta = 90.1 \pm 0.1°$, $\gamma = 124.3 \pm 0.05°$.

The available data on the density of the X-phase (3.0 ± 0.05 g cm^{-3}) was found to be insufficient for any new discussion of the exact chemical formula of the phase, which may well consist of fractional numbers of atoms over the whole range of homogeneity.

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*$R = \left[\sum_{i=1}^{n} (\sin^2\theta_{i\,\mathrm{obs.}} - \sin^2\theta_{i\,\mathrm{calc.}})/(n - n_0)\right]^{1/2}$, where n is the number of reflections used and n_0 is the number of refined parameters (6 for a triclinic structure).

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