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Two Phase Refinements of the Structures of α-Si_3N_4 and β-Si_3N_4 Made from Rice Husk by Rietveld Analysis

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Abstract: The crystalline structures of α-Si_3N_4 and β-Si_3N_4 made from rice husk were obtained at room temperature (300 K) from X-ray powder diffraction with CuKα radiation using Rietveld analysis for the two phase mixture. For α-Si_3N_4 at 300 K, crystal data: Mr = 140·285, the rhombohedral system, P31c, a = 7·7650(4) Å, c = 5.6275(2) Å, V = 293·85(2) Å^3, Z = 4, Dx = 3·1709 g cm^{-3}, μ = 133·474 cm^{-1} (λ = 1·5406 Å), F(000) = 280·0, the structure was refined with 29 parameters to R_b = 2·42%, R_f = 1·78% for 243 peaks. For β-Si_3N_4 at 300 K, crystal data: Mr = 140·285, the hexagonal system, P6$_3$/m, a = 7·6093(8) Å, c = 2·9079(2) Å, V = 145·81(2) Å^3, Z = 2, Dx = 3·1951 g cm^{-3}, μ = 134·492 cm^{-1} (λ = 1·5406 Å), F(000) = 140·0, the structure was refined with 17 parameters to R_b = 3·02%, R_f = 1·88% for 145 peaks. The whole diffraction was fitted and refined with 46 parameters to R_{wp} = 6·98%, R_p = 5·33% for 3301 step intensities and 'goodness of fit' S = 3·50.

1 INTRODUCTION

Si_3N_4 is important in industry because of its good refractory properties and high temperature ceramic properties and has been extensively studied.[1,2] Previous studies showed that there were two types of structures for Si_3N_4 with α phase (rhombohedral)[3,4] and β phase (hexagonal).[5–8] Moreover different space groups P6$_3$ and P6$_3$/m were assigned to β-Si_3N_4.[7,8]

This article presents the structural parameters of α-Si_3N_4 and β-Si_3N_4 at 300 K by Rietveld analysis from the diffraction of the mixed two phase powder.

2 SAMPLE PREPARATION

The submicrometer Si_3N_4 powder was prepared from rice husk.[9] The prewashed rice husk was digested with hot HNO_3 and then pyrolysed at 800°C to a constant weight under a flow of argon gas. Si_3N_4 powder was produced by the carbothermal reduction and nitridation of the pyrolysed digested husk at 1430°C. After nitridation, the product was burned in a muffle furnace at 700°C for 30 min in order to remove any excess carbon.

3 EXPERIMENT AND REFINEMENT

A standard Siemens D-5000 sample holder was used. The Si_3N_4 powder was gently pressed into the sample holder and then carefully serrated with a razor blade to make a smooth surface and to minimize any possible preferred orientation in the specimen.

The diffraction data for Rietveld analysis were collected at room temperature (300 K) with the Siemens D-5000 powder diffractometer, Bragg–Brentano geometry, diffracted-beam graphite (0002) monochromator, CuKα radiation, 40 KV of tube voltage and 30 mA of tube current, step-scan-size of 0·04°, radius of the diffractometer 216 mm. With counting time 70 s, divergence slit DS = 0·8°, anti-scattering slit AS = 1·0°, receiving slit

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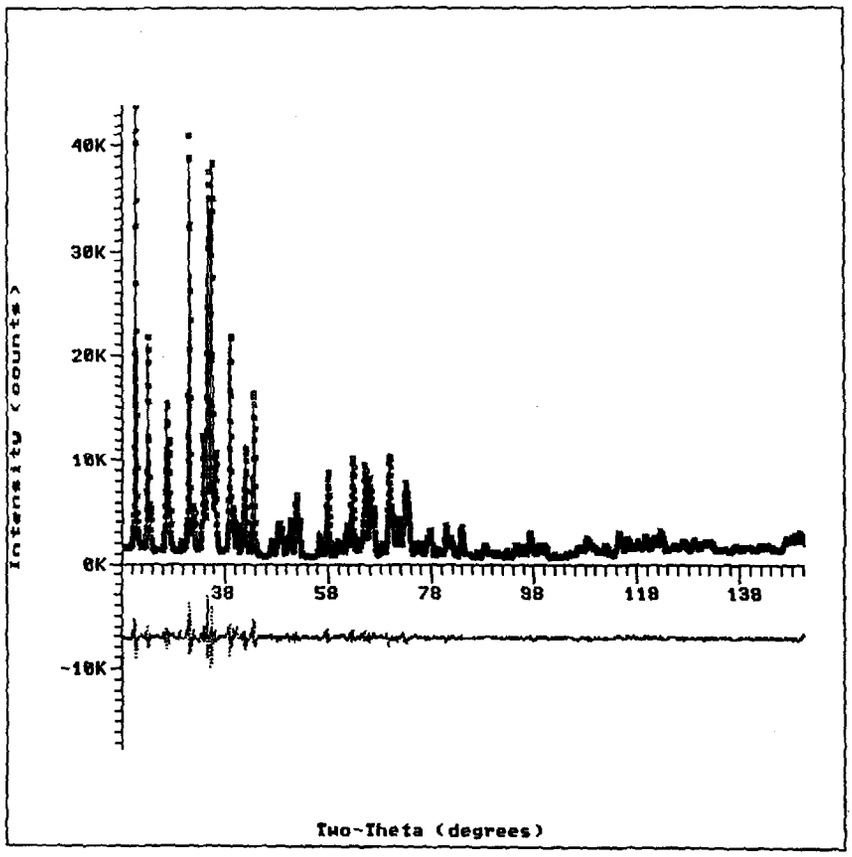

Fig. 1. Observed (dotted), calculated (curve) data and residuals of the powder diffraction patterns for α-Si_3N_4 and β-Si_3N_4. Residual is the difference between observed and calculated data: $I_{obs}-I_{cal}$.

Table 1. Structure parameters of α-Si_3N_4 by Rietveld analysis at 300 K with ESDs in parentheses

Formula:	Si_3N_4		
Temperature:	300 K		
Space group:	P31c	$Z = 4$	
Crystal Data*:	$Mr = 140{\cdot}285$	$Dx = 3{\cdot}1709$ g/cm^3	
	$F(000) = 280{\cdot}0$		
	$\mu = 133{\cdot}474$ cm^{-1} ($\lambda = 1{\cdot}5406$ Å)		
Cell parameters (Rietveld refinement):			
	$a = 7{\cdot}7650(4)$ Å	$V = 293{\cdot}85(2)$ Å^3	
	$c = 5{\cdot}6275(2)$ Å		

Refinements of the structure:
$R_b = 2{\cdot}42$ and $R_f = 1{\cdot}78\%$

Atom	Site	x	y	z	B_{iso} (Å^2)	Occupancy
Si(1)	6c	0·5106(3)	0·0815(3)	0·1904(4)	0·73(3)	1
Si(2)	6c	0·1658(2)	0·2520(2)	–0·0168(4)	0·54(3)	1
N(1)	2a	0	0	–0·029(2)	0·26(3)	1
N(2)	2b	1/3	2/3	0·634(2)	0·3(2)	1
N(3)	6c	0·3488(6)	–0·0383(8)	–0·022(1)	0·8(1)	1
N(4)	6c	0·3159(5)	0·3165(6)	0·241(1)	0·1(1)	1

Selected interatomic distances (Å) and angles (degrees)* for two types of the Si–N tetrahedra:

Bond lengths:			
Si(1)–N11:†	1·739(3)	Si(2)–N21:	1·724(3)
Si(1)–N12:	1·644(5)	Si(2)–N22:	1·709(5)
Si(1)–N13:	1·774(6)	Si(2)–N23:	1·929(6)
Si(1)–N14:	1·825(6)	Si(2)–N24:	1·766(7)
Bond angles:			
N13–Si(1)–N14:	102·4(3)	N23–Si(2)–N24:	115·3(3)
N12–Si(1)–N14:	111·0(3)	N22–Si(2)–N24:	100·2(3)
N12–Si(1)–N13:	114·5(3)	N22–Si(2)–N23:	103·2(2)
N11–Si(1)–N14:	112·1(2)	N21–Si(2)–N24:	110·6(2)
N11–Si(1)–N13:	101·9(2)	N21–Si(2)–N23:	111·2(2)
N11–Si(1)–N12:	114·2(2)	N21–Si(2)–N22:	115·9(2)

*Calculated using PARST.[12]
†The notations are for N atoms of the Si–N tetrahedra, similar to previous references.[4,7]

RS = 1·0 mm, the data were collected over the range from 18–150°. The powder diffraction pattern is as shown in Fig. 1, in which only α-Si_3N_4 and β-Si_3N_4 phases exist.

The Rietveld analysis program version DBWS-9006PC (release 12.8.91)[10,11] was used. The background was refined with a fifth order polynomial. The profile was refined with a pseudo-Voigt function. The preferred orientation (001) was refined with a March–Dollas function. No absorption correction was taken into account. The wavelengths of the $CuK\alpha_2$, $CuK\alpha_1$ and the intensity ratio were chosen as 1·5444 Å, 1·5406 Å and 0·497, respectively. The isotropic thermal parameters could be refined to the reasonable values. For α-Si_3N_4, the structure was refined with 29 parameters to R_b = 2·42%, R_f = 1·78% for 243 peaks. For β-Si_3N_4, the structure was refined with 17 parameters to R_b = 3·02%, R_f = 1·88% for 145 peaks. The whole diffraction pattern was fitted and refined with 46 parameters to R_{wp} = 6·98%, R_p = 5·33% for 3301 step intensities and 'goodness of fit' S = 3·50.

The refinement was performed according to the following group order: (1) scale factor; (2) background; (3) zero point shift/sample displacement, transparency coefficient; (4) cell parameters; (5) peak shape; (6) half width; (7) asymmetry parameter and preferred orientation; (8) atom position parameters, and (9) isotropic thermal parameters.

The refined structure parameters are listed in Tables 1 and 2. The data, fitting curves and the differences (residuals: $I_{obs} - I_{cal}$) are shown in Fig. 1. The numbers in the parentheses in the tables are the estimated standard deviations (ESDs). x, y, z are the fractional coordinates and B_{iso} the equivallent thermal parameter. R-values are defined as follows:

$$R_{wp} = \left[\frac{\sum w_i(Y_{io}-Y_{ic})_2}{\sum w_i Y^2_{io}}\right]^{1/2} \qquad R_p = \frac{\sum |Y_{io}-Y_{ic}|}{\sum Y_{io}}$$

$$R_b = \frac{\sum |I_{ko}-I_{kc}|}{\sum I_{ko}} \qquad R_f = \frac{\sum |F_{ko}-F_{kc}|}{\sum F_{ko}}$$

where Y_{io} and Y_{ic} are observed and calculated intensities at step i, I_{ko} and I_{kc} are the peak intensities observed and calculated for kth peak, F_{ko} and F_{kc} are the observed and calculated structure factors, w_i is the weight (= $1/Y_{io}$).

4 RESULTS AND DISCUSSION

The structures were refined with space group P31c for α-Si_3N_4 and $P6_3/m$ for β-Si_3N_4. The structural parameters are as listed in Tables 1 and 2. The (0001) projections of the structures are shown in

Table 2. Structure parameters of β-Si_3N_4 by Rietveld analysis at 300 K with ESDs in parentheses

Formula:	Si_3N_4					
Temperature:	300 K					
Space group:	$p6_3/m$			Z = 2		
Crystal data*:	Mr = 140·285			Dx = 3·1951 g/cm³		
	$F(000)$ = 140·0					
	μ = 134.492 cm⁻¹ (λ = 1·5406 Å)					
Cell parameters (Rietveld refinement):						
	a = 7·6093(8) Å			V = 145·81(2) Å³		
	c = 2·9079(2) Å					
Refinements of the structure:						
R_b = 3·02% and R_f = 1·88%						
Atom	Site	x	y	z	B_{iso} (Å²)	Occupancy
Si(1)	6h	0·1742(7)	−0·2322(7)	1/4	0·51(8)	1
N(1)	2c	1/3	2/3	1/4	0·9(5)	1
N(2)	6h	0·329(2)	0·039(2)	1/4	2·0(3)	1
Selected interatomic distances (Å) and angles (degrees)* for the Si–N tetrahedron:						
Bond lengths:						
Si(1)–N11:†	1·729(5)					
Si(1)–N12:	1·79(1)					
Si(1)–N13:	1·709(9)					
Si(1)–N14:	1·709(9)					
Bond angles:						
N13–Si(1)–N14:	116·6(5)					
N12–Si(1)–N14:	105·10(1)					
N12–Si(1)–N13:	105·10(1)					
N11–Si(1)–N14:	110·67(1)					
N11–Si(1)–N13:	110·67(1)					
N11–Si(1)–N12:	108·1(4)					

*Calculated using PARST.[13]
†The notations are for N atoms of the Si–N tetrahedra, similar to previous references.[4,7]

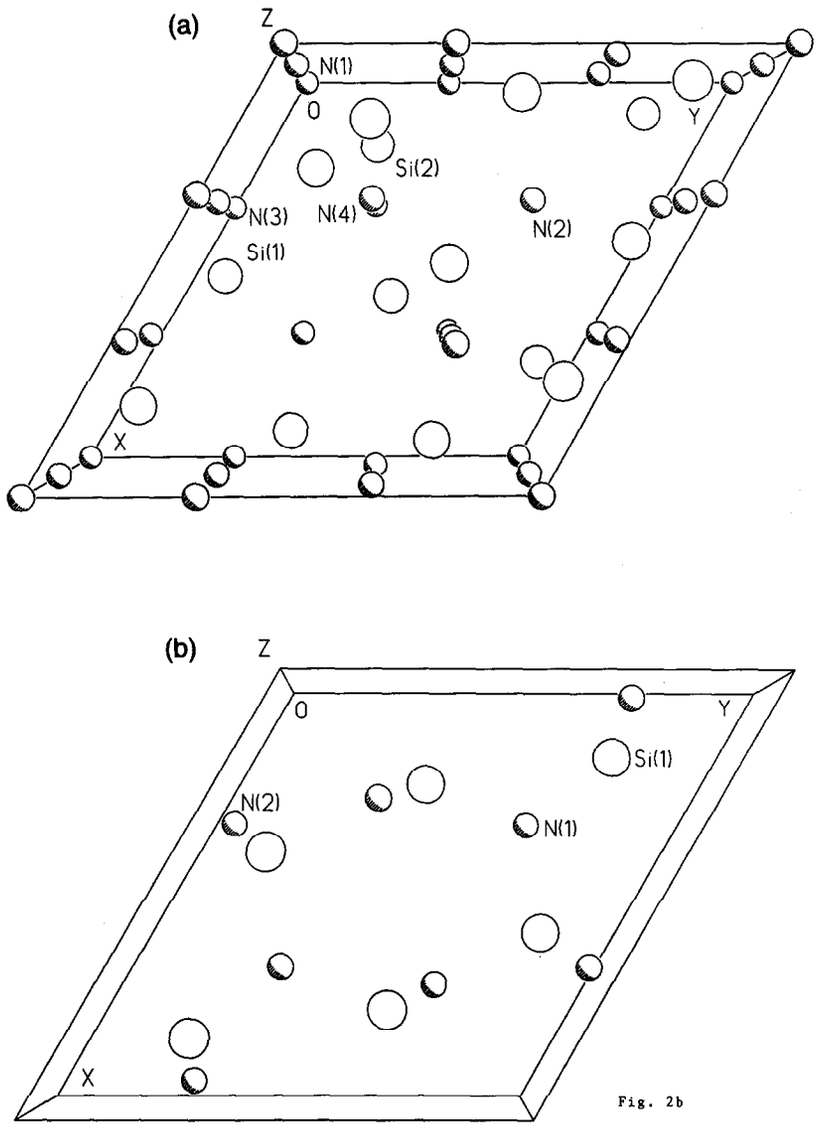

Fig. 2. Projections of the structures for, (a) α-Si_3N_4, and (b) β-Si_3N_4.

Fig. 2(a) and (b), respectively for α-Si_3N_4 and β-Si_3N_4. The results reveal that pure α-Si_3N_4 and β-Si_3N_4 can be made from rice husks and the structures are the same as those made from Si.[4,7] The ratio of crystalline α-Si_3N_4 and β-Si_3N_4 can be obtained by the following formula:[12]

$$S_j = \frac{K \cdot V_j}{\Omega_j^2 \cdot \bar{\mu}}$$

The scale factor S_j is obtained from

$$I_j = S_j \cdot [n \cdot |F|^2 \cdot Lp \cdot e^{-M}]_j$$

where I_j is the integrated intensity, S_j the scale factor, n the multiplicity factor, F the structure factor, Lp the Lorentz polarization factor and e^{-M} the Debye–Waller factor for phase j, K a constant, V_j the fractional volume of phase j in the powder, Ω_j the volume of unit cell of phase j and $\bar{\mu}$ the average absorption coefficient of the sample. From the refinements, the overall scale factors are 0·0323 and 0·0118, respectively for α-Si_3N_4 and β-Si_3N_4. The weight percentages are then calculated out to be 91·7 wt% (α-Si_3N_4) and 8·3 wt% (β-Si_3N_4).

The atomic coordinates, selected bond lengths and bond angles for Si–N tetrahedra are listed in Tables 1 and 2 for α-Si_3N_4 and β-Si_3N_4, respectively. The results are compared to the previous structure determinations.[4,7] One may notice that the coordinates and isothermal parameters of N atoms have less precision than those of Si atoms. This is because N atoms are very light and not very sensitive to the diffraction data.

Space group $P6_3$ for β-Si_3N_4 was also used for another refinement where the 2 coordinates were refined for the N atoms replacing the special position in the z =1/4 (mirror plane) in $P6_3/m$. Nearly the same R-values were obtained, i.e., R_b = 2·53, R_f = 1·83% for α-Si_3N_4, R_b = 3·19, R_f = 1·93% for β-Si_3N_4 and R_{wp} = 7·12, R_p = 5·40%. But the

Table 3. Observed and calculated intensities of the powder diffraction pattern for α-Si_3N_4 in P31c (λ = 1·5406Å)

2-theta (degree)	d (Å)	I_{obs} (observed)	I_{calc} (calculated)	h	k	l
13·16	6·7247	*	19·34	0	1	0
20·56	4·3157	100·00	95·34	0	1	1
22·89	3·8825	50·04	44·92	−1	2	0
26·49	3·3623	35·32	33·52	0	2	0
30·96	2·8864	96·69	99·08	0	2	1
31·78	2·8138	10·30	9·57	0	0	2
34·53	2·5957	89·13	94·46	0	1	2
35·28	2·5417	92·83	100·00	−1	3	0
38·85	2·3164	52·30	17·18	−1	3	1
38·85	2·3164		43·33	1	2	1
39·52	2·2783	10·15	3·70	−1	2	2
39·52	2·2783		5·17	1	1	2
40·20	2·2416	6·60	4·49	0	3	0
41·83	2·1579	24·80	32·82	0	2	2
43·42	2·0824	38·97	45·93	0	3	1
48·21	1·8861	7·35	0·33	−1	3	2
48·21	1·8861		9·29	1	2	2
48·79	1·8651	5·91	8·39	−1	4	0
50·47	1·8069	8·24	12·63	0	1	3
51·58	1·7704	14·31	19·48	−1	4	1
51·58	1·7704		0·11	1	3	1
56·10	1·6381	5·12	8·59	0	2	3
57·64	1·5979	20·61	21·58	−2	4	2
57·64	1·5979		7·06	2	2	2
62·36	1·4879	23·14	1·38	−2	5	1
62·36	1·4879		36·13	2	3	1
64·75	1·4386	20·07	31·81	0	3	3
65·70	1·4200	18·94	26·94	−1	5	1
65·70	1·4200		2·43	1	4	1
66·39	1·4069	11·61	16·52	0	0	4
69·42	1·3528	24·43	18·04	−2	5	2
69·42	1·3528		22·92	2	3	2
71·23	1·3227	8·61	5·17	−1	2	4
71·23	1·3227		0·81	1	1	4
71·24	1·3226		3·48	−1	4	3
71·24	1·3226		5·09	1	3	3
72·60	1·3011	17·83	7·94	−1	5	2
72·60	1·3011		16·72	1	4	2
73·05	1·2942	11·23	14·59	−3	6	0
76·84	1·2396	7·20	6·11	−2	6	1
76·84	1·2396		1·76	2	4	1
77·48	1·2309	6·30	6·76	−1	3	4
77·48	1·2309		4·56	1	2	4
80·55	1·1916	7·47	0·70	0	3	4
80·56	1·1915		10·75	−2	5	3
80·56	1·1915		2·78	2	3	3
83·59	1·1558	7·32	0·72	−1	5	3
83·59	1·1558		8·41	1	4	3
96·92	1·0291	5·51	3·61	−1	3	5
96·92	1·0291		3·74	1	2	5
96·94	1·0290		1·07	−3	7	2
96·94	1·0290		0·39	3	4	2
114·17	0·9176	5·60	1·79	−4	8	2
114·17	0·9176		2·27	4	4	2
122·19	0·8799	5·86	0·42	−1	3	6
112·19	0·8799		0·70	1	2	6
122·22	0·8798		2·99	−1	8	1
122·22	0·8798		0·89	1	7	1

The observed intensities were obtained directly from the Siemens D5000 powder diffractometer. The calculated intensities were obtained using XPOW, Version 4.2, Siemens Analytical X-ray Inst. Inc., 1990; with the structure parameters from Table 1 by Rietveld refinement. (The preferred orientation and monochromator correction are not taken into account. Atomic scattering factors are for Si and N and anomalous dispersion correction was used.) Only lines with observed intensities greater than 5% are listed.
*Out of the observation range.

Table 4. Observed and calculated intensities of the powder diffraction pattern for β-Si_3N_4 in $P6_3/m$ (λ = 1·5406 Å)

2-theta (degree)	d (Å)	I_{obs} (observed)	I_{calc} (calculated)	h	k	l
13·43	6·5898	*	31·21	0	1	0
23·36	3·8047	36·17	31·19	−1	2	0
27·04	3·2949	94·40	97·25	0	2	0
33·66	2·6604	100·00	94·84	0	1	1
36·03	2·4907	81·93	100·00	−1	3	0
41·38	2·1803	32·54	32·98	0	2	1
49·85	1·8277	9·34	13·07	−3	4	0
49·85	1·8277		0·25	−1	4	0
52·14	1·7527	28·43	46·08	0	3	1
61·26	1·5118	9·50	10·88	−3	5	0
61·26	1·5118		7·07	−2	5	0
63·98	1·4540	11·65	17·07	0	0	2
64·78	1·4380	6·30	6·02	−4	5	0
64·78	1·4380		3·46	−1	5	0
70·09	1·3414	30·38	46·40	−3	5	1
70·09	1·3414		6·25	−2	5	1
75·68	1·2557	8·94	0·45	−2	3	2
75·68	1·2557		20·31	−1	3	2
89·29	1·0962	3·26	0·00	−5	6	1
89·29	1·0962		5·70	−1	6	1
101·90	0·9919	2·67	3·02	−5	7	1
101·90	0·9919		0·27	−2	7	1
104·15	0·9765	2·35	3·38	0	5	2
123·91	0·8728	3·85	0·09	−7	8	0
123·91	0·8728		2·50	−1	8	0
141·47	0·8160	5·13	2·40	−3	5	3
141·47	0·8160		0·29	−2	5	3
146·80	0·8038	3·26	0·00	−4	5	3
146·80	0·8038		1·05	−1	5	3

The observed intensities were obtained directly from the Siemens D5000 powder diffractometer. The calculated intensities were obtained using XPOW, Version 4.2, Siemens Analytical X-ray Inst. Inc., 1990; with the structure parameters from Table 2 by Rietveld refinement. (The preferred orientation and monochromator correction are not taken into account. Atomic scattering factors are for Si and N and anomalous dispersion correction was used.) Only lines with observed intensities greater than 5% are listed.
*Out of the observation range.

coordinates were quite near the mirror plane (z = 1/4) in that z-1/4 = 0·06(1) for N1 and z-1/4 = 0·03(3) for N2. Furthermore, since z-1/4 = σ for N2, where standard error σ = 0·03, the difference from the mirror plane is not significant. Our Rietveld analysis favours β-Si_3N_4 belonging to the space group $P6_3/m$.[8] The observed and calculated intensities of the powder diffraction patterns for α-$Si_3N_4$and β-Si_3N_4 are listed in Tables 3 and 4, respectively.

5 CONCLUSION

The Rietveld analysis demonstrated conclusively that the Si_3N_4 powder produced from rice husk according to the method of Rahman[9] is a pure two-phase mixture of α-Si_3N_4 (91·7 wt%) and β-Si_3N_4 (8·3 wt%). No other impurities were detected.

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