PHYSICAL REVIEW B VOLUME 58, NUMBER 18 1 NOVEMBER 1998-II

Diffraction-pattern calculation and phase identification of hypothetical crystalline C_3N_4

Jianbo Wang, Jianlin Lei, and Renhui Wang
Department of Physics, Wuhan University, Wuhan 430072, People's Republic of China

(Received 20 April 1998)

In the present work we calculate x-ray powder-diffraction patterns and structure factors for electron diffraction of seven structures of hypothetical crystalline C_3N_4. Applying the same computational method, we calculate the x-ray powder-diffraction patterns of β-Si_3N_4 and α-Si_3N_4 that match the experimental ones taken from the Joint Committee on Powder Diffraction Standards cards indicating very well the reliability of our computational programs. The discrepancy between calculated diffraction intensities and the experimental ones from synthesized C-N compounds indicates that all the claims regarding successful synthesis of crystalline β-C_3N_4, α-C_3N_4, and defect zinc blende C_3N_4 are not convincing, at least from the point of view of phase identification by the diffraction method. All the calculated patterns can be used as standard reference patterns in the future synthesis of C_3N_4. [S0163-1829(98)00541-4]

I. INTRODUCTION

Since Cohen and Liu[1–3] predicted theoretically that β-C_3N_4 may possess a hardness superior to that of diamond, many efforts have been made to synthesize such a harder-than-diamond crystal of β-C_3N_4. As summarized by Fang[4] and DeVries,[5] about 65 papers claimed successful synthesis of crystalline β-C_3N_4, among which some papers[6–18] listed their x-ray and/or electron-diffraction patterns to confirm the consistency between experimental diffraction patterns from synthesized carbon nitrides and calculated ones from theoretically predicted crystal models of carbon nitrides. It is well known that any convincing phase identification by the diffraction method requires consistency of both the interplanar spacings and relative intensities between the diffraction pattern from crystals to be identified and the standard pattern of a known crystal. However, there have been no standard patterns of the hypothetical carbon nitride, so that all the claims regarding synthesis of the β-C_3N_4 phase[6–18] were based only on a consistency between the experimental interplanar spacings d and some selected d values calculated from the predicted structure. Obviously such claims are not convincing.

In addition to the structure model of β-C_3N_4 predicted by Liu and Cohen[3] in 1990, which is isostructural with β-Si_3N_4, studied by Borgen and Seip[19] with C substituted for Si, theoretical calculations[20,21] revealed that some other carbon nitride structures, including α-C_3N_4, cubic C_3N_4, and graphite C_3N_4, are also energetically favored. Recently, two papers[22,23] claimed synthesis of cubic C_3N_4 identified by electron diffraction.

In the present work we calculate theoretical x-ray powder-diffraction patterns and structure factors for electron diffraction of seven possible structures of C_3N_4 predicted by Liu and Cohen,[3] Liu and Wentzcovitch,[20] and Teter and Hemley.[21] The results are used to check the reliability of the claims regarding the synthesis of crystalline C_3N_4 and will be useful for future synthesis of C_3N_4 crystals.

II. DIFFRACTION-PATTERN CALCULATION

A. Structural models

Among the predicted seven structure types of crystalline C_3N_4 (Refs. 3, 20, and 21), two are β-C_3N_4 of space groups $P6_3/m$ (Refs. 3 and 20) and $P3$,[21] one is α-C_3N_4 of space group $P31c$,[21] one is a cubic defect-zinc-blende structure type,[20,21] one is a cubic willemite-II structure type of Zn_2SiO_4,[21] two are graphitic C_3N_4 of space groups of $R3m$ (Ref. 20) and $P\overline{6}m2$.[21] The structural parameters of these crystalline C_3N_4 are listed in Table I. The so-called pseudocubic C_3N_4 in Ref. 21 is the same as the cubic C_3N_4 in Ref. 20 when the origin is shifted to the $[\frac{1}{2}\frac{1}{2}0]$ position. The atomic arrangement in the basis plane of both types of graphite C_3N_4 is similar. When it is stacked according to the sequence of $ABCABC\ldots$, one obtains $3R$-type $R3m$ C_3N_4.[20] When the stacking sequence is $ABAB\ldots$, $2H$-type $P\overline{6}m2$ C_3N_4 results. Obviously many other polytypes of graphite C_3N_4 may be formed according to different stacking sequences.

B. Computational method

The relative intensity of (hkl) reflection in an x-ray powder-diffraction pattern is expressed as

$$I=n|F_{hkl}|^2L_p, \tag{1}$$

where n is the multiplicity, F_{hkl} the structure factor, and

$$L_p=\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}, \tag{2}$$

the Lorentz-polarization factor with θ being the Bragg angle of (hkl) reflection. In the calculation we omitted the Debye-Waller factor. This would cause a small systematic increase of the calculated intensity with the increase of θ. Since the C-N bond is rather strong, the effect of the Debye-Waller factor should be very small. In the calculation the wavelength of $\lambda=1.541\,838$ Å is used. In addition, we have calculated values of $|F_{hkl}|$ for electron diffraction that may be used for qualitative comparison with the experimental selected-area electron-diffraction patterns. In all the calcula-

TABLE I. Structural parameters of some predicted crystalline C_3N_4.

	β-C_3N_4	β-C_3N_4	α-C_3N_4	Cubic C_3N_4 (zinc blende)	Cubic C_3N_4	$3R$ graphitic C_3N_4	$2H$ graphitic C_3N_4
Space group	$P3(143)$	$P6_3/m(176)$	$P31c(159)$	$P\overline{4}3m(215)$	$I\overline{4}3d(220)$	$R3m(160)$	$P\overline{6}m2(187)$
Z	2	2	4	1	4	3	2
a (Å)	6.4017	6.44	6.4665	3.43	5.3973	4.744	4.7420
c (Å)	2.4041	2.467	4.7097			9.193	6.7205
$C1$	$3d$ (0.7732,0.1784,0.2499)	$6h$ (0.174,0.766,0.250)	$6c$ (0.5171,0.0813,0.2102)	$3c$ (0.500,0.500,0.000)	$12b$ (0.8750,0.0000,0.2500)	$9b$ (0.5000,0.5000,0.0000)	$3j$ (0.3517, 0.1759,0.0000)
$C2$	$3d$ (0.2271,0.8216,0.7501)		$6c$ (0.1656,0.2547,0.9905)				$3k$ (0.0197,0.5099,0.5000)
$N1$	$1b$ (0.3333,0.6667,0.7500)	$2c$ (0.333,0.667,0.250)	$2a$ (0.0000,0.0000,0.0000)	$4e$ (0.254,0.254,0.254)	$16c$ (0.2812,0.2812,0.2812)	$3a$ (0.0000,0.0000,0.3333)	$1a$ (0.0000,0.0000,0.0000)
$N2$	$1c$ (0.6667,0.3333,0.2500)		$2b$ (0.3333,0.6667,0.6278)			$9b$ (0.5000,0.5000,0.3333)	$1f$ (0.6667,0.3333,0.5000)
$N3$	$3d$ (0.0331,0.3309,0.2502)	$6h$ (0.321,0.025,0.250)	$6c$ (0.3471,0.9510,0.9706)				$3k$ (0.1694,0.3387,0.5000)
$N4$	$3d$ (0.9669,0.6705,0.7498)		$6c$ (0.3148,0.3188,0.2423)				$3j$ (0.5026,0.4974,0.0000)

TABLE II. Calculated x-ray powder-diffraction pattern of $P6_3/m$ β-Si_3N_4 compared with Joint Committee on Powder Diffraction Standards card 33-1160.

hkl	d (Å)		I/I_1	
	Calc.	Expt.	Calc.	Expt.
100	6.5856	6.583	32.5	34
110	3.8022	3.800	32.2	35
200	3.2928	3.293	95.1	100
101	2.6598	2.660	100.0	99
210	2.4891	2.489	87.2	93
111	2.3096	2.310	5.9	9
300	2.1952	2.1939	2.8	10
201	2.1795	2.1797	33.5	31
220	1.9011	1.9013	5.7	8
211	1.8909	1.8916	6.5	5
310	1.8265	1.8275	10.3	12
301	1.7519	1.7525	44.3	37
221	1.5912	1.5911	14.4	12
311	1.5466	1.5467	6.8	6
320	1.5108	1.5108	18.2	15
002	1.4538	1.4534	18.0	15
410	1.4371	1.4368	9.4	8
401	1.4327	1.4325	1.2	5
102	1.4196	1.4197	0.6	1
112	1.3579	1.3579	2.3	1
321	1.3406	1.3408	52.4	39
202	1.3299	1.3299	9.2	6
500	1.3171	1.3173	5.0	5
411	1.2883	1.2883	26.0	18
330	1.2674	1.2675	9.1	7
212	1.2553	1.2554	20.2	16
420	1.2446	1.2447	1.6	1
501	1.1998	1.1998	2.1	2
510	1.1828	1.1831	3.0	2
331	1.1618	1.1618	0.3	<1
222	1.1548	1.1551	2.4	2
421	1.1441	1.1445	7.1	3
312	1.1375	1.1377	4.1	3
511	1.0956	1.0957	5.7	4
430	1.0827	1.0828	4.5	3
520	1.0545	1.0545	0.9	<1
322	1.0476	1.0476	11.2	6
601	1.0269	1.0269	0.4	<1
412	1.0220	1.0219	7.1	4
431	1.0146	1.0147	0.7	1
610	1.0043	1.0043	3.0	2
521	0.9913	0.9914	3.9	3
502	0.9761	0.9761	5.1	4
103	0.9588	0.9589	4.4	3
332	0.9553	0.9554	9.1	5
440	0.9506		1.5	
611	0.9493	0.9492	15.5	8
422	0.9454	0.9455	2.0	1
530	0.9408	0.9408	3.0	1
203	0.9297	0.9298	4.1	2
512	0.9175	0.9175	3.9	1
620	0.9133	0.9132	4.4	3
441	0.9035	0.9034	7.5	4

TABLE II. (*Continued*).

hkl	d (Å)		I/I_1	
	Calc.	Expt.	Calc.	Expt.
531	0.8951	0.8950	1.6	3
303	0.8866	0.8866	8.5	5
710	0.8723	0.8722	10.9	6
621	0.8713	0.8712	7.3	5
432	0.8683	0.8682	8.2	5
223	0.8634	0.8634	3.2	1
313	0.8561	0.8561	2.3	1
522	0.8536	0.8537	1.9	2

tions, the dependence of the atomic-scattering factor on the value of $\sin\theta/\lambda=1/2d$ is considered.

In order to check the reliability of our computational programs, we calculated the x-ray powder-diffraction pattern of β-Si_3N_4 as listed in Table II compared with the experimental one taken from the Joint Committee on Powder Diffraction Standards (JCPDS) card 33-1160. In the calculation a structure model described in Ref. 19 is used that is isostructural with the $P6_3/m$ β-C_3N_4 listed in Table I. The calculated intensities match the experimental ones very well except there are somewhat higher calculated values for reflections with low interplanar spacings. This discrepancy may be caused by neglecting the Debye-Waller factor in the calculation. Table II also shows what is ''matched very well.'' Similarily, our calculated x-ray powder diffraction pattern of α-Si_3N_4 matches rather well the experimental one taken from the JCPDS card 41-360.

TABLE III. Calculated x-ray-diffraction pattern of $P6_3/m$ and $P3$ β-C_3N_4 compared with the experimental intensities.

hkl	$P6_3/m$		$P3$		$(I/I_1)_{Expt}$
	d (Å)	$I/I_1>6$ [a]	d (Å)	$I/I_1>6$ [a]	
100	5.5772	41.7	5.5440	51.6	
110	3.2200	34.6	3.2008	36.4	
200	2.7886	100.0	2.7720	100.0	vs
101	2.2561	71.0	2.2057	61.7	m
210	2.1080	33.9	2.0954	40.2	s
111	1.9583	55.8	1.9223	58.2	w
300	1.8591	43.4	1.8480	41.5	m
201	1.8477	0.1	1.8162	0.0	m
220	1.6100	1.0	1.6004	1.9	m
211	1.6026	14.0	1.5796	11.5	w
310	1.5468	7.1	1.5376	9.8	w
301	1.4847	11.8	1.4652	11.6	vw
221	1.3483	19.1	1.3322	17.3	m
311	1.3105	0.4	1.2954	0.1	vw
320	1.2795	11.5	1.2719	10.9	
002	1.2335	13.1	1.2020	12.5	
321	1.1358	31.9	1.1242	35.7	
411	1.0915	18.7	1.0807	16.9	
330	1.0733	9.6	1.0669	9.9	
302	1.0278	7.3	1.0076	6.9	
501	1.0164	<6.0	1.0069	7.6	
421	0.9692	6.5	0.9605	<6.0	
322	0.8880	11.9	0.8736	12.1	
610	0.8505	<6.0	0.8455	7.0	
103	0.8135	<6.0	0.7931	7.2	
332	0.8097	27.7	0.7980	34.6	
611	0.8041	22.3	0.7976	26.5	
113	0.7968	7.0	0.7774	<6.0	
530,700	0.7967	11.0	0.7920	13.3	

[a] Calculated intensities are larger than 6 except those reflections that appeared in the experiment.

TABLE IV. Calculated x-ray-diffraction pattern of α-C_3N_4 compared with the experimental intensities.

hkl	d (Å)	I/I_1	
		Calc.>5 [a]	Expt.
100	5.6002	19.1	
101	3.6045	100.0	
110	3.2332	45.5	
200	2.8001	33.3	
201	2.4068	87.4	s
002	2.3548	4.0	w
102	2.1707	43.5	m
210	2.1167	55.2	s
211	1.9306	14.4	m
112	1.9035	82.2	w
300	1.8667	56.5	m
202	1.8022	0.3	m
301	1.7354	15.2	w
212	1.5742	9.9	w
310	1.5532	5.5	
103	1.5116	6.5	
311	1.4751	5.2	
222	1.3328	26.1	w
321	1.2395	22.2	
303	1.2015	6.5	
004	1.1774	10.7	
322	1.1278	25.1	
114	1.1063	7.1	
412	1.0847	24.3	
330	1.0777	12.8	
214	1.0289	6.1	
323	0.9943	7.6	
511	0.9836	7.2	
324	0.8680	6.9	
215	0.8606	8.0	
334	0.7950	22.8	
433	0.7942	12.9	
531,701	0.7887	14.5	
405	0.7815	5.8	
106	0.7774	5.1	
620	0.7766	24.2	

[a] Calculated intensities are larger than 5 except those reflections that appeared in the experiment.

C. X-ray powder-diffraction patterns and structure factors for electron diffraction from hypothetical C_3N_4

Tables III–VIII list calculated x-ray powder-diffraction patterns from hypothetical crystalline C_3N_4, namely, from $P6_3/m$ β-C_3N_4, $P3$ β-C_3N_4 (Table III), α-C_3N_4 (Table

TABLE V. Calculated x-ray-diffraction pattern of cubic defect zinc blende C_3N_4.

hkl	d (Å)	$I/I_1>1$
100	3.4300	20.2
110	2.4254	9.3
111	1.9803	100.0
200	1.7150	5.3
210	1.5339	2.2
211	1.4003	2.1
220	1.2127	34.9
221	1.1433	1.3
311	1.0342	22.9
320	0.9513	1.3
321	0.9167	1.6
400	0.8575	12.1
410	0.8319	1.8
330,411	0.8085	2.2
331	0.7869	55.5

IV), cubic defect-zinc-blende structure-type C_3N_4 (Table V), cubic willemite-II structure-type C_3N_4 (Table VI), $3R$-type graphite C_3N_4 (Table VII), and $2H$-type graphite C_3N_4 (Table VIII), respectively.

By comparing two calculated diffraction patterns in Table III one finds similar relative intensities for both $P6_3/m$ and $P3$ β-C_3N_4. The reason lies in that the atomic positions of both structures have only a minor difference as shown in Table I.

As an example, we list in Table IX calculated structure factor amplitudes $|F_{hkl}|$ for electron diffraction of defect zinc blende C_3N_4 that will be used to check the claims regarding successful synthesis of defect-zinc-blende-type C_3N_4.

D. Comparison with diffraction patterns from synthesized C-N crystals

Based on the calculated powder-diffraction patterns listed in Tables III–VIII we can compare them with experimental powder-diffraction patterns from synthesized C-N crystals.

TABLE VI. Calculated x-ray-diffraction pattern of cubic willemite-II C_3N_4.

hkl	d (Å)	$I/I_1>1$
211	2.2034	100.0
220	1.9082	56.6
310	1.7068	1.0
321	1.4425	15.7
400	1.3493	11.5
420	1.2069	6.0
332	1.1507	19.8
422	1.1017	17.3
431,510	1.0585	12.9
521	0.9854	7.4
530	0.9256	4.9
532,611	0.8756	8.8
541	0.8328	20.7

TABLE VII. Calculated x-ray-diffraction pattern of $3R$ graphite C_3N_4.

hkl	d (Å)	$I/I_1>1$
101	3.7509	8.8
003	3.0643	100.0
102	3.0632	4.6
110	2.3720	1.8
201	2.0048	18.8
113	1.8757	1.4
202	1.8754	14.2
006	1.5322	6.5
204	1.5316	5.8
205	1.3700	3.5
220	1.1860	6.8
207	1.1065	1.5
223	1.1060	10.8
009	1.0214	1.5
401	1.0208	1.3
208	1.0029	1.2
402	1.0024	1.2
226	0.9379	8.6
404	0.9377	1.2
405	0.8967	1.2
$20\underline{10}$	0.8391	1.6
407	0.8091	2.0

TABLE VIII. Calculated x-ray-diffraction pattern of $2H$ graphite C_3N_4.

hkl	d (Å)	$I/I_1>1$
100	4.1067	2.6
101	3.5042	9.9
002	3.3602	100.0
102	2.6006	1.1
110	2.3710	1.2
200	2.0533	3.8
103	1.9666	1.2
201	1.9637	19.1
112	1.9373	1.1
202	1.7521	3.9
004	1.6801	7.2
203	1.5137	6.1
204	1.3003	1.0
220	1.1855	4.8
205	1.1246	1.8
006	1.1201	1.4
222	1.1180	8.0
401	1.0149	1.4
224	0.9686	6.1
403	0.9333	1.3
207	0.8697	1.5
405	0.8159	2.1
226	0.8142	9.9

TABLE IX. Calculated structure factor amplitudes for electron diffraction of defect zinc blende C_3N_4.

hkl	d (Å)	$\|F_{hkl}\|$
100	3.4300	33.7
110	2.4254	23.9
111	1.9803	100.0
200	1.7150	21.0
210	1.5339	12.5
211	1.4003	12.6
220	1.2127	73.5
300	1.1433	5.8
221	1.1433	9.8
310	1.0847	8.1
311	1.0342	40.9
222	0.9902	11.3
320	0.9513	8.6
321	0.9167	6.1
400	0.8575	40.6
410	0.8319	5.6
322	0.8319	3.2
330	0.8085	4.6
411	0.8085	5.2
331	0.7869	25.2
420	0.7670	7.5
421	0.7485	3.6
332	0.7313	4.1
422	0.7001	28.1
500	0.6860	5.6
430	0.6860	2.2
510	0.6727	3.3
431	0.6727	3.7
511	0.6601	18.3
333	0.6601	18.3

As examples we list the experimental relative intensities in Tables III and IV, selected from Ref. 10 that match the calculated patterns better than those of Refs. 6–9 and 11–18. In these tables, vs means very strong, s strong, m medium, w weak, and vw very weak. However, Table III still reveals an obvious discrepancy in diffraction intensities. The calculated intensities of (110) and (111) reflections are rather strong while in experiment they were weak [(111) reflection] or even not observed [(110) reflection]. On the contrary, the calculated intensities of (201) and (220) reflections are very weak while they showed medium intensities in experiment. This discrepancy cannot be explained by possible texture because reflections (110) and (220) possess the same orientation for a textured specimen. Table IV reveals a similar situation where the calculated strongest (101) reflection was not observed while the calculated very weak (202) reflection showed a medium intensity, in spite of the same orientation of both (101) and (202) lattice planes. Other experimental intensities from synthesized crystalline C-N compounds published in Refs. 6–18 deviated much more seriously from the calculated ones.

Martin-Gil *et al.*[22] and Yamamoto *et al.*[23] claimed successful synthesis of a C_3N_4 compound with defect-zinc-blende structure ($P\overline{4}3m$). Their experimental electron-diffraction patterns show strong 111, 200, 220, 311, ... reflections and extinct 100, 110, ... reflections, typical for face-centered-cubic crystals. However, as listed in Table IX, for defect zinc blende C_3N_4 of space group $P\overline{4}3m$, the structure factors $|F_{hkl}|$ for 100 and 110 reflections should possess measurable values comparable to 200 and 311 reflections.

III. CONCLUSION

The coincidence between our calculated x-ray powder-diffraction patterns and the experimental ones taken from JCPDS cards for α-Si_3N_4 and β-Si_3N_4 indicates the reliability of our computational programs. And the discrepancy between calculated diffraction intensities and the experimental ones from synthesized C-N compounds indicates that all the claims in Refs. 6,18,22, and 23 regarding successful synthesis of crystalline β-C_3N_4, α-C_3N_4, and defect zinc blende C_3N_4 are not convincing, at least from the point of view of phase identification by the diffraction method. Tables III–VIII and our programs for the calculation of structure factors $|F_{hkl}|$ of electron diffraction are useful in the future synthesis of C_3N_4 crystals to confirm which structure type is synthesized. In the case that the measured diffraction patterns arise from more than one phase, one can confirm the existence of a phase only when the strongest reflections of this phase are observed in the experimental pattern.

ACKNOWLEDGMENT

Dr. M. Gao, in Beijing Laboratory of Electron Microscopy, is thanked for his helpful discussions.

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