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On the Crystal Structures of the Nitrides of Silicon and Germanium

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The X-ray powder diffraction patterns of the two phases, α and β, of each of the nitrides Si_3N_4 and Ge_3N_4 have been separated and indexed. The structure of the β phase is confirmed to be of the phenacite (Be_2SiO_4) type. A structure for the α phase is proposed which is related to that of the β phase.

Introduction

Germanium nitride, Ge_3N_4, was described by Juza & Hahn (1939, 1940) as isomorphous with phenacite, Be_2SiO_4. This conclusion was contradicted by Leslie, Carroll & Fisher (1952), who pointed out that two of the line positions quoted by Juza & Hahn could not be indexed on the phenacite basis. These authors showed the resemblance between the X-ray powder diffraction patterns of silicon nitride and germanium nitride and suggested an orthorhombic unit cell, with $a = 13{\cdot}38$, $b = 8{\cdot}60$, $c = 7{\cdot}74$ Å for Si_3N_4 and $a = 13{\cdot}84$, $b = 9{\cdot}06$, $c = 8{\cdot}18$ Å for Ge_3N_4, containing twelve molecules.

The formation of two nitrides of silicon by nitriding the metal at about 1400° C. was reported by Vassiliou & Wilde (1957) and by Turkdogan & Ignatowicz (1957). We found the same two phases of silicon nitride and also the corresponding two phases of germanium nitride (Popper & Ruddlesden, 1957, referred to as I) and showed that the powder diffraction photographs of Juza & Hahn and of Leslie *et al.* could be interpreted as resulting from mixtures of these two phases.

The composition of the two phases was discussed in I, where the high electrical resistivity of α-silicon nitride ($> 10^{12}$ ohm cm.) was mentioned and the probability expressed that both phases were of composition M_3N_4. This conclusion has been confirmed by the work of Turkdogan, Bills & Tippett (1958), whose chemical analysis showed no detectable difference between the compositions Si_3N_4 of the two phases of silicon nitride.

The β phases (referred to in I as phase II) were shown to be in substantial agreement with the original assignment by Juza & Hahn of a phenacite-type structure for germanium nitride and were indexed according to the rhombohedral, phenacite-type unit cell. However, our more recent diffraction photographs show certain systematic absences which confirm the expected change in unit cell from the rhombohedral to the smaller hexagonal cell on replacing Be and Si by like atoms and are in agreement with the recent work of Hardie & Jack (1957).

The powder diffraction patterns of the α phase (previously referred to as phase I) were indexed on the basis of an orthorhombic unit cell containing two M_3N_4 molecules. The relation $b = a\sqrt{3}$ between the lattice parameters of this cell suggested a hexagonal cell, but the hexagonal unit cell of half the orthorhombic cell volume was not allowed since the orthorhombic cell is not *C*-face centred, i.e. lines with $h+k$ odd are present. Attempts based on the orthorhombic unit cell to devise a trial structure with tetrahedral coordination of metal atoms indicated that this cell (which could not be determined unambiguously from powder line positions only) was too small. Hardie & Jack (see also Turkdogan *et al.*) and also Decker & Forgang (private communication) have since proposed a hexagonal unit cell which is related to the orthorhombic cell by $a = 2a_0$, $c = c_0$, and of double the volume. This hexagonal cell agrees with all the data and appears the most reasonable.

We suggest a crystal structure for the α-nitrides which is based on this hexagonal cell and is related to the phenacite-type structure of the β-nitrides.

Preparation of the nitrides

Silicon nitride has been prepared by nitriding the metal in nitrogen or ammonia at 1350–1450° C. and by the reaction, at the same temperatures, of ammonia with silicon tetrachloride. α-Si_3N_4 is predominant in the product, which frequently contains traces of β-Si_3N_4. On one occasion, when a pellet of powdered silicon had been kept at 1400° C. for 2 days in an atmosphere of nitrogen, β-Si_3N_4 was found concentrated at the edges of the pellet. A third phase of unknown composition is sometimes produced by the same nitriding processes; the *d* values 2·43 and 2·39 Å are characteristic of this phase. Until recently, attempts to control the formation of the phases have been unsuccessful. Turkdogan, Bills & Tippett have reported the conversion of α-Si_3N_4 to β-Si_3N_4 at temperatures in the region of 1550° C., which are higher than those we have used. We have, however, now produced a number of single crystals of β-Si_3N_4 by heating pure silicon in ammonia at 1500° C. for 3 days.

Germanium nitride is formed at lower temperatures, but attempts to control the formation of its α and β phases also met with little success although, in our initial experiments, heating the metal in ammonia at

750° C. gave largely α-Ge_3N_4 whilst heating the oxide under the same conditions gave largely β-Ge_3N_4.

Structure of the β-nitrides

X-ray powder diffraction photographs of the β-nitrides, using Co $K\alpha$ radiation and a 9 cm. camera, were compared with those of Zn_2SiO_4 and Zn_2GeO_4, which are known to be phenacite-type. The resemblance was so close that no intensity calculations were made, the observed line positions being indexed in terms of a rhombohedral cell with

$$a = 8{\cdot}15 \text{ Å}, \quad \alpha = 108{\cdot}0° \quad \text{for} \quad Si_3N_4$$

and

$$a = 8{\cdot}62 \text{ Å}, \quad \alpha = 108{\cdot}0° \quad \text{for} \quad Ge_3N_4\,.$$

Bragg & Zachariasen (1930) pointed out that if both the Be and Si positions of phenacite were occupied by identical atoms the unit cell would be reduced from the rhombohedral phenacite-type cell to the related hexagonal cell of one-third the volume. The dimensions of this cell are related to those of the hexagonal pseudo-cell circumscribing the unit rhombohedron by $a = a'/\sqrt{3}$, $c = c'/3$, where a' and c' are the pseudo-cell dimensions. Such a reduction in cell size would be associated with the absence from the powder diffraction pattern of lines with $l \neq 3n$, indexed according to the large hexagonal pseudo-cell. Juza & Hahn looked for this reduction of cell size but found that they had to index many Ge_3N_4 lines with $l \neq 3n$ and attributed this to distortions from the ideal phenacite-type structure. However, all but one of these lines either belong to the other phase or can be indexed with $l = 3n$.

Our powder pattern of Ge_3N_4 was indexed with $l = 3n$ only, whilst our original powder diffraction photograph of β-Si_3N_4 showed a number of very weak lines which were indexed with $l \neq 3n$. However, the recent diffraction photographs of the single crystals show no lines with $l \neq 3n$, i.e. they can be indexed according to the smaller unit cell. They are in agreement with the recent complete structure determination of β-Si_3N_4 by Hardie & Jack (1957). The extra lines on the original photograph were due to the impurities α-Si_3N_4, Si and cristobalite (SiO_2). The lattice parameters of this cell, determined by extrapolation to $\theta = 90°$ of $1/a^2$ versus $\sin^2\theta$ for various a^2/c^2, are

$$a = 7{\cdot}606 \pm 0{\cdot}003, \quad c = 2{\cdot}909 \pm 0{\cdot}002 \text{ Å} \quad \text{for} \quad Si_3N_4$$

and

$$a = 8{\cdot}038 \pm 0{\cdot}004, \quad c = 3{\cdot}074 \pm 0{\cdot}002 \text{ Å} \quad \text{for} \quad Ge_3N_4\,.$$

Table 1 shows the comparison between calculated and observed line positions.

Structure of the α-nitrides

Table 1. *The X-ray powder diffraction patterns of the β nitrides*

The dimensions of the hexagonal unit cells are $a = 7{\cdot}606$, $c = 2{\cdot}909$ Å for Si_3N_4 and $a = 8{\cdot}038$, $c = 3{\cdot}074$ Å for Ge_3N_4

	Si_3N_4			Ge_3N_4		
hkl	d_c (Å)	d_o (Å)	I_o	d_c (Å)	d_o (Å)	I
100	6·587	6·61	*mw*	6·960	6·95	*m*
110	3·803	3·81	*w*	4·019	4·03	*m*
200	3·293	3·30	*s*	3·480	3·48	*s*
101	2·661	2·66	*m*	2·812	2·81	*vs*
210	2·490	2·50	*s*	2·631	2·62	*vs*
111	2·311	2·31	*vvw*			
201	2·180	2·18	*w*	2·304	2·31	*s*
220	1·901	1·90	*vw*	2·010	2·01	*vw*
211	1·892	1·88	*vw*			
310	1·827	1·83	*vw*	1·931	1·93	*vw*
301	1·753	1·75	*m*	1·852	1·85	*s*
221	1·592	1·59	*vw*	1·682	1·68	*w*
311	1·547	1·55	*vvw*	1·635	1·63	*w*
320	1·511	1·51	*w*	1·597	1·59	*w*
002	1·454	1·453	*w*	1·537	1·54	*w*
410	1·437	1·435	*vw*	1·519	1·514	*w*
401	1·433			1·514		
321	1·341	1·340	*m*	1·417	1·415	*m*
202	1·330	1·329	*vvw*	1·406	1·406	*vvw*
500	1·317	1·317	*vvw*	1·392	1·391	*vvw*
411	1·289	1·287	*mw*	1·362	1·359	*mw*
330	1·268	1·266	*vw*	1·340	1·339	*vvw*
212	1·256	1·254	*w*	1·327	1·324	*mw*
501	1·200	1·200	*vvw*			
510	1·183	1·183	*vvw*	1·250	1·247	*vvw*
222	1·155	1·154	*vvw*	1·221	1·218	*w*
421	1·144	1·145	*vvw*	1·209	1·208	*vw*
312	1·138	1·137	*vvw*	1·202	1·199	*vvw*
511	1·096	1·095	*vvw*	1·158	1·157	*vw*
430	1·083	1·082	*vvw*	1·144	1·143	*vw*
322	1·048	1·046	*vw*	1·107	1·106	*w*
412	1·022	1·021	*vw*	1·080	1·080	*w*
431	1·015	1·015	*vvw*			
610	1·004	1·003	*vvw*	1·062	1·061	*vw*
521	0·992	—	—	1·048	1·047	*vw*
502	0·976	0·975	*vvw*	1·032	1·031	*w*
103	0·959	0·958	*vvw*			
332	0·956	0·955	*vw*	1·010	1·009	*vvw*
611	0·950	0·949	*mw*	1·003	1·002	*mw*
700	0·941	0·941	*vvw*			
203	0·930	0·929	*vw*	0·983	0·985	*w*
512	0·918	0·917	*vvw*	0·970	0·970	*w*
620	—	—	—	0·965	0·966	*w*
213	0·904	0·903	*w*	0·955	0·955	*w*
701	—	—	—	0·946	0·946	*vvw*
303	—	—	—	0·937	0·937	*w*
710	—	—	—	0·922	0·922	*mw*

Trial structures for the α phase were looked for in which SiN_4 (or GeN_4) tetrahedra were joined by their corners in threes as in the phenacite-type structure of the β phase, by analogy with the formation of different silica and silicate structures by the linking of SiO_4 tetrahedra.

The proposed structure consists of an arrangement of SiN_4 tetrahedra in the hexagonal unit cell, the arrangement in the lower half of the cell corresponding to that of phenacite whilst in the upper half, instead of repeating this layer, tetrahedra cover spaces of the lower layer. (The relationship between this structure and the phenacite-type structure is similar to the relationship between cristobalite and tridymite.) The structure has trigonal symmetry (space group $P31c$) and, as in the phenacite-type structure, in such an arrangement of identical tetrahedra these cannot be regular, although nearly so. Hardie & Jack have indicated a similar structure for α-Si_3N_4.

The double layer of tetrahedra in this cell means that edges of the tetrahedra need not lie exactly parallel to the c axis, as they must for the single-layer, phenacite-type of structure, but may deviate from this to allow the individual tetrahedra to become more regular, with an accompanying distortion of their geometric arrangement. Such a hypothetical distortion would reduce the c dimension whilst increasing the a dimension, i.e. would give $c_\alpha < 2c_\beta$, $a_\alpha > a_\beta$. The parameters determined for the hexagonal unit cell of the α phase are

$$a = 7{\cdot}753 \pm 0{\cdot}004,\ c = 5{\cdot}618 \pm 0{\cdot}004\ \text{Å} \quad \text{for} \quad Si_3N_4$$

and

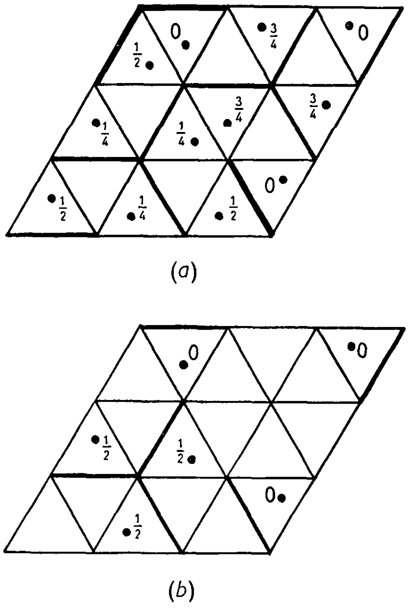
$$a = 8{\cdot}202 \pm 0{\cdot}004,\ c = 5{\cdot}941 \pm 0{\cdot}003\ \text{Å} \quad \text{for} \quad Ge_3N_4.$$

Thus the inequalities mentioned are observed in both Si_3N_4 and Ge_3N_4:

	α			β (phenacite type)	
	Si_3N_4	Ge_3N_4		Si_3N_4	Ge_3N_4
a (Å)	7·753	8·202	a (Å)	7·606	8·038
c (Å)	5·618	5·941	$2c$ (Å)	5·818	6·148
a^2c (Å^3)	337·7	399·7	$2a^2c$ (Å^3)	336·6	397·2

It may be noted that the cell volume of the α phase exceeds that of the β phase by only about ½%, giving an only slightly lower density for the α phase.

The X-ray densities of the α and β phases of Si_3N_4 are 3·18 and 3·19 g.cm.$^{-3}$ respectively. The measured density of the α phase is 3·0 g.cm.$^{-3}$. A value often quoted is 3·44 g.cm.$^{-3}$, measured by Weiss & Engelhardt in 1910. The X-ray densities of α- and β-Ge_3N_4 are 5·25 and 5·28 g.cm.$^{-3}$ respectively.



(a)

(b)

Fig. 1. Schematic diagrams of (a) α-Si_3N_4, (b) β-Si_3N_4.

To check the correctness of the proposed structure, calculations of the intensities of powder diffraction lines were made, not for the most probable atomic positions considering distortions of the tetrahedral arrangement (which are not known) but for the simplest positions, corresponding to the ideal geometric arrangement, in which all tetrahedra have one edge parallel to the c axis and one edge parallel to one of the three possible a axes. Fig. 1 (a) illustrates the structure schematically, indicating the heights of the Si (or Ge) atoms above the basal plane. Heavy lines indicate edges parallel to the basal plane of tetrahedra surrounding the silicon atoms. Nitrogen atoms lie at the corners of these tetrahedra. The corresponding diagram for the β phase, whose c axis is approximately half that of the α phase, is shown in Fig. 1(b).

Table 2. *X-ray powder diffraction patterns of the α nitrides*

The dimensions of the hexagonal unit cells are $a = 7{\cdot}753$, $c = 5{\cdot}618$ Å for Si_3N_4 and $a = 8{\cdot}202$, $c = 5{\cdot}941$ Å for Ge_3N_4. Lines hhl with l odd and lines hkl with $l = 4n+2$, $h = 3n'$, $k = 3n''$ are absent, from considerations of space group and special atomic positions. Lines hkl and $hk\bar{l}$ etc. have been combined in the table

	Si_3N_4				Ge_3N_4			
hkl	d_c (Å)	d_o (Å)	I_c	I_o	d_c (Å)	d_o (Å)	I_c	I_o
100	6·715	—	25	—	7·103	~7·04	17	*w*
101	4·308	4·32	98	*s*	4·557	~4·53	97	*s*
110	3·877	3·88	38	*mw*	4·101	4·08	31	*m*
200	3·357	3·36	18	*m*	3·552	3·54	18	*mw*
201	2·882	2·90	47	*s*	3·048	3·05	64	*vs*
002	2·809	2·82	0	*vw*	2·971	2·97	0	*w*
102	2·591	2·59	100	*s*	2·741	2·74	100	*s*
210	2·538	2·54	60	*s*	2·685	2·68	86	*vs*
211	2·313	2·32	54	*m*	2·446	2·44	87	*vs*
112	2·274	2·28	2	*vw*	2·406	—	7	—
300	2·238	2·24	7	*vw*	2·368	2·36	2	*vvw*
202	2·154	2·16	35	*mw*	2·279	2·27	62	*ms*
301	2·079	2·08	45	*m*	2·200	2·20	60	*ms*
220	1·938	1·95	1	*vvw*	2·051	2·05	2	*vw*
212	1·883	1·89	1	*vw*	1·992	1·99	2	*vw*
310	1·862	1·86	4	*vw*	1·970	1·97	4	*vw*
103	1·803	1·80	7	*vw*	1·908	1·90	7	*vw*
311	1·768	1·77	23	*w*	1·870	1·87	26	*mw*
400	1·679	—	0	—	1·776	—	0	—
203	1·635	1·63	8	*vw*	1·730	1·73	10	*vw*
401	1·608	—	0	—	1·702	—	0	—
222	1·595	1·60	31	*mw*	1·688	1·70	19	*w*
312	1·552	1·55	6	*vvw*	1·642	1·64	8	*vw*
320	1·540	1·54	4	*vvw*	1·630	1·63	4	*vvw*
213	1·507	1·51	14	*vvw*	1·594	1·59	20	*vw*
321	1·486	1·485	21	*m*	1·572	1·57	20	*m*
410	1·465	—	1	—	1·550	—	0	—
402	1·441	—	0	—	1·524	—	0	—
303	1·436	1·437	14	*mw*	1·519	1·52	17	*m*
411	1·418	1·418	27	*mw*	1·500	1·497	32	*m*
004	1·404	1·405	21	*w*	1·485	1·481	16	*vw*
104	1·375	1·377	0	*vvw*	1·454	1·451	0	*vvw*
322	1·351	1·351	23	*ms*	1·429	1·426	22	*m*
500	1·343	—	1	—	1·421	—	1	—
114	1·320	—	2	—	1·397	—	2	—
313	1·320	1·323	9	*w*	1·397	1·395	10	*w*
501	1·306	1·306	3	*vvw*	1·382	1·380	4	*vw*
412	1·299	1·298	35	*m*	1·374	1·372	23	*w*
204	1·296	—	2	—	1·370	—	2	—
330	1·292	1·293	3	*w*	1·367	1·365	7	*vw*

Table 2 (*cont.*)

	Si_3N_4				Ge_3N_4			
hkl	d_c (Å)	d_o (Å)	I_c	I_o	d_c (Å)	d_o (Å)	I_c	I_o
420	1·269	1·269	9	*vvw*	1·342	1·341	10	*vw*
403	1·250	—	0	—	1·322	—	0	—
421	1·238	1·239	8	*vw*	1·309	1·308	9	*vw*
214	1·229	1·228	14	*w*	1·300	1·298	16	*w*
502	1·212	1·211	1	*vvw*	1·282	—	1	—
510	1·206	—	3	—	1·276	1·278	3	*vvw*
304	1·190	—	0	—	1·258	—	1	—
323	1·190	1·190	12	*mw*	1·258	1·256	12	*mw*
511	1·179	1·179	10	*w*	1·247	1·247	12	*vw*
422	1·156	1·156	10	*m*	1·223	1·227	8	*m*
413	1·154		17		1·221		18	
224	1·137	—	0	—	1·203	1·201	1	*vvw*
314	1·121	1·121	2	*vvw*	1·186	1·183	1	*vw*
600	1·119	—	0	—	1·184	—	0	—
105	1·108	—	2	—	1·172	—	1	—
512	1·108	1·106	7	*vw*	1·172	1·172	8	*w*
430	1·104		4		1·168	1·168	5	*vw*
601	1·098	—	0	—	1·165	—	0	—
503	1·091	—	3	—	1·154	1·154	3	*vw*
431	1·083	1·082	1	*vvw*	1·146	1·145	3	*vvw*
404	1·077	—	0	—	1·139	—	0	—
520	1·075	1·074	2	*vvw*	1·137	1·137	1	*vvw*
205	1·066	1·065	3	*vw*	1·127	1·125	3	*vvw*
521	1·056	—	0	—	1·117	—	0	—
423	1·051	1·050	5	*w*	1·111	1·110	6	*w*
324	1·038	1·039	4	*vw*	1·098	1·097	3	*vw*
215	1·027	1·027	9	*w*	1·087	1·086	9	*mw*
432	1·027	—	1	—	1·087	—	2	—
610	1·024	—	3	—	1·033	—	8	—
513	1·014	1·014	10	*vw*	1·072	1·071	9	*vw*
414	1·014	—	1	—	1·072	—	0	—
611	1·007	1·007	10	*vvw*	1·066	1·064	9	*vw*
305	1·004	—	9	—	1·062	1·061	9	*vvw*
522	1·004	—	0	—	1·062	—	2	—
504	0·971	~0·971	2	*vvw*	1·027	—	2	—
440	0·969		8		1·025	1·025	6	*vvw*
315	0·962	0·962	9	*vw*	1·017	1·017	7	*w*
612	0·962		0		1·018		3	
603	0·961		0		1·016		0	
530	0·960		7		1·015		6	
334	0·951	0·951	32	*w*	1·006	1·006	11	*vw*
433	0·951		3		1·006		9	
531	0·946	0·946	7	*vw*	1·000	1·000	6	*vvw*
424	0·942	0·941	23	*vw*	0·996	0·994	18	*vw*
405	0·934	—	0	—	0·988	0·989	0	*vvw*
523	0·932	—	0	—	0·986	—	0	—
620	0·931	—	13	—	0·985	0·984	9	*w*
106	0·927	—	16	—	0·981		9	
621	0·919	0·918	14	*vvw*	0·972	0·972	9	*vw*
442	0·916	0·916	30	*mw*	0·969	0·969	29	*mw*
514	0·915		13		0·968		7	
116	0·910	—	0	—	0·963	—	2	—
325	0·908	0·908	33	*mw*	0·960	0·959	15	*w*
532	0·908		8		0·960	—	3	—
206	0·902	0·902	26	*vvw*	0·954	0·956	13	*vw*
613	0·898	0·898	51	*w*	0·950	0·950	15	*w*
415	—	—	—	—	0·943	0·942	28	*w*
710	—	—	—	—	0·941	—	1	—
622	—	—	—	—	0·935	0·935	14	*w*
711	—	—	—	—	0·929	0·929	32	*mw*
216	—	—	—	—	0·929	—	1	—
604	—	—	—	—	0·926	—	2	—
434	—	—	—	—	0·918	0·918	21	*vw*
505	—	—	—	—	0·911	0·912	8	*vvw*
540	—	—	—	—	0·910	0·909	13	*vw*
533	—	—	—	—	0·903	0·903	20	*vw*
541	—	—	—	—	0·899	—	12	—

The simplified atomic positions can be written, in terms of the positions

(*a*) $0, 0, z;\ 0, 0, \frac{1}{2}+z;$
(*b*) $\frac{1}{3}, \frac{2}{3}, z;\ \frac{2}{3}, \frac{1}{3}, \frac{1}{2}+z;$
(*c*) $x, y, z;\ \bar{y}, x-y, z;\ y-x, \bar{x}, z;$
$y, x, \frac{1}{2}+z;\ \bar{x}, y-x, \frac{1}{2}+z;\ x-y, \bar{y}, \frac{1}{2}+z$

of the space group *P*31*c* as:

$2N_{I}$ in (*a*) with $z = 0$;
$2N_{II}$ in (*b*) with $z = \frac{3}{4}$;
$6N_{III}$ in (*c*) with $x = \frac{1}{3},\ y = 0,\ z = 0$;
$6N_{IV}$ in (*c*) with $x = \frac{1}{3},\ y = \frac{1}{3},\ z = \frac{1}{4}$;
$6Si_{I}$ in (*c*) with $x = \frac{1}{2},\ y = \frac{1}{12},\ z = \frac{1}{4}$;
$6Si_{II}$ in (*c*) with $x = \frac{1}{6},\ y = \frac{1}{4},\ z = 0$.

The extent of the agreement between calculated and visually observed X-ray line intensities (shown in Table 2 for both Si_3N_4 and Ge_3N_4) is considered sufficient to confirm the proposed structure whilst illustrating the necessity of refinement. The observation of a 002 reflexion indicates a deviation of the atoms from the heights 0, $\frac{1}{4}$. .

Conclusions

The nitrides of silicon and germanium occur in two polymorphic forms of composition M_3N_4, which are generally found mixed. The structure of the β phases is of the phenacite (Be_2SiO_4) type with the unit cell reduced to the smaller hexagonal one on account of the substitution of like atoms for Be and Si. The structure proposed for the α phases is related to that of phenacite, one layer of phenacite type alternating with another similar but differently oriented layer in a hexagonal cell. A third phase is sometimes formed whose composition is not known but, if it were a nitride of composition M_3N_4, it might perhaps be related to the α and β phases by a different stacking sequence of phenacite-type layers.

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