Letters

The crystal structures of $CeSiO_2N$ and $LaSiO_2N$

In a recent note in this journal [1], the X-ray powder diffraction pattern of "$3Ce_2O_3 \cdot 2Si_3N_4$" was presented, with the conclusion that the substance was orthorhombic: $a = 7.257$ Å, $b = 9.460$ Å, $c = 4.184$ Å*. It is apparent that the substance is actually $CeSiO_2N$, pseudo-hexagonal with $a = 7.256$ Å, $c = 9.459$ Å.

The crystal has the α-$CaSiO_3$ pseudo-wollastonite structure, as does $YSiO_2N$ [2]. Earlier patterns in the La–Si–O–N system were published [3] which contain the compound $LaSiO_2N$ mixed with other phases [2]. Table I gives the measured and calculated d values and intensities for this structure for both $CeSiO_2N$ and $LaSiO_2N$. Table II gives the approximate atom positions used in the computer intensity calculation [4]. We note that in $CeSiO_2N$, cerium is trivalent. If cerium were tetravalent then, nominally, $CeSiON_2$ is possible with the same large cation:small cation:anion ratios. Thus a solid solution, $Ce^{3+}_{1-x}Ce^{4+}_{x}SiO_{2-x}N_{1+x}$, may occur. In $CeSiO_2N$ the bond strength (Pauling's second crystal rule) arriving at nitrogen is 2–3/4, at oxygen 2–1/8 [2]. In "$CeSiON_2$" half of the nitrogens would receive a bond strength of 3 while the other half would receive 2–1/2, as would oxygen. This would be a more unstable condition so that the range of x is probably quite small.

TABLE II, Atom positions used in intensity calculation

Ce(or La)	O
0, 0, 0	0.666, 0.015, 0.082 & 0.418
0, 0, 1/2	0.318, 0.318, 0.082 & 0.418
1/3, 2/3, 0	0.015, 0.666, 0.082 & 0.418
1/3, 2/3, 1/2	0.652, 0.666, 0.582 & 0.918
2/3, 1/3, 0	0.000, 0.318, 0.582 & 0.918
2/3, 1/3, 1/2	0.349, 0.015, 0.582 & 0.918
Si	N
0.666, 0.935, 0.250	0.666, 0.463, 0.250
0.398, 0.398, 0.250	0.870, 0.870, 0.250
0.935, 0.666, 0.250	0.463, 0.666, 0.250
0.732, 0.666, 0.750	0.204, 0.666, 0.750
0.000, 0.398, 0.750	0.000, 0.870, 0.750
0.269, 0.935, 0.750	0.797, 0.463, 0.750

TABLE I

$LaSiO_2N$					$CeSiO_2N$				
hkl	d_0	d_c	I_0 [3]	I_c	hkl	d_0	d_c	I_0 [1]	I_c
0 0 2	4.81	4.78	17	37	0 0 2	4.733	4.729	27	37
1 1 0	3.65	3.655	84	62	1 1 0	3.630	3.628	79	63
1 1 1	3.41	3.413	14	10	1 1 1	3.383	3.387	11	10
1 1 2	2.90	2.902	100	100	1 1 2	2.882	2.879	100	100
0 0 4	2.381	2.388	18	14	0 0 4	2.366	2.365	17	14
0 30	2.110	2.110	43	37	0 3 0	2.094	2.094	39	37
1 1 4	1.996	1.999	31	35	1 1 4	1.981	1.981	26	35
0 3 2	1.928	1.930	30	32	0 3 2	1.915	1.915	26	32
2 2 0	1.826	1.827	15	9	2 2 0	1.814	1.814	15	10
2 2 2	1.708	1.707	15	21	2 2 2	1.695	1.694	12	21
0 3 4	1.584	1.581	8	17	0 3 4	1.564	1.568	10	17
1 1 6	1.447	1.459	14	17	1 1 6	1.442	1.445	18	17
2 2 4		1.451		12	2 2 4		1.439		12
					1 4 0	1.370	1.371	8	8
					1 4 2	1.317	1.317	14	19

$LaSiO_2N$	$CeSiO_2N$
pseudo-hexagonal $R = 0.25$	pseudo-hexagonal $R = 0.21$
$a = 7.31$ Å	$a = 7.256$ Å
$c = 9.55$ Å	$c = 9.459$ Å

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* These axes are, in fact, orthohexagonal with $a = \sqrt{3}c$

References

1. R. R. WILLS and J. A. CUNNINGHAM, *J. Mater. Sci.* 12 (1977) 208.
2. P. E. D. MORGAN, P. J. CARROLL and F. F. LANGE, *Mat. Res. Bull.* 12 (1977) 251.
3. R. R. WILLS, R. W. STEWART, J. A. CUNNINGHAM and J. M. WIMMER, *J. Mater. Sci.* 11 (1976) 749.
4. K. YVON, W. JEITSCHKO and E. PARTHE, Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia (1969).

Received and accepted 2 February 1977.

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Comments on "Silicon cerium oxynitride"

Wills and Cunningham [1] report the existence of a new phase in the silicon–cerium–oxygen–nitrogen system obtained by reacting together 3 : 1 molecular proportions of CeO_2 and Si_3N_4 at 1550° C. They indexed the X-ray diffraction pattern of this phase on the basis of an orthorhombic cell with dimensions

$$a = 7.257, \quad b = 9.460, \quad c = 4.184\,\text{Å},$$

but were unable to correlate it with any known silicate crystal structure.

Two points are apparent from the indexing proposed by Wills and Cunningham. Firstly the sum of h and l indices for each line is even (except for 3 1 2 which has the alternative indexing 3 4 1); and secondly, the a/c ratio (1.734) is exactly $\sqrt{3}$. These observations show that the pattern can be reindexed on a simpler hexagonal cell with

$$a_\text{H} = b_\text{H} = c_\text{O} = 4.184\,\text{Å},$$
$$c_\text{H} = b_\text{O} = 9.460\,\text{Å}$$

where H and O refer to hexagonal and orthorhombic respectively.

When indexed in this way (Table I) the unit cell is similar to those of the rare-earth borates [2, 3] and aluminates [4] and can be related to the group of 3-membered ring silicates [5, 6]. All these structures have a characteristic formula of the type ABO_3, where A is a rare-earth metal and B is a small network-forming cation (B, Al, Si). It is noteworthy that the formula proposed by Wills and Cunningham [1], $3Ce_2O_3 \cdot 2Si_3N_4$ or $SeCeO_{1.5}N_{1.33}$ which was derived on the assumption that oxygen was the non-metallic species lost during the $Ce^{IV} \rightarrow Ce^{III}$ transformation reduces to an $AB(O, N)_3$-type formula, $CeSiO_2N$, if nitrogen is lost in place of oxygen. This is in fact extremely likely in these type of reactions.

A similar compound, $YSiO_2N$, has recently been reported by Rae [7] and Lange *et al.* [8]. This compound has the structure of α-wollastonite (3-membered rings) with a monoclinic unit cell related to a simpler hexagonal pseudocell of dimensions

TABLE I Alternative indexing of the diffraction pattern for "$3Ce_2O_3 \cdot 2Si_3N_4$"

d_obs	I_obs	d_calc	$hkl_\text{W\&C}$	hkl_DPT
4.733	27	4.730	0 2 0	0 0 2
3.630	79	3.628	1 0 1, 2 0 0	1 0 0
3.383	11	3.387	1 1 1, 2 1 0	1 0 1
2.882	100	2.879	1 2 1, 2 2 0	1 0 2
2.366	17	2.365	0 4 0	0 0 4
2.094	39	2.095	0 0 2, 3 0 1	1 1 0
1.981	26	1.981	1 4 1, 2 4 0	1 0 4
1.915	26	1.915	0 2 2, 3 2 1	1 1 2
1.814	15	1.814	2 0 2, 4 0 0	2 0 0
1.695	12	1.694	2 2 2, 4 2 0	2 0 2
1.573	7	1.572	2 3 2, 4 3 0	2 0 3
1.564	10	1.568	3 1 2, 3 4 1	1 1 4
1.442	18	1.446, 1.439	4 4 0, 2 6 0, 1 6 1	1 0 6, 2 0 4
1.370	8	1.371	1 0 3, 4 0 2, 5 0 1	2 1 0
1.317	14	1.317	1 2 3, 4 2 2, 5 2 1	2 1 2

Orthorhombic: $a = 7.257, b = 9.460, c = 4.184$ Å. Hexagonal: $a = 4.189, c = 9.460$ Å.