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P. E. D. MORGAN
Metallurgy and Materials Engineering,
University of Pittsburgh,
Pittsburgh, USA
P. J. CARROLL
Department of Chemistry,
Temple University
Philadelphia, USA

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.

by

$$a_{\mathrm{H}} = 4.05, \quad c_{\mathrm{H}} = 9.10\,\text{Å}$$

$$a_{\mathrm{M}} = \sqrt{3a_{\mathrm{H}}}, \quad b_{\mathrm{M}} = 3a_{\mathrm{H}},$$

$$c_{\mathrm{M}} = 2c_{\mathrm{H}}, \quad \beta \sim 90^\circ$$

The distortion from hexagonal in $\mathrm{YSiO_2N}$ is so slight that on X-ray powder photographs the superlattice reflextions are extremely weak, and the splitting of $hk0$ lines is only apparent at high Bragg angles. It is therefore very probable that the new cerium compound has this larger monoclinic cell. In fact the $c_{\mathrm{H}}/a_{\mathrm{H}}$ ratios for the yttrium and cerium compounds are in very good agreement (2.252 and 2.259 respectively).

On the basis of the foregoing chemical, structural and crystallographic evidence, it is concluded that the silicon cerium oxynitride phase reported by Wills and Cunningham has the formula $\mathrm{CeSiO_2N}$, with a monoclinic unit cell of dimensions:

$$a = 7.26, \quad b = 12.57, \quad c = 18.93\,\text{Å}; \beta \sim 90^\circ$$

and a crystal structure of the 3-membered ring type similar to α-wollastonite.

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D. P. THOMPSON
The Wolfson Research Group for
High-strength Materials,
Crystallography Laboratory,
The University,
Newcastle-upon-Tyne, UK

Reply to "Comments on 'Silicon cerium oxynitride'"

Our designation of the compound as "$\mathrm{3Ce_2O_3 \cdot 2Si_3N_4}$" was intended only to indicate the approximate composition of this phase. As Dr. Thompson [1] has mentioned this formula can be written as $\mathrm{SiCeO_{1.5}N_{1.33}}$, which is very close to the true composition $\mathrm{SiCeO_2N}$. It is apparent that we may have misindexed the pattern but the true indexing is certainly not known at this time. The possibility of a monoclinic cell seems most likely as it would concur with findings for a similar compound, $\mathrm{YSiO_2N}$, and explain why Morgan and Carroll [2] obtain such high R factors in their studies.

Morgan and Carroll [2] have suggested that the diffraction patterns for the silicon lanthanide oxynitrides were due to mixtures containing $\mathrm{LaSiO_2N}$. This is incorrect. The compound designated "$\mathrm{2Si_3N_4 \cdot La_2O_3}$" was the only one which we were uncertain of the true composition. Although its diffraction pattern certainly contains some of the d spacings given for the $\mathrm{LaSiO_2N}$ the compositions of these two oxynitrides ($\mathrm{2Si_3N_4 \cdot La_2O_3}$ and $\mathrm{Si_3N_4 \cdot SiO_2 \cdot 2La_2O_3}$) are grossly different. Furthermore, there is no practical evidence as yet for existence of "$\mathrm{LaSiO_2N}$."

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R. R. WILLS
Batelle Columbus Laboratories,
Columbus, Ohio, USA
J. A. CUNNINGHAM
Air Force Materials Laboratory,
Wright-Patterson Air Force Base,
Ohio, USA