The silicon-cerium-oxynitride $Ce_5(SiO_4)_3N$ with fluorapatite structure

The existence of a new group of silicon lanthanide oxynitrides of the general formula $Ln_{10}Si_6O_{24}N_2$ (Ln = La, Nd, Sm and Gd) has been proposed by Hamon *et al.* [1] who reported that these rare-earth sesquioxides form oxynitrides with structures based on the hexagonal fluorapatite $Ca_5(PO_4)_3F$ and thus can be represented by the formula $Ln_5(SiO_4)_3N$. Mitomo *et al.* [2] have also prepared the compound $La_{10}Si_6O_{24}N_2$ and indexed the X-ray powder diffraction pattern of the compound with *hkl* indices that are the same as for fluorapatite. A yttrium analogue $Y_{10}Si_6O_{24}N_2$ which was first identified by Rae *et al.* [3] and later confirmed by Wills *et al.* [4] also has a hexagonal structure similar to that of the fluorapatite. The purpose of the present communication is to show that a silicon cerium oxynitride exists in the pseudoternary system Si_3N_4–SiO_2–Ce_2O_3 and its X-ray powder diffraction pattern bears a close resemblance to those of the lanthanide and yttrium analogues with fluorapatite structure and thus may be represented by the formula $Ce_5(SiO_4)_3N$.

The existence of a compound with the probable composition of $Ce_{10}Si_6O_{24}N_2$ was first observed when a number of hot-pressed Si_3N_4 samples containing variable proportions of CeO_2 were analysed by X-ray powder diffraction. The compound was subsequently prepared as a single-phase material using high-purity Si_3N_4 (Ventron Corporation, USA), SiO_2 (Pierce Chm. Products, USA) and Ce_2O_3 (obtained by reduction of CeO_2 at 1300° C). Identical samples containing the powder materials in the molar ratio of $10Ce_2O_3$:$9SiO_2$:Si_3N_4 were pressed into pellets which were supported on a bed of boron nitride and heated at temperatures between 1400 and 1550° C in a stream of pure nitrogen with intermittent cooling, crushing and pressing to promote homogeniety and to attain equilibrium. At the end of the firing, the pellets were cooled inside the furnace and the product obtained was analysed by X-ray powder diffraction using CuK_α radiation. The indexing of the powder pattern for the compound was accomplished by a combination of Ito's technique and the computerized version of Visser [5]. The final lattice parameters were ascertained by the least-square refinement of the powder data. The apparant density of the powder samples was determined by pycnometric method using ethyl alcohol as the immersion liquid and the average value obtained from three separate determinations was compared with the calculated density value.

TABLE I X-ray powder diffraction data for $Ce_{10}Si_6O_{24}N_2^*$

I/I_0	$d_{obs.}$	$d_{calc.}$	$h\ k\ l$
5	4.83	4.824	1 1 0
15	4.179	4.178	2 0 0
12	4.005	4.004	1 1 1
8	3.590	3.590	0 0 2
45	3.300	3.299	1 0 2
40	3.159	3.158	2 1 0
100	2.890	2.891	2 1 1
35	2.783	2.785	3 0 0
3	2.721	2.723	2 0 2
2	2.411	2.412	2 2 0
5	2.316	2.316	3 1 0
2	2.284	2.286	2 2 1
6	2.200	2.200	3 0 2
10	2.145	2.144	1 1 3
5	2.088	2.089	4 0 0
45	2.003	2.002	2 2 2
12	1.946	1.947	3 1 2
10	1.915	1.917	3 2 0
40	1.908	1.907	2 1 3
12	1.851	1.852	3 2 1
20	1.822	1.823	4 1 0
40	1.803	1.805	4 0 2
20	1.795	1.795	0 0 4
2	1.698	1.699	2 2 3
2	1.683	1.682	1 1 4
3	1.649	1.649	2 0 4
2	1.624	1.625	4 1 2
3	1.579	1.579	4 2 0
5	1.567	1.569	3 3 1
6	1.561	1.560	2 1 4
10	1.510	1.509	3 0 4
5	1.495	1.495	3 2 3
8	1.466	1.467	3 3 2
2	1.416	1.415	1 0 5
2	1.385	1.384	5 1 2
2	1.374	1.374	4 3 0
2	1.360	1.361	4 0 4
3	1.334	1.334	3 3 3
7	1.308	1.307	2 1 5
3	1.296	1.298	6 0 2
12	1.278	1.279	4 1 4
5	1.271	1.271	5 1 3
8	1.252	1.253	5 2 2
4	1.203	1.203	6 0 3

* Hexagonal: $a = 9.649$ Å and $c = 7.181$ Å

The X-ray powder diffraction data for the compound $Ce_{10}Si_6O_{24}N_2$ together with the relative intensities are given in Table I. The data have been indexed on the basis of a hexagonal unit-cell with

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dimensions: $a = 9.649$ Å and $c = 7.181$ Å. The indexing gives a unit-cell volume of 579 Å^3 and with the number of molecules per unit cell $z = 2$, a calculated density value of $5.68\,\mathrm{g\,cm^{-3}}$ was obtained which is in good agreement with the experimental density value of $5.61\,\mathrm{g\,cm^{-3}}$.

The cell parameters proposed for the compound $Ce_{10}Si_6O_{24}N_2$ are found to be close to the values for the analogous silicon lanthanide oxynitride [1] and silicon yttrium oxynitride [4]. As can be expected, the lattice parameter values show an increasing trend with increasing "ionic" radii of the rare-earth cation Ln^{3+} and Y^{3+}. It is noteworthy that a cerium oxysilico–apatite having a formula of $Ce_{4.67}(SiO_4)_3O$ which occurs in the pseudobinary join SiO_2–Ce_2O_3 has a fluorapatite structure [6] similar to that of the nitrogen-containing apatite phase $Ce_5(SiO_4)_3N$ reported here and thus the X-ray diffraction pattern for one could be easily mistaken for the other. The nature and characteristics of various apatite-type phases in the system Ce–Si–O–N and compatibility relations between them will be described in detail in a separate publication.

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On the adsorption processes in the selective etching of MgO and CaF$_2$ crystals

In a detailed study of the etching of LiF, Gilman *et al.* [1] found trivalent cations in water to be effective agents in the formation of etch pits at dislocation sites. It was suggested that these cations chemisorb at kink sites in a ledge and thus inhibit its motion. Since their work, many observations [2–4] of the etching phenomenon have been reported on alkali halides, which indicate that the inhibition process is not simple chemisorption. Etchants of semiconductors and metals are still more complicated and, consequently, are less suited for the study of the mechanism of adsorption and etch-pit formation. Etchants of periclase, fluorites and barytes are aqueous acidic solutions and hence etching studies on these crystals may be hoped to provide considerably fruitful information on the dissolution process.

In the present communication the adsorption process taking place on MgO and CaF_2 crystals is analysed from a study of the dependence of selective etch rates on the concentration and temperature of HCl. Etching was conducted on $\{1\,0\,0\}$ faces of MgO and $\{1\,1\,1\}$ faces of CaF_2 crystals in the temperature range 20 to 80° C. The rate of lateral etching, v_t, at dislocations in MgO was determined using the procedure employed earlier [5]. In the case of CaF_2, the rate was computed from the distance between a side and the opposite corner of a triangular etch pit, and from the distance between the opposite sides of a hexagonal pit.

The dependence of v_t on concentration, c, at different etchant temperature is shown in Figs. 1 and 2 for MgO and CaF_2 crystals, respectively. It may be noted from these figures that v_t attains a maximum value, v_{max}, and then decreases with a further increase in c. The values of v_{max} and c_{max} depend on the nature of the acid (Fig. 2), the crystal, and on the etching temperature. The value of c_{max} decreases with an increase in etching temperature.

It was also observed that the etch-pit mor-

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