structural units, elongated perpendicular to the draw direction, are the features responsible for the four-lobed pattern at low aximuthal angle.

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Comments on "New compound in the system La–Si–O–N"

In a recent note [1], the "discovery" of the apatite phase $La_5(SiO_4)_3N$ was disclosed. Not, unfortunately, for the first time, as a variety of rare earth nitrogen apatites have been announced before [2]. It is considered that the authors are mistaken in suggesting that the formula $La_5(SiO_4)_3N$ should be thus written to show the similarity to the isotypic $Ca_5(PO_4)_3F$. It can readily be shown that the site occupied by F in fluorapatite is a low bonded site (with a valence sum of 1 by Pauling's second crystal rule) which is why the crystal is stable with F (or (OH) or Cl) in this position. The equivalent site in $La_5(SiO_4)_3N$ has a valence bond sum of 1.29 to 1.50, depending on the exact method of calculation [3]. Sites in the silicon tetrahedra have values or 2.33 to 2.60, again depending slightly on method of calculation. Recent work [4, 5] has shown that bond sum calculation in oxides (and by extension oxynitrides) can be made rather exact, for example, they work precisely in apatites [3] but lacking accurate bond-length/bond-strength values for M–N bonds we can only use approximate Pauling type values. Nevertheless, it is clear that the N atoms in these apatites *all* go to the silicon tetrahedra sites. Oxygen* or vacancies are to found at the F sites and vacancies at the low bonded sites can, of course, readily explain the excess of nitrogen atoms at the silicon tetrahedra sites and, indeed, stabilize the structure. Limiting cases would be represented by the formulae:

$$La_5(SiO_{3.67}N_{0.33})_3O–La_5(SiO_3N)_3\square$$

The formula type given by the authors is not based upon normal crystallographic rules as understood to apply in the multitude of substituted mineral structures that have been studied.

The citation of Morgan [6] implies that the compound had been overlooked in that work; in fact we knew of reference [2]. Our study was concerned with the crystallography of $CeSiO_2N$ using, not results obtained by us, but taking the data of Wills *et al.* [7]. We suggested [6] that $LaSiO_2N$ existed and was present in the X-ray data of [8]; in addition an examination of the X-ray patterns in [8], those of "$Si_3N_4 \cdot La_2O_3$" and "$La_4Si_2O_7N_2$", suggests that, not only was $LaSiO_2N$ present in the seeming mixtures [6], but also many of the *d*-values of the apatite "$La_5(SiO_4)_3N$" as published in [1] appear, so that the compound under discussion was also present.

*Several rare earth mineral apatites with O at the low bonded sites are well known.

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Reply to 'Comments on "New compound in the system La–Si–O–N"'

Our claim to finding a new compound [1] was incorrect, although a preceding report [2] was not available to us. Our work on the present compound was to show that $La_5(SiO_4)_3N$ was formed by the reaction of Si_3N_4 and La_3O_3 despite a high oxygen content in the compound. It is likely that N atoms substitute O atoms in SiO_4 tetrahedra as suggested by Morgan [3], although the problem of the site and degree of substitution might require further work.

We have no evidence to show that "$Si_3N_4 \cdot La_2O_3$" and "$La_4Si_2O_7N_2$" phases published by Wills *et al.* [4] were not single phase, but contain $LaSiO_2N$ or apatite. The presence of Morgan's $LaSiO_2N$ phase [5] is unlikely, because we could not form the phase at any region in the Si_3N_4–SiO_2–La_2O_3 system.

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