

consolidated by heat treatment. A special aspect of Si_3N_4 processing is the use of both phase types: when α powder is used, it converts during heat treatment to the β form to yield the acicular crystal morphology.

The application in which Si_3N_4 has been most successfully exploited is for cutting tools which make use of its hardness and resilience. In this area, attention has turned to the so-called sialons³, which are based on silicon nitride (both α and β types) but in which substitutions of aluminium and oxygen are made respectively on the silicon and nitrogen sublattices. As well as providing a basis for wide-ranging and subtle use of additive elements, the sialons have opened doors to a greater range of properties, including improved hardness and resistance to corrosion.

The original objective of using Si_3N_4 to produce engine components for operation at high temperatures and pressures has not yet been reached. Despite the 'ceramic fever', during which intensive international effort was expended for more than a decade, the current high-profile use of Si_3N_4 in engines is limited to valves. Moreover, the use of Si_3N_4 in failure-critical components in aircraft continues to be ruled out by their susceptibility to brittle fracture, namely the risk of sudden and total failure under impact as a result of some small — fractions of a mil-

limetre — processing flaw within a component.

So what of the new form that has been identified by Zerr *et al.*¹? The 'spinel' form of Si_3N_4 that results from high-pressure fabrication (15 gigapascals at temperatures over 2,000 K) offers several avenues of interest. The first is the structure (Fig. 1b). In the spinel system, the nitrogen anions adopt a close-packed, cubic crystal structure, and the silicon cations occupy spaces in the lattice between the anions. The silicon cations are arranged in an unusual two-sublattice system, with two-thirds of the cations surrounded by six anions (an octahedral array) and one-third surrounded by four anions (a tetrahedral array).

In contrast to the other forms of Si_3N_4 , the structure of cubic Si_3N_4 is more dense, stiffer and with every expectation of being considerably harder, perhaps even as hard as stishovite (the third hardest material after diamond and cubic boron nitride). Most surprising is the existence of silicon in an octahedral sublattice. The higher-density spinel structure results from using high pressures during fabrication, as predicted by Le Chatelier's principle, which says that if a system in chemical equilibrium is disturbed, it will react in a way that tries to neutralize the disturbance and restore the equilibrium. But a key benefit is that, once the pressure is removed, the material survives in a metastable state and is, indeed, stable to at least 700 K.

In areas where hardness and wear resistance are required (such as cutting tools), the new spinel structure offers advantages over current Si_3N_4 phases. The work by Zerr *et al.*¹ also demonstrates particularly well the trend in materials science, where experimental studies and theoretical studies march closely in step and with mutual benefit. Their theoretical calculations throw light both on why the high-density form of Si_3N_4 should be spinel and on the stiffness and hardness of the new material.

The quest for ever more reliable processing methods has had several consequences. In seeking to avoid the presence of any flaws, greater attention has been given to precursor materials that are themselves free of flaws. This demands new techniques for producing advanced ceramics. Sol-gel processing for oxides⁴, in which small particles in a liquid suspension are converted into an amorphous solid, and polymer precursors for non-oxides⁵ are just two examples. It can be expected that following these avenues will lead to a remarkable array of metastable intermediate structures. Heat treatment of polymer precursors, for example, provides an accessible route to compounds containing silicon, nitrogen, carbon or boron, where amorphous structures of remarkable resilience have already been identified. In this sense, the finding of the new cubic sili-

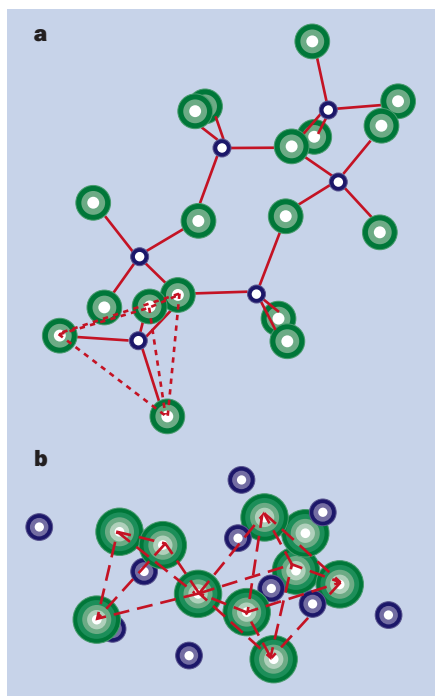


Figure 1 Phases of silicon nitride, showing the silicon atoms in purple and the nitrogen atoms in green. a, In the β form of Si_3N_4 , the relatively open packing of the nitrogen results from the corner-sharing tetrahedra, one of which is outlined. b, In the new cubic form of Si_3N_4 created by Zerr *et al.*¹, the nitrogen is close packed and silicon occurs in both tetrahedral (shown on the left) and octahedral (shown on the right) surroundings.



100 YEARS AGO

So far as the details of practical cultivation are concerned, we are not so much in advance of our forefathers. We have infinitely greater advantages, and we have made use of them, but if they had had them they would have done the same. We are able to bring to bear on our art not only the "resources of civilization" to a degree impossible to our predecessors, but we can avail ourselves also of the teachings of science and endeavour to apply them for the benefit of practical gardening. We are mere infants in this matter at present, and we can only dimly perceive the enormous strides that gardening will make when more fully guided and directed by scientific investigations. One object of this conference is to show that cultural excellence by itself will not secure progress, and to forward this progress by discussing the subject of cross-breeding and hybridisation in all their degrees, alike in their practical and in their scientific aspects. To appreciate the importance of cross-breeding and hybridisation we have only to look round our gardens and our exhibition-tents, or to scan the catalogues of our nurserymen.

From *Nature* 20 July 1899.

50 YEARS AGO

To find a principle common to a science of physics which, according to some thinkers, is nearing completion, and a science of psychology which, according to all, has scarcely begun, is inevitably to put oneself in the company of the dialectical materialists, the kinematical relativists and others, whose universal, fundamental principles of Nature are alike seductive and baseless and are further alike in being all incompatible with one another. If one likes that kind of thing, one can take a choice between the principle that all things generate their contraries with which they then identify themselves, the principle that all experience must be expressible in terms of intuitive apprehension of the passage of time ... and any other principle that one can think of. I know no way of choosing between them; it seems to depend on which siren's voice sounds the sweetest. I can only recommend, in the strongest possible terms, a liberal use of wax and straps.

From *Nature* 23 July 1949.