

Combined infra-red and X-ray studies of β -silicon nitride and β' -sialons

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Previous investigations of the replacement of silicon by aluminium and nitrogen by oxygen in β -silicon nitride have been based primarily on X-ray powder diffraction studies. In the present work this technique is coupled with parallel infra-red studies. X-ray analyses of sialons over a wide composition range confirm previous observations that increasing substitution of aluminium for silicon and nitrogen for oxygen in β -silicon nitride is accompanied by an increase in cell size, with no evidence of any other structural modification. Parallel infra-red analyses show shifts in certain of the infra-red absorption bands to lower wavenumbers as the degree of substitution increases. Changes in the infra-red spectra at the composition $\text{Si}_2\text{Al}_4\text{N}_4\text{O}_4$ indicate structural modifications which are not apparent from the X-ray investigations. It is suggested that these changes are a result of the ordering of the different atom types at this composition.

1. Introduction

1.1. The β' -sialons

A number of workers [1–3] have shown that β -silicon nitride can take into solid solution relatively large amounts of aluminium and oxygen. The accepted composition (first reported by Lumby [2]) for the series of solid solutions is $\text{Si}_{6-z}\text{Al}_z\text{N}_{8-z}\text{O}_z$ and the solubility limit is given by Jack [1] as $z \sim 4.2$. These solid solutions form part of a wide ranging group of materials called sialons (after Jack) which have as their basic structural unit the $(\text{Si,Al})(\text{O,N})_4$ tetrahedron.

A large proportion of the data which have been reported on these systems is based on X-ray powder diffraction studies. Such studies, whilst providing important and detailed information, have certain limitations. For example, using standard X-ray powder diffraction techniques it is only possible to detect the presence of crystalline phases, so that the formation of an undetected glassy phase can lead to errors in the estimation of the composition of the crystalline phase. The substitution of aluminium for silicon, and oxygen

for nitrogen in β -silicon nitride produces an increase in the hexagonal unit-cell dimensions [1], but there is no evidence of any other type of structural change such as lowering of symmetry due to either order or anisotropic cell distortion.

It was considered by the present authors that infra-red absorption studies of β -silicon nitride and β' -sialons may not only complement the existing X-ray data but may also provide information, not apparent from X-ray studies, of any structural changes occurring in the substituted phase. Also, as infra-red absorption studies will detect the presence of glassy phases it was thought that the formation of such phases would be clearly indicated.

1.2. Infra-red spectra of crystalline solids

The infra-red spectrum of a crystal is determined in the main by the symmetry properties of the crystal and the geometrical character of the vibrations involved. The normal modes of vibration of an extended crystal lattice comprise low frequency acoustic modes and high frequency optical

modes. The optical vibrations, which are of interest in the present work, are relative displacements of the atoms within a unit cell, whereas the acoustic modes arise from translatory movements of the individual cells. Thus in the optical case the deformations of the unit cell are independent of each other and produce absorption of radiation at discrete frequencies.

For a discrete polyatomic ion or a discrete molecule the number and type of vibrations of the atoms is dictated by the symmetry of the point group. When such a group is built into a crystal lattice having a lower degree of symmetry some of the degenerate normal modes may be split, but the vibrational spectrum can still be interpreted in terms of the vibrations of the original unit. This approach is only valid, however, where the unit remains in the structure as a discrete strongly bonded unit. Where the atoms in the group are coordinated to other atoms in the structure to produce a continuously bonded solid such as silicon nitride, then a more general approach, that of factor group analysis, is required (see [4]). Factor group analysis gives the number of bands expected in the spectrum of a structure and the selection rules, i.e. whether the vibrations are active or inactive in the infra-red and Raman. Thus, two solids which are isostructural should exhibit the same number of absorption bands in the infra-red. Group theoretical analysis however makes no statement of either frequency or intensity of absorption bands, therefore the pattern of absorption bands for the two isostructural materials will not necessarily be identical.

TABLE I

Type of substitution	Expected spectral behaviour
Random	No new bands. Frequency shifts
Ordering on non-equivalent sites	No new bands. Frequency shifts
Ordering on equivalent sites	New bands. Frequency shifts

1.3. The effects of ordering on the infra-red spectra of solids

According to White [5], if atoms of one type on a given crystallographic site within a crystal are substituted randomly by atoms of another type then each position is occupied by an average atom whose mass, X-ray scattering factor and force constants are weighted averages of the two atom types. No

rotational symmetry is lost, there is no change in the space group symmetry and therefore no change in the number of infra-red and Raman bands. If, however, the substituted atoms take on special positions in the sub-lattice this systematic arrangement of atoms will result in a loss of rotational symmetry because all symmetry elements which exchange atoms in adjacent sites no longer exist. Different types of ordering might be expected to have different effects on the absorption spectrum (Table I).

This approach is, however, not universally applicable to all systems and there are a considerable number of examples of solid solutions which do not conform to the factor group analysis. Although it is not possible to predict the detailed changes in infra-red spectra that will occur due to the effects of ordering, it is clear that ordering will produce significant modifications in the spectra.

2. Experimental techniques

2.1. Preparation of silicon and germanium nitrides and β' -sialons

β -silicon nitride was prepared by reacting silicon powder with nitrogen in an alumina tube furnace for 2 h at 1350° C followed by 16 h at 1500° C. β -germanium nitride was produced by reaction of ammonia with germanium dioxide powder at 800° C.

The β' -sialons were kindly supplied by Dr J. Lumby of Joseph Lucas Ltd., and Professor K. H. Jack of the Department of Metallurgy and Engineering Materials, University of Newcastle-upon-Tyne. They were prepared by hot pressing, at temperatures between 1700 and 1800° C, three component mixtures of the compounds AlN, Al₂O₃, SiO₂ and Si₃N₄ in the appropriate proportions to give β' -sialons of the required compositions. The z-values of the reacted samples estimated from the composition of the starting materials ranged from 0.5 to 4.5. Most specimens showed little or no evidence from either X-ray or infra-red analysis of any impurity phases. Small amounts of α -alumina, 8H, and 15R (see [1]) were present in specimens of high z, and in particular the specimen z = 4.5 contained a substantial proportion (~ 40%) of 8H. Although there was no evidence from the infra-red spectra of any glassy phase, the broadness of the infra-red absorption bands, especially at high z-values, make it impossible to detect small amounts of vitreous material.

2.2. X-ray and infra-red measurements

Routine X-ray powder diffraction work was carried out on a Raymax RX 3D generator using a 9 cm powder camera and CrK α radiation. This technique was found inadequate for obtaining very accurate unit cell dimensions. The latter were therefore determined using a 19 cm powder camera.

Samples for infra-red analysis were in the form of 13 mm diameter disks produced by pressing an intimate mixture of 0.001 g of powdered sample and 0.25 g CsI.

Infra-red spectra were recorded on a Perkin-Elmer 457 Spectrophotometer. The positions of the infra-red absorption bands were measured on a Perkin-Elmer 580 Infra-red Spectrophotometer. Repeat scans were carried out on each individual absorption peak using a vertical scale expansion of up to 10 \times and the positions of the peaks were recorded to within ± 1 cm^{-1} from a digital wavenumber readout.

3. Results

3.1. Infra-red spectra of β -silicon and germanium nitrides

The infra-red spectra of β -silicon and germanium nitrides are presented in Fig. 1. Scans were made

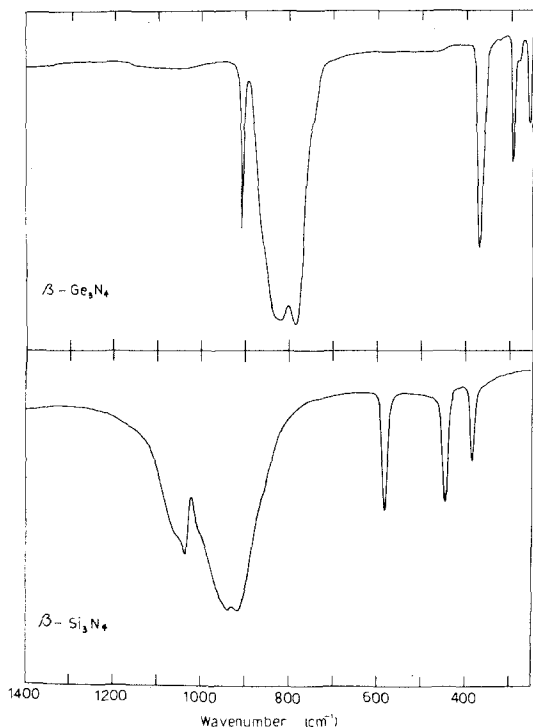


Figure 1 Infra-red spectra of β -silicon and germanium nitrides.

over a wavenumber range of 4000 to 40 cm^{-1} and the absorption bands shown in the diagram are the only ones observed in this range. Scans in the range 200 to 40 cm^{-1} were obtained at the Department of Chemistry, University of Bristol, by kind permission of Dr P. Goggin.

β -silicon nitride [6] and isomorphous β -germanium nitride [7] are hexagonal with two formula units (M_6N_8) in the unit cell. The space group is $P6_3/m$. From factor group analysis it is found that of the 42 degrees of freedom there are 4 vibrations of class A_g , 2 of class A_u , 3 of class B_g , 4 of class B_u , 2 of class E_{1g} , 4 of class E_{1u} , 5 of class E_{2g} , 2 of class E_{2u} and two translations. Of these only $4E_{1u} + 2A_u$ are predicted to be active in the infra-red and $4A_g + 2E_{1g}$ in the Raman.

A comparison of the infra-red spectra in Fig. 1 confirms that the two compounds are isostructural. Both compounds show the same pattern of absorptions and both exhibit six principal absorption bands, which is in agreement with the factor group analysis. The bands for β -germanium nitride are shifted to lower wavenumbers relative to those of β -silicon nitride which is consistent with the larger mass of germanium (relative to that of silicon) and the lower force constants of Ge-N bonds.

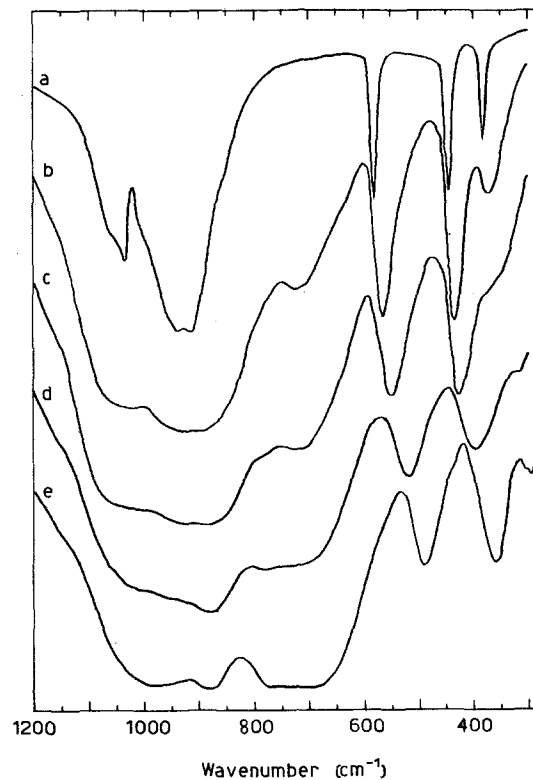


Figure 2 Infra-red spectra of β' -silalons.

Some of the absorption bands of β -silicon nitride, however, show small shoulders which are absent in the germanium nitride spectrum. These can be explained by the presence of small traces of α -silicon nitride and silica, both of which are normally present in β -silicon nitride preparations.

3.2. Infra-red spectra of β' -sialons

A series of infra-red spectra of materials ranging from $z = 0$ to $z = 4$ are presented in Fig. 2. The changes in the spectra which occur with increasing substitution of silicon by aluminium, and nitrogen by oxygen are:

(i) The bands at 578.5 cm^{-1} and 442 cm^{-1} (designated ν_1 and ν_2) shift to lower wavenumber values. The shift over the whole range $z = 0$ to $z = 4$ is about 100 cm^{-1} , which is very large compared with observed shifts in other similar systems [8, 9]. As z increases all the bands become much broader although as z approaches 4 there is a slight sharpening of the absorption bands.

(ii) The band at 376.5 cm^{-1} (designated ν_3) broadens considerably and is reduced in height as z increases (see Fig. 3) until at $z = 2$ it has virtually disappeared. As z increases above 2 a new broad band appears which increases in sharpness as z approaches 4. At $z = 4$ the new band is fully resolved at 303 cm^{-1} and for $z > 4$ the band again broadens and is reduced in intensity.

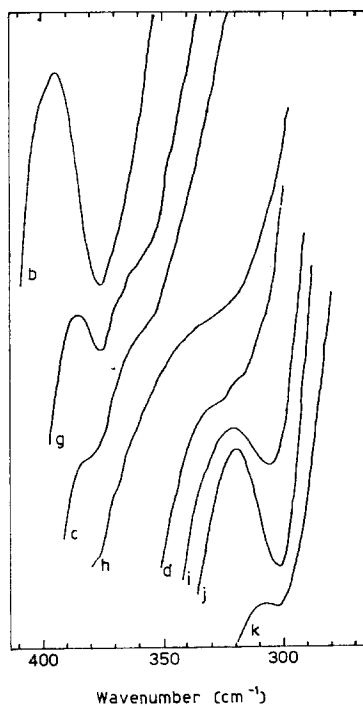


Figure 3 Changes observed in band ν_3 with increasing z .

(iii) A group of new bands appears in the spectral region, 650 to 800 cm^{-1} , the relative intensity of these bands increasing with increasing z .

(iv) The shift in ν_1 with composition is not identical with that of ν_2 . The graph of ν_2 against ν_1 (Fig. 4) shows that $\Delta\nu_2/\Delta\nu_1$ increases uniformly as z approaches 4. For $z > 4$, although ν_1 continues to decrease, ν_2 remains constant at 362 cm^{-1} .

3.3. Variation of band positions with cell constants for β' -sialons

It has been shown by Jack [1] that the a and c dimensions of the hexagonal unit cell increase at approximately the same rate with increasing z . The variation between the cell constants and z does not, however, appear to follow a simple linear relationship, although relatively large errors involved in the estimation of z make it difficult to obtain a very accurate correlation. The same difficulties arise in correlating infra-red band positions with composition. However, a very accurate correlation of band position with cell constants can be obtained over the complete compositional range.

The X-ray and infra-red data are presented in Table II. Fig. 5 shows the relationship between the cell constants and the infra-red band position ν_1 . There is a perfectly linear relationship at the lower values of z , but as z approaches 4 $\Delta\nu_1/\Delta a$ and $\Delta\nu_1/\Delta c$ increase significantly.

4. Discussion

4.1. Parameters influencing frequency shifts

An investigation of isotopic substitution of germanium in $\beta\text{-Ge}_3\text{N}_4$ shows a decrease in frequency in both ν_1 and ν_2 of about 6 cm^{-1} in the range $^{70}\text{Ge}_3\text{N}_4$ to $^{76}\text{Ge}_3\text{N}_4$ [10]. This effect is solely due to the difference in mass of the different germanium isotopes. Because the cation mass is greater than that of the anion, small changes in the cation mass have little effect on the vibrational frequencies.

In β -silicon nitride the cation mass is much closer to the anion mass and therefore the vibrational frequencies will be more sensitive to small cation mass changes. In addition, in the β' -sialons not only does the average cation mass decrease with increasing z , but also the average anion mass increases. The change in average mass in the

TABLE II

z estimated from composition of starting materials	Figure code	Unit-cell dimensions (Å)		Wavenumber [‡] (cm ⁻¹)		
		a	c	ν_1	ν_2	ν_3
0	a	7.6035 (6)	2.9079 (3)	578.5	442	376.5
0.5	—	7.6161 (6)	2.9169 (3)	573	438	377
1.15	b	7.6253 (10)	2.9260 (4)	564	434	375
1.45	g	7.6351 (8)	2.9346 (3)	556	427	376
1.9	c	7.6486 (10)	2.9464 (4)	550	423	—
2.0	—	†7.660	2.957	539	416	—
2.5	h	7.6782 (8)	2.9729 (3)	527	407	—
3.3	d	7.6912 (15)	2.9833 (7)	517.5	398	—
3.75	—	7.7057 (12)	2.9961 (5)	506	379	310
3.97	i	7.7107 (5)	3.0046 (2)	498	376	306
4.0	e	7.7169 (8)	3.0085 (4)	496	371	304
4.0	j	7.7181 (6)	3.0094 (3)	494.5	367.5	303
x = 5.5*	—	7.7189 (10)	3.0113 (4)	489.5	362.5	304
4.5	k	†7.7259 (12)	3.0190 (5)	481.5	362.5	303

*Based on Jack's originally reported composition $\text{Si}_{(6-0.75x)}\text{Al}_{0.67x}\text{N}_{(8-x)}\text{O}_x$.

† Measurement using Hagg Guinier camera, all other measurements made with 19 cm powder camera.

*Maximum error of measurement $\pm 1 \text{ cm}^{-1}$.

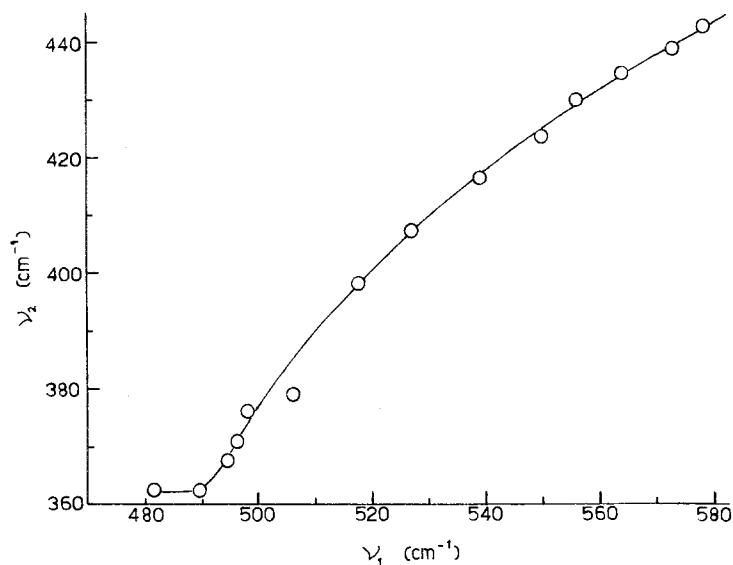


Figure 4 Plot of ν_2 against ν_1 over the full range of sialon compositions.

range $z = 0$ to 4 for both cations (28.09 to 27.35) and anions (14.01 to 15.00) is, however, relatively small and could in no way account for the large shift in infra-red absorption frequencies ($\sim 100 \text{ cm}^{-1}$) which are observed over this composition range.

Thus the observed frequency changes must mainly be a result of changes in force constants which, as indicated by Fig. 5, are related to changes in interatomic distances and bonding. In a continuously bonded three-dimensional solid the

relationship between vibrational frequencies, force constants and interatomic distances is highly complex. Simple relationships have been found to apply for certain compounds but these are diatomic and simple polyatomic molecules [11]. A large number of mixed crystal systems of the type $\text{AB}_{1-x}\text{C}_x$ have been studied [12–14] and many of these systems appear to show a simple linear relationship between absorption frequency and cell constant. These systems are, however, much simpler than the present system and deal mainly

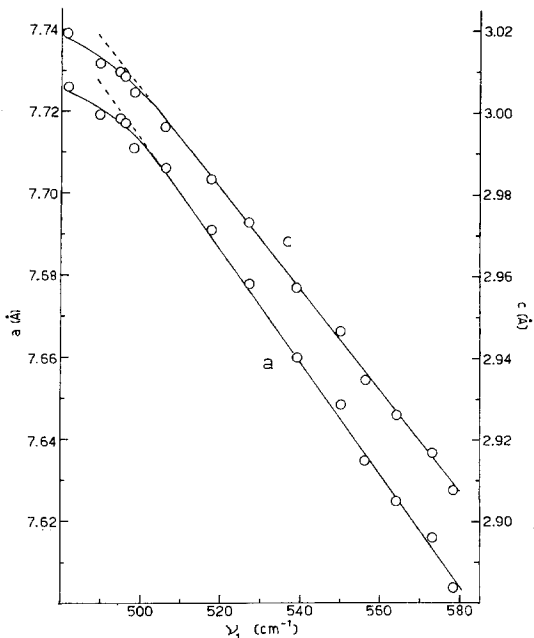


Figure 5 Plot of cell constants a and c against ν_1 .

with ionic crystals. White and Keramidis [15] have also reported a similar type of relationship for a series of garnets, but no attempt is made to explain the relationship.

In order to attempt to explain the present observations it is first necessary to assign the spectral bands in the pure nitride phases. Rigorous assignment requires the availability of both Raman and polarized infra-red data. So far attempts to obtain Raman spectra of the pure nitride phases have been totally unsuccessful and the authors have not been able to obtain suitable single crystals for polarized infra-red work.

4.2. Ordering in β' -sialons

X-ray analysis of the β' -sialons show that β -silicon nitride can take into solid solution relatively large amounts of aluminium and oxygen (up to about $z = 4.2$ according to Jack) without evidence of any structural changes. The only observable change is a general increase in the a and c dimensions of the hexagonal cell with increasing z .

The results of the infra-red studies reported in Section 3 do, however, indicate that structural changes are occurring. The type of structural changes which could occur and which would not be apparent from routine X-ray studies but would produce changes in the infra-red spectra are (a) small localized regions differing in both compo-

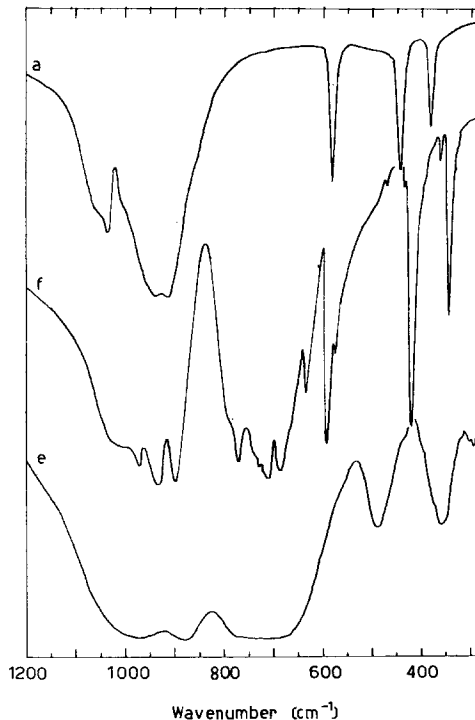


Figure 6 Comparison of the infra-red spectra of pure β -silicon nitride, phenacite and $z = 4$ sialon.

sition and structure from the bulk materials, and (b) long range ordering of both the cations and the anions on the available crystallographic sites.

In the latter case such long range ordering would normally produce superlattice reflections observable by X-ray diffraction methods. However, the difference in scattering power between silicon and aluminium, and nitrogen and oxygen is so small that these superlattice reflections would be too weak to observe.

One aspect of the infra-red data is that all marked changes occur at around the composition $z = 4$, and the possibility of ordering of the silicon and aluminium atoms and also the nitrogen and oxygen atoms at this composition cannot be discounted. An interesting analogy exists with the mineral phenacite (Be_2SiO_4). The arrangement of the cations and anions in phenacite [16] is identical with that in β -silicon nitride. However, because of the ordering of the beryllium and silicon atoms there is a reduction in symmetry and subsequent increase in the number of predicted infra-red absorption bands (see Fig. 6).

The composition of $z = 4$ sialon is $\text{Al}_2\text{SiO}_2\text{N}_2$ which, neglecting the fact that there are two types of anion, is the same as the phenacite composition

Be₂SiO₄. The close similarity between both the structure and composition of these two materials and the fact that substantial changes in the β'-sialon spectrum occur at the z = 4 composition, whilst not in themselves proving the existence of ordering, do suggest a possible model.

Attempts to obtain z = 4 sialon in its disordered state by heating at 1800°C followed by rapid quenching have produced no changes in the infra-red spectrum. This is however not surprising as the high stability of such phases makes it unlikely that they could be obtained in their disordered state at room temperature.

5. Conclusions

The present investigation shows that although X-ray analysis of β'-sialons produces no evidence of any structural changes with composition, infra-red studies suggest that structural changes are occurring. The changes in the infra-red spectrum at the composition near z = 4 are probably a result of ordering of the different types of atoms in the structure and an analogy with phenacite suggests an ordering scheme. It is, however, not possible without a detailed analysis of the allowed vibrational modes in β-silicon nitride, to confirm this. Assignment of the vibrational modes in the β structure would be aided by both polarized infra-red and Raman studies, but it is at present not possible to obtain data from either of these techniques.

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