

***In situ* study of amorphization and changes in coordination in Si₂N₂O at high pressure**

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Silicon oxynitride was investigated by x-ray powder diffraction and infrared absorption spectroscopy at pressures close to 50 GPa. Gradual amorphization was found to occur above 25 GPa. This process is associated with the disappearance of the strong B_1 Si-O stretching mode of the SiN₃O tetrahedra at close to 1130 cm⁻¹ and the appearance of additional modes at lower frequencies with respect to the Si-O stretching modes. This is evidence of an increase in the coordination of Si. Whereas the silicon atom appears to revert to a fourfold coordination below 7 GPa, the material remains amorphous.

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I. INTRODUCTION

The phenomenon of pressure-induced amorphization occurs in a variety of paradigmatic solid materials ranging from simple molecular systems such as CO₂,¹ C₆H₆,² and N₂ (Ref. 3) to open framework structures such as α -quartz⁴⁻¹⁴ and ice.¹⁵⁻¹⁹ One of the most intriguing open questions in condensed matter physics is whether these amorphous systems are temperature quenched states of high-pressure fluids or whether they arise from the pressure-induced mechanical collapse of ordered phases. Recently, it has been shown that for ice,¹⁹ pressure-induced amorphization is related to mechanical melting at low temperatures, whereas at high temperature, the amorphization mechanism changes and thermal melting prevails. In the case of quartz, for example, amorphization has been linked to elastic and dynamical instabilities in the α -quartz structure.⁶⁻¹¹ However, other models have also been proposed; they include the passage across the intersection of the melting curve with the pressure axis at room temperature,^{5,12} frustrated phase transitions¹³ involving an increase in silicon coordination number (CN), and the formation of a ferroelectric glass.¹⁴ Tetrahedrally coordinated open network structures are among the best candidates to exhibit pressure-induced amorphization, thereby providing unique opportunities for investigating transformations in out-of-thermodynamic equilibrium metastable systems. Among these, silicon oxynitride is a model system. The framework structure of Si₂N₂O is orthorhombic, with the space group $Cmc2_1$, and is composed of SiN₃O tetrahedra²⁰ (Fig. 1). These corner-sharing tetrahedra are linked by oxygen atoms in the **a** direction. The Si and N atoms form puckered hexagonal two-dimensional layers. The Si, N, and O atoms are in fourfold, threefold, and twofold coordinations, respectively. Si₂N₂O is a refractory material, which is particularly stable at a high temperature in the presence of oxygen.²¹⁻²³ It exhibits relatively high hardness, corrosion resistance, and electrical resistivity. Both neutron irradiation²⁴ and shock waves²⁵ are found to induce amorphization in this material.

Si₂N₂O was previously studied up to 2.3 GPa by neutron diffraction.^{26,27} The main compression mechanism was found

to be a cooperative rotation of the SiN₃O tetrahedra with a consequent reduction in the Si-O-Si angle. Shock-recovery experiments indicate that Si₂N₂O is stable up to about 28 GPa and becomes gradually amorphous between 34 and 41 GPa.²⁵ A theoretical study predicted phase transitions to a defect spinel structure and then to a corundum-type structure at a high pressure.²⁸ The present study was intended to investigate *in situ* the process of high-pressure amorphization in this material and the behavior of the amorphous form on decompression.

II. EXPERIMENT**A. High-pressure x-ray diffraction**

The high-pressure, angle-dispersive, x-ray powder diffraction experiments on Si₂N₂O were performed in a diamond anvil cell (DAC). X-ray diffraction with Cu $K\alpha$ radiation indicated trace impurities of Si₃N₄ in the initial sample at ambient pressure. The powder was placed in 150 μ m diameter holes, which had been drilled in Inconel or stainless steel gaskets pre-indented to a thickness of 100 μ m. Powdered ruby was added as a pressure calibrant. Pressures were measured based on the shifts of the ruby R₁ and R₂ fluorescence lines.²⁹ The 16:3:1 methanol:ethanol:H₂O (MEW) mixture was used as a pressure-transmitting medium up to 25 GPa (Figs. 2 and 3). Runs at pressures above 25 GPa were performed with vacuum grease or with no pressure-transmitting medium (Fig. 2).

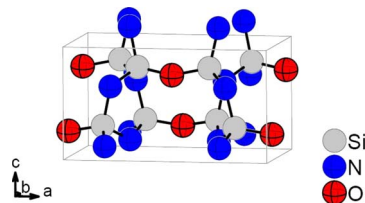


FIG. 1. (Color online) The crystal structure of orthorhombic Si₂N₂O.

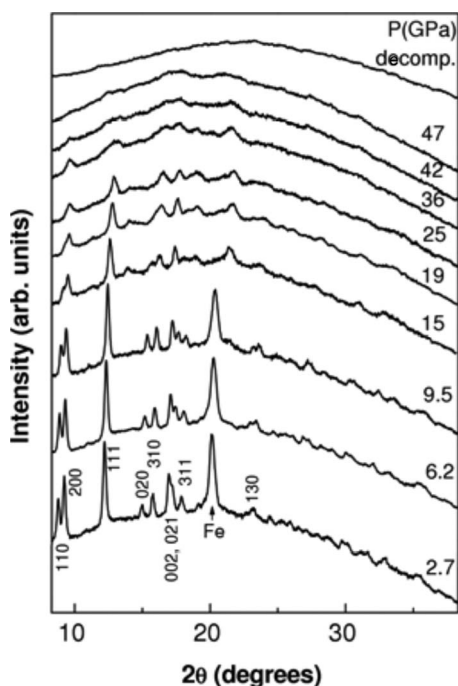


FIG. 2. X-ray diffraction patterns of $\text{Si}_2\text{N}_2\text{O}$ as a function of pressure on compression and that of the recovered sample upon decompression. The principal diffraction lines of orthorhombic $\text{Si}_2\text{N}_2\text{O}$ are indexed (Fe=iron from the gasket). The disappearance of the signal from iron at high pressure is due to an increase in the diameter of the gasket hole and the consequent absence of iron in the x-ray beam.

Angle-dispersive x-ray diffraction patterns were obtained with zirconium-filtered molybdenum radiation from an 800 W microfocus tube. X-ray capillary optics were used, which gave a 100 μm diameter beam. Detection was performed with an imaging plate placed at 143.59–143.78 mm from the sample. Exposure times were typically between 48 and 60 h. A DAC in which the rear diamond was mounted over a 16° wide slit that allows access to an angular range of $4\theta=80^\circ$ was used for these experiments. All x-ray diffraction patterns were obtained at ambient temperature. Exposures on the materials recovered in the gasket after the experiment were obtained by using the same installation.

The observed intensities on the imaging plates were integrated as a function of 2θ in order to give conventional one-dimensional diffraction profiles. The individual peaks were thus fitted to pseudo-Voigt functions, and unit cell refinements were performed by using the program U-FIT.³⁰ All figures in parentheses refer to estimated standard deviations.

B. High-pressure infrared measurements

A membrane-type DAC equipped with IIa diamonds was used for the high-pressure infrared measurements. Re gaskets with initial hole diameters and thicknesses of typically 80–100 and 40–50 μm , respectively, were used to contain the sample. Infrared spectra were measured by using a Fourier transform infrared spectrometer (Bruker IFS-120 HR) equipped with a mercury cadmium telluride detector, a glow-

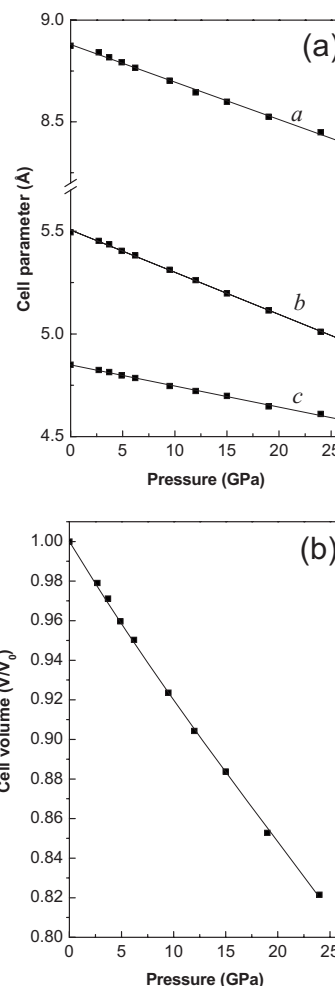


FIG. 3. (a) Cell parameters and (b) relative volume of orthorhombic $\text{Si}_2\text{N}_2\text{O}$ as a function of pressure.

bar lamp, and a KBr beam splitter. An optical beam condensing system based on two ellipsoidal aluminum coated mirrors was used to focus and collect the infrared beam through the gasket hole. Samples were diluted in a solid solution of 1% in weight of NaNO_2 in NaBr , which served as a pressure calibrant and a pressure-transmitting medium.^{31,32} The pressures were also checked by the ruby fluorescence method.²⁹ Runs with different dilutions were performed in order to properly observe peaks of different intensities. 400 scans were performed at each pressure point. All IR spectra were obtained at ambient temperature.

III. RESULTS AND DISCUSSION

A. Compression of orthorhombic $\text{Si}_2\text{N}_2\text{O}$ and high-pressure amorphization

1. X-ray diffraction

The compression of orthorhombic $\text{Si}_2\text{N}_2\text{O}$ was studied by x-ray diffraction up to 47 GPa (Fig. 2). A broadening of the diffraction lines due to nonhydrostatic stress was found to occur above 12 GPa. A further increase in pressure resulted in a gradual decrease in the intensity of the diffraction lines.

The unit cell parameters and volume could be reliably measured up to 24 GPa, above which the diffraction lines were too broad and weak.

Orthorhombic $\text{Si}_2\text{N}_2\text{O}$ undergoes anisotropic compression [Fig. 3(a)] with the following relationship between the linear compressibilities: $k_b[3.72(4) \times 10^{-3} \text{ GPa}^{-1}] > k_c[2.10(4) \times 10^{-3} \text{ GPa}^{-1}] = k_a[2.07(5) \times 10^{-3} \text{ GPa}^{-1}]$. The higher compressibility along **b** is in agreement with a previous neutron study of up to 2.3 GPa.²⁶ In the same study, an unusual compression behavior was reported along **a**, with the compressibility increasing with increasing pressure. This is not inconsistent with the first high-pressure point in the present study, which lies above the curve. The present work indicates that in the higher-pressure region, compression in the *ac* plane becomes more isotropic. Refinements of neutron diffraction data of up to 2.3 GPa (Ref. 26) indicated that the principal compression mechanism is a cooperative antiphase tilting of the SiN_3O tetrahedra with a preferential reduction in the Si-O-Si angle. The compression along **b** is enhanced by the shortening of one Si-N bond. These processes may be expected to continue up to higher pressure as there is no evidence of saturation of compression mechanisms from the close to the linear dependences of the cell parameters.

The pressure-volume data [Fig. 3(b)] of orthorhombic $\text{Si}_2\text{N}_2\text{O}$ were fitted to a Birch–Murnaghan equation of state³³ as follows:

$$P = 1.5B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]\{1 + 0.75(B'_0 - 4) \times [(V/V_0)^{-2/3} - 1]\},$$

where V_0 , B_0 , and B'_0 are the volume, bulk modulus, and the first derivative of the bulk modulus at ambient pressure. A bulk modulus of 115(2) GPa was obtained with a pressure derivative of 1.2(2). The B_0 value compares well with a linear fit of up to 2.3 GPa in a previous work, which yielded a value of 127(6) GPa.²⁶ The pressure derivative obtained is rather low and may be sensitive to the appearance of nonhydrostatic stress above 10 GPa in the MEW pressure-transmitting medium.

Beginning at above 25 GPa, a significant decrease in the intensity of the diffraction lines is observed, with only a very weak, broad residual pattern at 47 GPa. This indicates that most of the material is highly disordered or amorphous. No significant differences were obtained when using either vacuum grease or no pressure-transmitting medium. The latter is shown in Fig. 2 for the highest pressure (>35 GPa) as such loadings resulted in a larger sample in the x-ray beam and a better signal/noise ratio over the pressure range in which the sample was partially amorphous. No remaining features apart from extremely weak peaks, which are due to the ruby pressure calibrant and the traces of Si_3N_4 in the sample, were present in the data obtained after a full decompression of the sample. The present *in situ* data are thus in very good agreement with the shock-recovery experiments of Sekine *et al.*,²⁵ who reported, based on x-ray diffraction and Raman spectroscopy, that in recovered samples the starting phase was obtained for shock pressures of up to 28 GPa, partial amorphization for pressures between 34 and 41 GPa, and complete amorphization for higher pressures.

2. Infrared spectroscopy

Group theory predicts that orthorhombic $\text{Si}_2\text{N}_2\text{O}$, with space group $Cmc2_1$, (C_{2v}^{12}) with $Z=4$, should exhibit 30 vibrational modes, as follows:

$$\Gamma = 8A_1 + 7A_2 + 7B_1 + 8B_2.$$

All of these modes are infrared and Raman active except for the A_2 modes, which are Raman active only. The three modes A_1 , B_1 , and B_2 correspond to acoustic modes, and 20 modes are thus expected in the infrared spectrum of orthorhombic $\text{Si}_2\text{N}_2\text{O}$. A total of 16 modes have previously been observed in the infrared spectrum of $\text{Si}_2\text{N}_2\text{O}$ (1400–200 cm^{-1}), of which 14 are fundamental vibrations.^{34,35} In the present study, ten modes in the 1300–500 cm^{-1} region were studied as a function of pressure [Figs. 4(a) and 4(b)].

In the pressure range of up to 25 GPa, the principal changes in the infrared spectrum of orthorhombic $\text{Si}_2\text{N}_2\text{O}$ concern the increase in intensity and/or the appearance of additional peaks in the 900–600 cm^{-1} region, in which the symmetric ν_{SiO} vibration is observed at 679 cm^{-1} (Ref. 34) at ambient pressure. In particular, the very weak fundamental mode at 648 cm^{-1} strongly increases in intensity with increasing pressure and is essentially as intense as the ν_{SiO} mode at 25 GPa. An additional mode that was initially a shoulder on the lower frequency side of the ν_{SiO} mode is clearly resolved above 11 GPa. The weak peak, which is initially at 730 cm^{-1} , also increases in intensity. These two latter modes do not correspond to fundamental vibrations based on lattice dynamical calculations.³⁵ The observed changes in intensity arise from the structural changes that occur over this pressure range and, in particular, to the important reduction in the Si-O-Si angle.^{26,27}

Very important changes in the infrared spectrum occur above 25 GPa. Certain modes strongly decrease in intensity and disappear with further increases in pressure. In particular, these include the ν_{SiO} modes, which were initially observed at 1130 and 679 cm^{-1} . This indicates that the Si-O-Si linkages are strongly affected. In contrast, the broad bands between 900 and 1100 cm^{-1} , which correspond to the ν_{SiN} stretching modes, continue to broaden but remain intense up to the highest pressure reached (the observed overall decrease in intensity can be linked to sample thinning). In addition, the δ_{SiN} bending modes below 600 cm^{-1} are also retained. A series of additional broad peaks appear between 600 and 900 cm^{-1} . Additional ν_{SiO} modes in this region may be expected if the coordination number of silicon were to increase with respect to oxygen. Such modes will be shifted to a lower wave number with respect to the modes of the initial orthorhombic crystalline form due to the increase in the Si-O distance linked to the increase in coordination number. This is similar to what was observed at high pressure in quartz, in which the modes above 1080 cm^{-1} disappear and additional broad bands appear below 900 cm^{-1} .³⁶ The pressure at which these changes are observed in $\text{Si}_2\text{N}_2\text{O}$ is in good agreement with the amorphization pressure determined by shock-recovery experiments²⁵ and with the gradual disappearance of the x-ray reflections in the present study. The broad nature of the peaks observed for the high-pressure form of $\text{Si}_2\text{N}_2\text{O}$ is consistent with the appearance of an

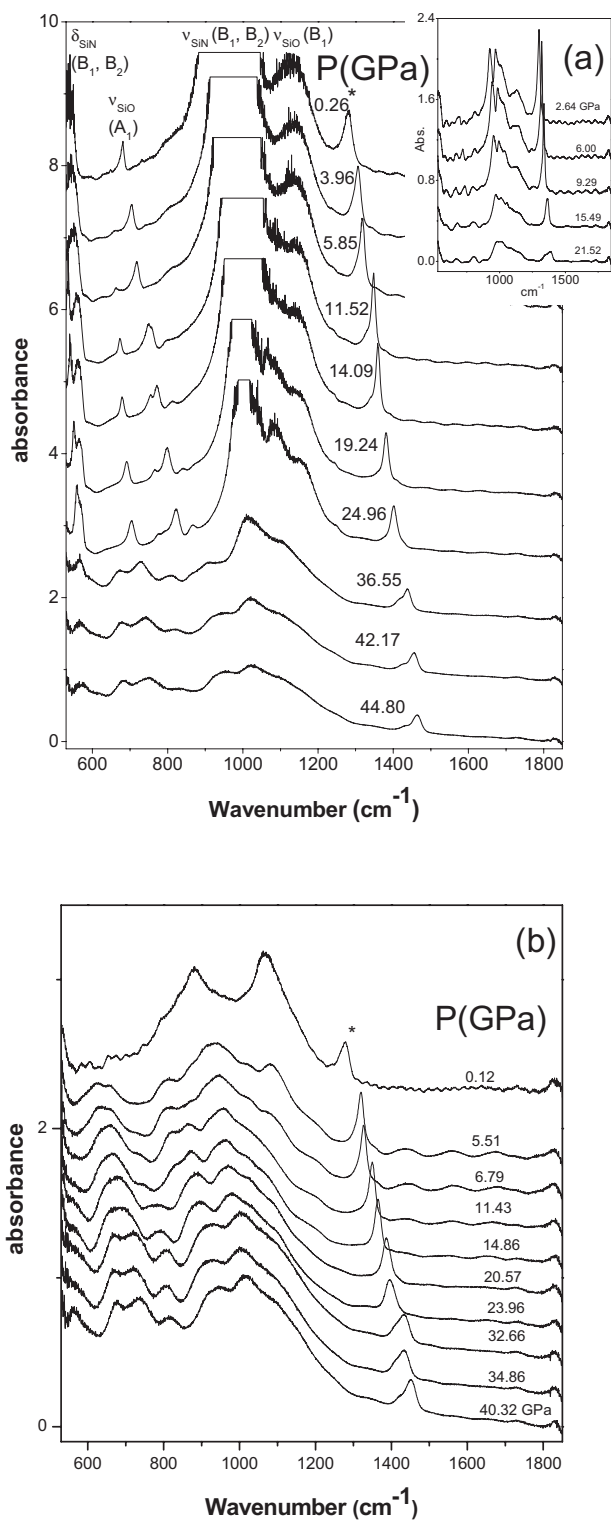


FIG. 4. Infrared absorption spectra of Si₂N₂O measured upon pressure (a) increase and (b) decrease. Mode assignment of the peaks is indicated (*=the NO₂⁻ stretching vibration of 1% NaNO₂/NaBr). The broadening of the NO₂⁻ stretching peak at high pressure is an indication of a pressure gradient in the compressed solid. The absorption of the ν_{SiN} modes in the 950–1000 cm⁻¹ region is saturated up to 25 GPa. In a different high-pressure run [inset in (a)], a more diluted sample in the pressure transmitting media was used (see text) in order not to saturate the absorption.

amorphous form as contributions from all *k* vectors in the Brillouin zone will now be present.

B. Spectral changes in the amorphous phase upon decompression

Upon decompression, the spectrum of the high-pressure amorphous form of Si₂N₂O does not exhibit significant changes down to close to 15 GPa, below which a shoulder appears near 830 cm⁻¹ and the peak that was previously near 780 cm⁻¹ shifts to a lower wave number [Fig. 4(b)]. Below 11 GPa, important modifications to the infrared spectrum are observed. A different intense broad peak near 1100 cm⁻¹ begins to appear close to 7 GPa. This peak is the strongest observed in the spectrum of the recovered form on pressure release. This band is very close in wave number to that of the highest energy ν_{SiO} stretching mode of the SiN₃O tetrahedra in the low-pressure orthorhombic phase. In addition, in the 600–900 cm⁻¹ region, there is evidence of a reduction in the coordination number to its initial value of 4. The broad band between 600 and 650 cm⁻¹ essentially disappears over the same pressure range upon decompression and a weak feature grows close to the 670 cm⁻¹ ν_{SiO} mode in the starting material. The replacement of the lower wave number modes by such a feature at a higher wave number is evidence of the strengthening of the Si-O bond as would be expected due to the shorter Si-O bonds obtained with a reduction in the CN of silicon. Both of these characteristic ν_{SiO} modes (~1100 and ~670 cm⁻¹) are thus observed at similar values to those in the starting material (CN=4) and the additional bands, which appeared at high pressures, disappear. These important changes indicate that major structural modifications, in particular, a change in the coordination number of silicon, occur in the amorphous form as no recrystallization on pressure release was observed by x-ray diffraction or in the shock-recovery experiments. These results may be an indication of the presence of polymorphism in amorphous Si₂N₂O, which is linked to a change in the coordination number of silicon upon decompression, and thus may provide a further example of polymorphism in addition to materials such as SiO₂,^{4,5} H₂O,^{15–19} silicon,³⁷ phosphorus,³⁸ and Al₂O₃-Y₂O₃.³⁹ Further studies of the amorphous phase with complementary techniques are, however, necessary to characterize this phenomenon and, in particular, to know whether the observed modifications to the infrared spectrum correspond to gradual changes in one amorphous state or a transformation from a high-density to a low-density form with a pressure range of coexistence between the two forms.

C. High-pressure amorphization process

The present results are consistent with an increase in coordination number of silicon, possibly to 5 as has been found in oxides,^{40–42} at the crystalline to amorphous transformation, followed by a decrease in coordination number to 4 upon pressure release in the amorphous phase. The rigid Si-N puckered hexagonal two-dimensional layers appear to be conserved as the changes in Si-N modes are relatively minor. In contrast, major changes occur at the level of the Si-O-Si linkages with a disappearance of the ν_{SiO} modes and

the appearance of modes at a lower wave number. Amorphization may be linked to relative displacements of the rigid Si-N puckered hexagonal two-dimensional layers (Fig. 1) in a disordered manner. Such shifts can result in an extra oxygen atom entering the coordination sphere of silicon leading to the formation of SiN_3O_2 polyhedra, which are unstable on pressure release.

In contrast with the present study, density functional theory calculations²⁸ indicate that a defect spinel modification may be stable between 11 and 16 GPa, whereas between 6 and 11 GPa and above 40 GPa, the decomposition into various forms of SiO_2 and Si_3N_4 , including stishovite SiO_2 and spinel-type $\gamma\text{-Si}_3\text{N}_4$ with sixfold coordinated silicon, may be favored. There is experimental evidence of a quenchable primitive, cubic phase with $a=7.350$ Å (at ambient pressure) based on the appearance of a few weak additional peaks after a laser heating experiment at 15 GPa.⁴³ These limited data do not permit the structure nor chemical composition of the phase to be identified. The major difference with respect to the present study is that in the absence of thermal activation, the stable phases are not observed and instead an amorphous form is obtained.

IV. CONCLUSIONS

The present results obtained *in situ* at high pressure by x-ray diffraction and infrared spectroscopy are in agreement with previous shock-recovery experiments²⁵ and permit the amorphization process in this material to be described in detail. The infrared spectroscopic measurements, in particular, provide evidence of an increase in the coordination number of silicon upon compression. This change in coordination number is found to be reversible; however, the material remains amorphous upon complete decompression.

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