Low-Energy Floppy Modes in High-Temperature Ceramics

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Enhancement of the phonon density of states due to low-energy floppy modes in crystalline and glassy states of the high-temperature ceramic Si_3N_4 is investigated using the molecular-dynamics method. Floppy modes appear continuously in the glass as the connectivity of the system is reduced. In the crystal, they appear suddenly at 20% volume expansion. The density of states due to the floppy modes varies linearly with energy, and the specific heat is significantly enhanced by the floppy modes.

Silicon nitride is a very promising material for high-temperature applications [1,2]. It has a strong resistance against thermal shock, high strength at high temperatures, corrosion resistance against fused metals, chemical inertness, and oxidation resistance at high temperatures. Because of these excellent characteristics, there are numerous applications of silicon nitride as engineering components.

In this Letter we report an investigation of the low-energy modes in silicon nitride based on molecular-dynamics (MD) simulations. Low-energy modes play an important role in determining the properties of glasses. Phillips introduced the idea of *underconstrained* and *overconstrained* glasses in terms of the number of constraints, n_c, and the degrees of freedom, n_d [3]. Thorpe extended these ideas and introduced the notion of rigidity percolation, where a glass at lower coordinates may be viewed as consisting of rigid and floppy regions [4,5]. In an idealized random network model, the rigidity percolation transition is found when the average coordination $\langle r \rangle$ reaches a critical value $\langle r_c \rangle = 2.4$; for $\langle r \rangle$ less than 2.4, there is a finite fraction of zero-energy modes in the network. If additional stabilizing interactions are added to improve the mechanical stability of the network, the rigidity percolation transition is washed out [5]. However, even for $\langle r \rangle$ greater than $\langle r_c \rangle$ there are floppy regions in the glass which give rise to low-energy modes rather than zero-energy modes, as envisioned in the original analysis [6–9].

In our MD simulations for the high-temperature ceramic silicon nitride, low-energy modes emerge in the amorphous and crystalline systems under uniform external negative pressures. In the glass the number of low-energy floppy modes increases continuously with a decrease in the density and the average coordination of the system. The behavior of the Si_3N_4 crystal is quite unusual; Upon expansion from 3.2 to 2.8 g/cm^3, the crystal undergoes distortions due to stretched N-N bonds (Si-N bond length remains unchanged) and the maximum energy ω_{max} in the density of states (DOS) shrinks by 20%. With further

expansion to 2.6 g/cm^3, the crystal undergoes sudden decohesion which transforms it into an "amorphous state." At the same time, the DOS at low energy exhibits a linear region due to floppy modes. In addition, ω_{max} increases by more than 30% and it continues to increase as the density of the system is further lowered. ω_{max} for the amorphous system at 2.0 g/cm^3 is 15% higher than ω_{max} for the crystal at the normal density (3.2 g/cm^3). Low-energy floppy modes cause a substantial enhancement in the specific heat over the temperature range of 50–400 K.

Molecular-dynamics simulations for silicon nitride were performed with interparticle interactions which consist of two-body and three-body terms [10]. The two-body potentials combine steric repulsion, long-range Coulomb interactions due to charge-transfer effects, and the charge-dipole interaction due to large electronic polarizability of negatively charged nitrogen ions. Three-body covalent interactions include the effects of bond bending and stretching. (Details of the interaction potentials will be discussed elsewhere [10].) Crystalline silicon nitride exists in two polymorphs: the α and β phases [11]. The crystal structure of both phases consists of slightly distorted, corner-sharing SiN_4 tetrahedra. In the β phase Si-N layers parallel to the hexagonal basal plane are stacked in an alternate sequence $ABABAB\ldots$. In the α phase the sequence becomes $ABCDABCD\ldots$, where the CD layers are related to the AB layers by a c-glide plane. The simulated systems consisted of 1344 particles in orthorhombic cells with periodic boundary conditions.

Two classes of low-density and low-coordination systems were generated via MD simulations. First the α-Si_3N_4 crystal [11,12] at 3.2 g/cm^3 was heated to 6000 K and the molten system (large silicon and nitrogen diffusion was observed) was thermalized for 60 000 time steps. A 1000 K glass at 3.2 g/cm^3 was obtained from the melt by quenching and thermalizing the system for 30 000 time steps. The glass was thermalized at 1000 K for another 15 000 time steps. From this well-thermalized glass at 3.2 g/cm^3, systems at 3.0, 2.8, 2.6, 2.4, 2.2,

and 2.0 g/cm^3 were prepared by successively decreasing the density and thermalizing each system for 15 000 time steps. Structural and dynamical correlations of these systems were calculated at 1000 K. These systems were then cooled to 280 K, and they were further thermalized for 8000 time steps each before calculating structural and dynamical correlations. Another set of low-coordination systems was obtained from the α-Si$_3$N$_4$ crystal at 3.2 g/cm^3 and 280 K. Maintaining the temperature of the system at 280 $\pm$ 20 K, the density of the well-equilibrated crystal was decreased in steps of 0.2 g/cm^3 and each new system was thermalized for 9000 time steps before further decreasing the density. In this manner systems at densities 3.0, 2.8, 2.6, 2.4, 2.2, and 2.0 g/cm^3 were generated from the 280 K α crystal. The DOS and low-energy floppy modes were obtained by two methods: (1) by directly diagonalizing the dynamical matrices, and (2) by Fourier transforming the velocity autocorrelation functions $\langle V(0)V(t)\rangle$ for the crystalline and glassy systems. The two methods gave the same results. We choose to present the results for DOS obtained by diagonalizing the dynamical matrix to avoid any uncertainty in the low-energy part of the spectrum.

Figures 1(a)–1(d) show structural correlations for Si$_3$N$_4$ glass at 2.8 g/cm^3 and 282 K. In Fig. 1(a), MD results for the neutron static structure factor, $S_n(q)$, are compared with the only available neutron experiment (Misawa et al. [12]). The calculated positions of the first and second peaks at 2.65 and 4.7 Å^{-1} and their respective heights agree well with the experiment. Figures 1(b), 1(c), and 1(d) show Si-Si, Si-N, and N-N pair-distribution functions and the corresponding coordination numbers, respectively. The nearest-neighbor distances and full widths at half maximum (FWHM) are found to have the following values: Si-N = 1.73 Å (0.13 Å), N-N = 2.84 Å (0.31 Å), and Si-Si = 2.98 Å (0.31 Å). The Si-N, N-N, and Si-Si distances in the crystalline α phase at 3.2 g/cm^3 are 1.73, 2.83, and 2.94 Å, respectively, and the corresponding nearest-neighbor coordinations are 4, 8, and 11.5. Clearly the Si-N bond is robust in the glassy state at 2.8 g/cm^3. However, the broader first peaks in $g_{Si-Si}(r)$ and $g_{N-N}(r)$ and slightly longer nn distances indicate the presence of distorted tetrahedra. The short-range order is further examined through bond-angle distributions, shown in Figs. 1(e) and 1(f). The N-Si-N and Si-N-Si distributions have peaks (FWHM) at 108° (17°) and 118° (18°), respectively. In the crystalline α phase, the N-Si-N bond angles range from 101.91° to 114.19° with an average value of 109° and the Si-N-Si from 113.48° to 127.36° with an average value of 120°. The above structural analysis reveals that despite the robustness of the Si-N bond the tetrahedra are considerably more distorted in the glass at 2.8 g/cm^3 than in the crystalline state.

To investigate the vibrational DOS, we applied the steepest descent quench (SDQ) to all 14 crystalline and glassy systems (SDQ brings a system to an underlying force-free mechanically stable structure) and then their dy-
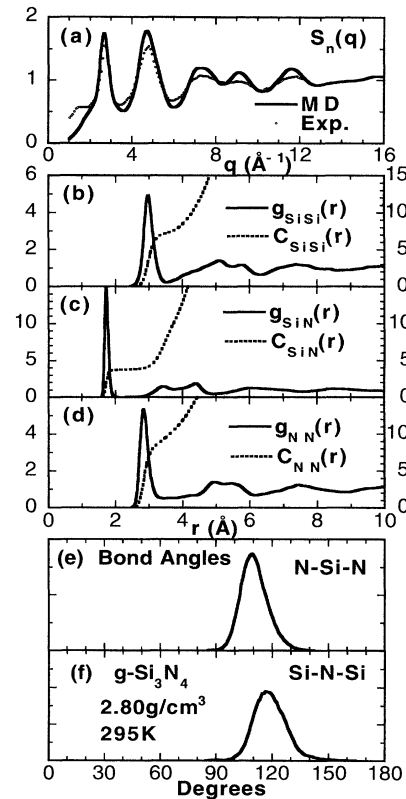

FIG. 1. Structural correlations for Si$_3$N$_4$ glass at 2.8 g/cm^3 and 282 K. (a) Neutron static structure factor $S_n(q)$. (b)–(d) Partial pair-distribution functions $g_{\alpha\beta}(r)$ and coordination numbers $C_{\alpha\beta}(r)$. (e) and (f) N-Si-N and Si-N-Si bond-angle distributions.

namical matrices (4032 × 4032) were diagonalized. Figures 2(a), 2(b), and 2(c) show the DOS for α- and β-crystalline phases and the glass at 3.2 g/cm^3, respectively. Wada et al. have measured Raman and infrared spectra of polycrystalline samples of α and β phases [13]. The calculated DOS reflects the lower symmetry of the α phase with respect to the β phase (the so-called high-temperature phase), and there is a clear energy gap, from approximately 100 to 110 meV, in the crystalline DOS. The experimental maximum energy of 140 meV is in reasonable accord with our simulations. We have also computed the average phonon frequencies $\langle\omega\rangle_{Si}$ and $\langle\omega\rangle_N$ for Si and N vibrations in the crystalline and glassy systems. For α and β phases, $\langle\omega\rangle_{Si}$ = 69.64 and 69.86 meV and $\langle\omega\rangle_N$ = 103.25 and 103.60 meV, respectively. Examination of eigenvectors reveals that N vibrations make the dominant contributions to high-energy modes above 110 meV. Larger value of $\langle\omega\rangle_N$ in the β phase is also consistent with a slightly larger value of the energy gap in Fig. 2(b). What is remarkable is the change in the phonon DOS when the system is in the glassy state. The 10 meV energy gap in the crystalline phases disappears and the high-energy part of the spectrum shifts from 145 meV in the crystals to 170 meV in the glass. However, the average
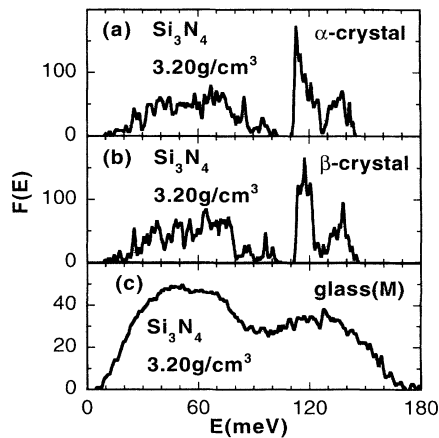
FIG. 2.   MD phonon density of states (DOS) $F(E)$: (a) α crystal, (b) β crystal, and (c) glass prepared from a 6000 K melt.

Si and N phonon frequencies in the glass are only slightly modified ($\langle\omega\rangle_{Si}$ = 70.25 meV and $\langle\omega\rangle_N$ = 103.87 meV).

Let us now examine the behavior of the phonon DOS in uniformly expanded glassy and crystalline Si_3N_4. Figures 3(a), 3(b), and 3(c) show the DOS for glasses at densities ranging from 3.2 to 2.0 g/cm^3. Two features are quite evident in the DOS as the density and, therefore, the connectivity of the glass is reduced: (i) The linear part of the DOS below 15 meV grows uniformly in magnitude as the density is reduced from 3.2 to 2.0 g/cm^3, and (ii) the maximum frequency in the DOS decreases as the density is reduced from 3.2 to 2.6 g/cm^3, and then it increases with a decrease in the density from 2.6 to 2.0 g/cm^3. The reduction in the density of the glass from 3.2 to 2.0 g/cm^3 covers two regimes. In the first regime between 3.2 and 2.6 g/cm^3 the glass stretches, but no major bond breaking occurs. In this regime, the average frequencies $\langle\omega\rangle_{Si}$ and $\langle\omega\rangle_N$ decrease from their
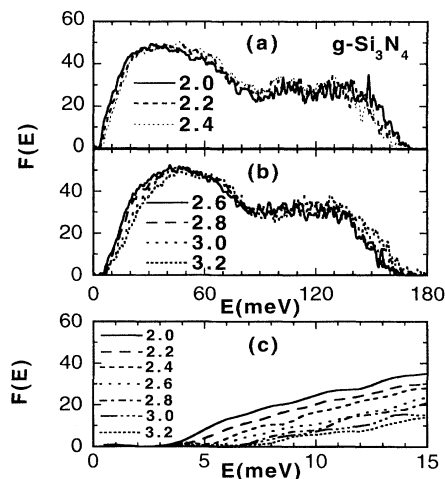

FIG. 3.   Phonon DOS $F(E)$ for Si_3N_4 glasses. (a) 2.0, 2.2, and 2.4 g/cm^3. (b) 2.6, 2.8, 3.0, and 3.2 g/cm^3. (c) Linear behavior of the low-energy part of the DOS.

values at 3.2 g/cm^3. When the density of the glass is reduced below 2.6 g/cm^3, the system begins to undergo decohesion and a substantial number of bonds are broken. Small pores or voids develop to reduce the strain in the system. Since the nitrogen ion is large and its mass is considerably smaller than that of Si, the effect of density reduction is more pronounced in nearest-neighbor N-N coordination numbers and in the average frequency of nitrogen vibrations, $\langle\omega\rangle_N$. Figure 3(c) shows the DOS in the frequency region below 15 meV: As the connectivity is reduced, low-frequency floppy modes give rise to a linear energy dependence of the DOS.

Results for the silicon and nitrogen partial and total DOS including the low-energy floppy modes in the α crystal are shown in Figs. 4(a)–4(d). As mentioned earlier, the DOS for the normal crystal is in good agreement with Raman and IR experiments of Wada et al. [13]. Figure 4(b) shows that, although the system at 2.8 g/cm^3 is stretched, there are still sharp peaks in the DOS indicating the crystalline nature of the system. However, at 2.8 g/cm^3 the 10 meV gap in the DOS of the normal crystal disappears, the point group symmetry of the original crystal is destroyed, and the maximum frequency in the DOS is reduced from 145 to 115 meV. Note that the Si-N bond is robust and the nearest-
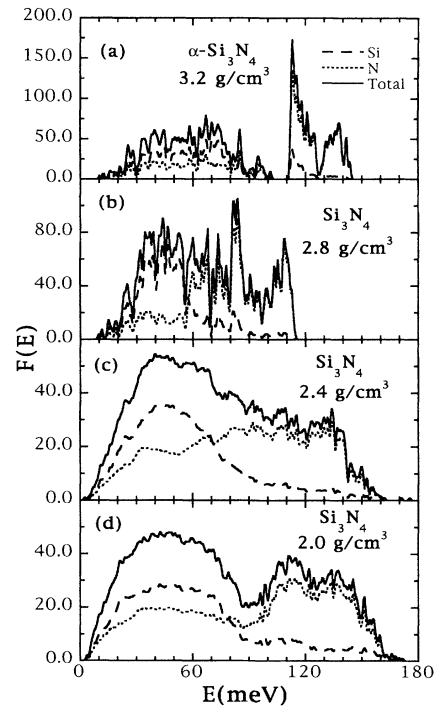

FIG. 4.   Silicon and nitrogen partial and total phonon DOS at different stages of decohesion of the α crystal due to volume expansion at 300 K.   (a) Crystal at normal density.   (b) Expanded crystal.   (c) At 2.4 g/cm^3 an abrupt decohesion of the crystal has occurred and a linear region in the DOS due to low-energy floppy modes has emerged.   (d) DOS for the system at 2.0 g/cm^3 from decohesion of the α crystal is practically the same as for the glass at 2.0 g/cm^3 which was obtained from the melt.

neighbor N-N and Si-Si distances change to accommodate expansion, thereby distorting the tetrahedra. (This is different from the early stages of uniform expansion of a monatomic crystal where all bonds stretch uniformly and the point group symmetry of the crystal are maintained.) As the density is further reduced to 2.6 g/cm^3, the system undergoes an abrupt decohesion. This represents the most profound rearrangement of the system—voids/pores grow and bonds are broken and reassembled within the clusters and in the intercluster regions. The crystalline symmetry is completely lost and a linear part in the DOS appears below 20 meV in both Si and N partial DOS. At the same time the maximum frequency in the DOS increases from 115 to 160 meV. As the connectivity of the system is further reduced at 2.0 g/cm^3 [Fig. 4(c)], the magnitude of the linear part of the DOS increases, the spectrum from 100 to 160 meV acquires more weight, and the maximum frequency increases to 170 meV.

The specific heat of the α crystal at normal density is calculated from the DOS [Fig. 2(a)], and the results along with experimental data [1] are shown in Fig. 5(a). The MD results for the specific heat agree very well with the experimental results. The specific-heat results, calculated from the DOS shown in Figs. 3(a) and 3(b), are plotted in Fig. 5(b); the differences in specific heats at different densities are shown in Fig. 5(c). The main contribution in Fig. 5(c) is due to low-energy floppy modes, and the maximum is around 150 K for the reduced coordination glass at 2.0 g/cm^3.

To confirm the existence of low-energy floppy modes in Si_3N_4, we propose the following experiments: Amor-

phous Si_3N_4 samples at different densities should be prepared by chemical vapor deposition on a cold substrate and diffraction [14,15], and inelastic neutron scattering [16,17] experiments should be carried out to determine the structure and DOS as a function of the sample density. Low-temperature specific heat should be measured [18] on the same samples to determine the excess specific heat in the temperature range of 50 to 400 K. After these initial measurements, the samples should be densified at high temperatures and annealed. Diffraction and inelastic neutron scattering and specific-heat measurements should be repeated on the densified and annealed samples to analyze their structures, and to observe the reduction in the contribution of low-energy floppy modes to the linear part of the phonon DOS and the specific heat.
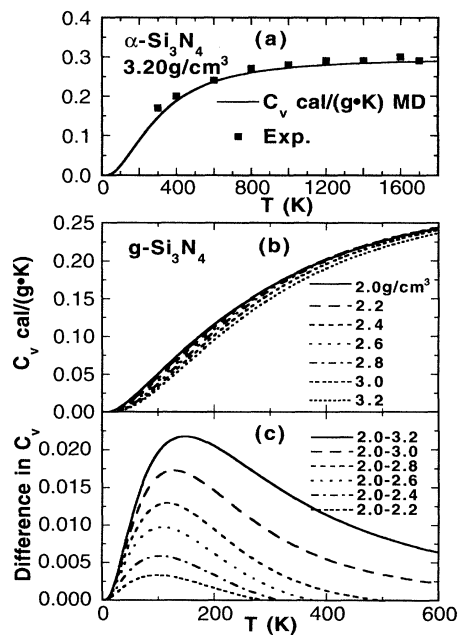
FIG. 5. Specific heat for Si_3N_4: (a) α crystal, (b) for seven glasses at densities between 3.2 and 2.0 g/cm^3, and (c) enhancement in the specific heat at different densities with a maximum around 150 K.

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