High-Resolution Transmission Electron Microscopy of Pressure-Amorphized α-Quartz

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α-quartz becomes x-ray amorphous when compressed, at ambient temperature, by pressures of 25 to 30 GPa [Hemley *et al.*, Nature **334**, 5 (1988)]. The relationship between pressure-amorphized and melt-quenched silica is of great interest. The most fundamental characteristic of melt-quenched silica is its lack of periodicity at the atomic level. We report here that high-resolution electron microscopy shows that α-quartz, pressure amorphized at 30.5 GPa is, as is conventional melt-quenched silica, amorphous at the atomic level.

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A novel method for producing amorphous solids is by compression at ambient temperature [1–10]. A central unanswered question is the relationship between pressure-induced amorphous solids and amorphous materials produced by conventional methods. While there are many aspects to consider, e.g., the existence of a glass transition, anisotropicity, the defining characteristic is the structure at the atomic level. Melt-quenched amorphous solids have no long-range order or translational periodicity [11–13]. It is common to assume that amorphous materials prepared by nonconventional methods are microcrystalline. Chen and Spaepan have stated this tendency best: "Invariably [a microcrystalline model] is resurrected when a new type of amorphous material is discovered, only to be put aside in most cases in favor of a truly amorphous structure (one without lattice periodicity). [14]" Our goal in this Letter is to show definitively that pressure-amorphized materials can be truly amorphous. Determining the length scale over which the translational order is absent depends on the structural probe used. For example, materials that appear amorphous by conventional x-ray diffraction methods may contain crystallites with an average diameter below ~20 Å [15]. Electron diffraction techniques probe order on a scale much smaller than x rays: High-resolution transmission electron microscopy (HRTEM) measurements have a resolution on the order of an angstrom [16].

The most highly studied pressure-induced amorphization is of α-quartz [17–19]. Raman and energy dispersive x-ray diffraction show that it becomes amorphous between 25 and 30 GPa, while single-crystal studies detect the onset of amorphization at ~15 GPa [1,2,20]. We have used HRTEM to study the pressure-induced x-ray amorphous state of α-quartz. We studied a sample of α-quartz before (20.0 GPa) and after (30.5 GPa) amorphization.

The sample of α-quartz powder (from Johnson Matthey, Alpha Products, 99.999%) was pressurized using a Merrill-Bassett style diamond anvil cell [21]. A 4:1 mixture of methanol and ethanol was used as the pressure-transmitting fluid. While our experiments are at pressures above the hydrostaticity limit of this medium, Hemley *et al.* found that amorphization occurred with either the alcohol mixture or the more hydrostatic neon pressure-transmitting medium [1,2]. Quasihydrostaticity of the 4:1 methanol-ethanol mixture above ~10.0 GPa simply causes the amorphization to occur at a lower pressure. Additionally, McNeil and Grimsditch reported no significant differences between the argon and the alcohol pressure-transmitting media in their Brillouin scattering measurements [22]. The high-resolution transmission electron microscopy was performed with a JEOL 4000EX instrument operating at 400 kV with a spherical aberration coefficient of 1.1 mm and a point-to-point resolution of ~1.8 Å. The pressurized samples, after the load was released, were drilled onto 200 mesh copper grids with a 100-Å holey carbon coating. Pieces of the Inconel gasket, with grains ~150 Å in diameter, can contaminate sections of the quartz sample after being transferred to an electron microscopy grid. These sections are easily identified with either energy dispersive spectroscopy or by indexing the diffraction pattern (JCPDS card 33-945). The pressure-amorphized samples were coated on one side with a thin layer of amorphous carbon to prevent charging in the beam.

Figure 1 is a high-resolution image representative of the 20.0-GPa sample. Quartz lattice fringes can be seen; the grains range from ~20 to 50 Å in diameter. The observation of microcrystallites is in agreement with the work of Hemley *et al.* who observed x-ray diffraction peaks from α-quartz samples at this pressure [2]. We found that the 30.5-GPa sample showed diffuse halos in its electron diffraction patterns. A typical image and the corresponding diffraction pattern are shown in Fig. 2. The inserted diffraction pattern shows clearly that the 30.5-GPa α-quartz sample is amorphous. The larger section of Fig. 2 is an image of the pressure-amorphized quartz. A through-focus series of images was taken to ensure that there were no artifacts in the image. The general morphology of the images, like that shown in Fig. 2, is similar to other high-resolution micrographs of melt-quenched and sol-gel prepared amorphous silica samples [12,23].

It is well known that electron irradiation can amor-

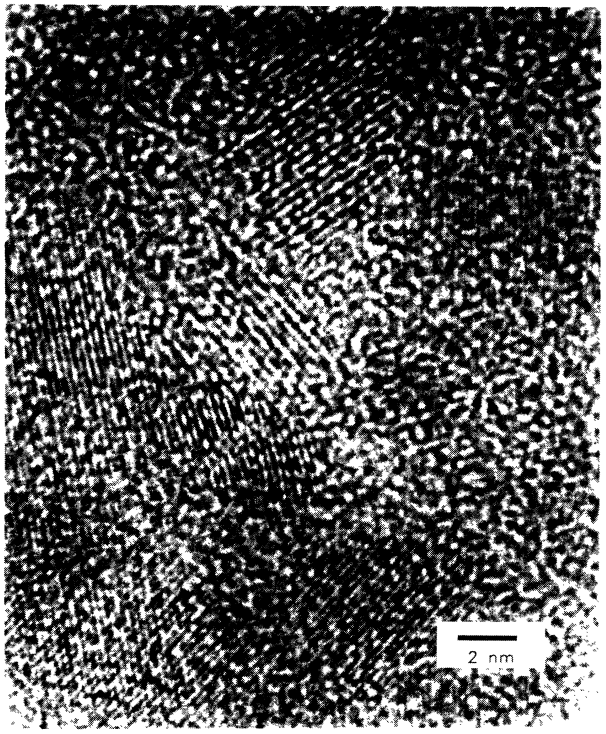

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FIG. 1. High-resolution electron micrograph of α-quartz after pressurization to 20.0 GPa.

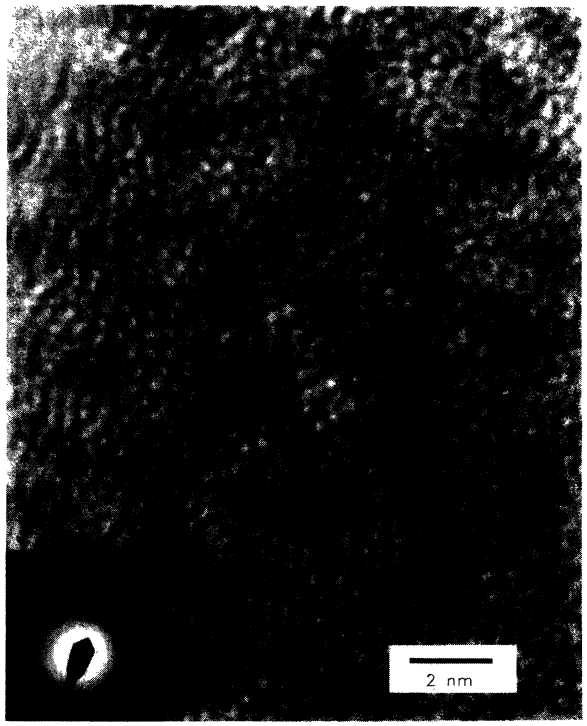

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FIG. 2. High-resolution electron micrograph of α-quartz after pressurization to 30.5 GPa. Inset: The diffraction pattern from this section. The image shown here was taken from a particle sitting over a hole in the holey carbon grid.

phize α-quartz [24–26]. Gopal and Mitchell reported that the total electron flux, at 400 kV, must be greater than 10^{18} $e/\mathrm{cm}^2\mathrm{sec}$ to induce a crystalline-to-amorphous transformation [24]. Accordingly, we kept the electron irradiation below this value during our measurements; typically, the electron flux was on the order of 10^8 $e/\mathrm{cm}^2\mathrm{sec}$ as calculated from the screen current of 19 $\mathrm{pA/cm}^2$. Additionally, α-quartz has been successfully imaged by electron microscopy without beam damage at 200 kV [27–29]. The electron flux threshold for amorphization is lower for 200-kV than for 400-kV accelerating voltages.

We conclude that the α-quartz sample pressure amorphized at 30.5 GPa has no translational order down to the atomic level: There are no vestiges of the sample's initial crystallinity. While the measurements reported here do not show that pressure-amorphized α-quartz and silica glass have the same microstructure, the results do show that both amorphous solids lack translational order on the same length scale. Although the x-ray diffraction patterns and Raman spectra of pressure-amorphized α-quartz and densified silica glass are very similar, there are some fundamental differences between the two amorphous states [1,2,22,30]. McNeil and Grimsditch's high-pressure Brillouin scattering measurements showed that pressure-amorphized (25 GPa) α-quartz, unlike silica glass, is not elastically isotropic: It retains a memory of its initial crystal orientation [22]. The combination of the HRTEM measurements reported here and the results of the Brillouin scattering studies document a most unusual material: an anisotropic solid that is amorphous at the atomic level. Indeed, a unique aspect of pressure-induced amorphization is the preparation of solids that have properties not often found in their melt-quenched analogs [8].

Last, a controversial aspect of amorphous solids is the degree of structural order present at length scales of 20 Å [31]. Pressure-induced amorphous states offer the promise of a deeper understanding of the medium-range ordering present in amorphous solids because the materials are prepared in a smooth and continuous fashion from a well-characterized crystalline state. It would be interesting to compare the images reported here to high-resolution images calculated by multislice methods based on the high-pressure structures of α-quartz as predicted by first-principles calculations [17–19].

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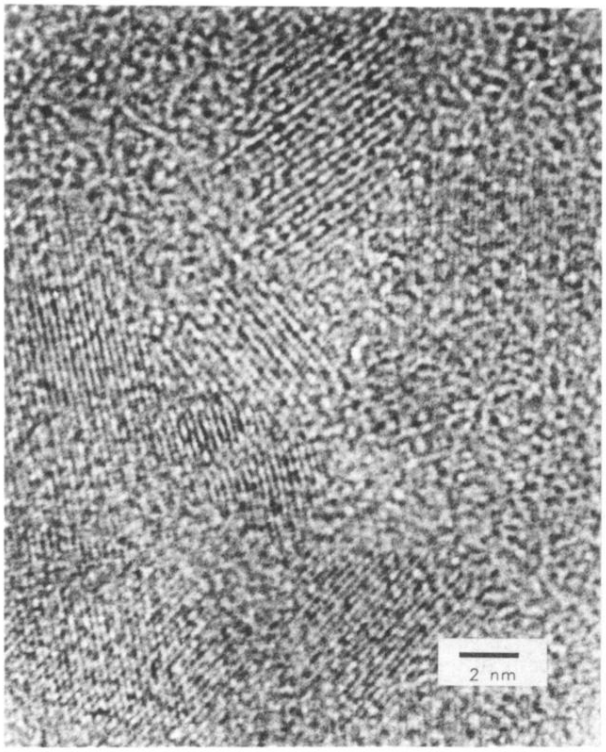

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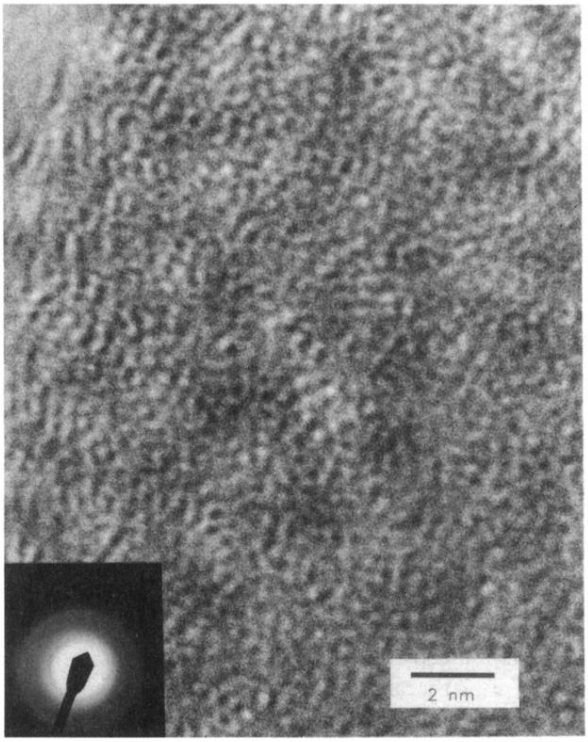

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FIG. 2. High-resolution electron micrograph of α-quartz after pressurization to 30.5 GPa. Inset: The diffraction pattern from this section. The image shown here was taken from a particle sitting over a hole in the holey carbon grid.