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Phase changes induced in hexagonal boron nitride by high energy mechanical milling

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Six crystallographic forms of BN have been reported: hexagonal (*h*-BN), cubic (*c*-BN), rhombohedral, wurtzite, orthorhombic, and monoclinic. Only the first two of these have engineering applications. Cubic BN is prepared by a high-pressure, high-temperature process and is valued as an ultrahard material for cutting and grinding tools. Hexagonal BN is the most common form of the material and serves as a soft refractory material with high lubricity and high electrical resistivity. BN has also been prepared in an amorphous state (*a*-BN) [1, 2]. Bulk *a*-BN prepared by a process similar to that used to produce *c*-BN has been reported to be exceptionally hard [3].

The equilibrium phase diagram for BN indicates that *c*-BN is the thermodynamically stable phase under ambient conditions [4]; however, the transformation of *h*-BN to *c*-BN is difficult to achieve. This transformation is hindered by the sluggish kinetics of the process; commercial *c*-BN production uses high temperatures, high pressures, and catalysts to transform *h*-BN to *c*-BN [5, 6].

Mechanical milling of powders can lead to formation of new equilibrium or metastable phases [7–9]. Previous work has shown that ball milling *h*-BN can transform it to *c*-BN [1, 2]. In one study, *h*-BN milled in a planetary mill transformed completely to *c*-BN at 1170 K without a catalyst; in other studies milled *h*-BN transformed to nano-crystalline *h*-BN, turbostratic BN, and *a*-BN [10]. In yet another investigation, an Ar ion beam created such high defect densities in an *h*-BN film that it transformed to *c*-BN [11, 12] without the high pressures and temperatures needed in commercial *c*-BN production.

Although the *h*-BN to *c*-BN transformation has received considerable attention, less study has been devoted to formation and characterization of the *a*-BN phase. This project was designed to produce *a*-BN by high energy milling, measure its properties, and study its stability at elevated temperature. These experiments milled −325 mesh *h*-BN powder in Spex 8000 mills with hardened steel vials and balls. All Spex milling was done with a 5:1 ball-to-charge mass ratio. The powders were maintained in a dry, inert gas atmosphere throughout powder loading and milling.

The Spex-milled powder specimens were analyzed by XRD to determine the degree of amorphization induced by the milling. XRD alone cannot provide a definitive determination of amorphization in nano-sized crystalline powder due to the peak broadening effect from very fine particle size, but it does provide a general indication of the degree of amorphization. The XRD patterns generated from *h*-BN powders Spex-milled for

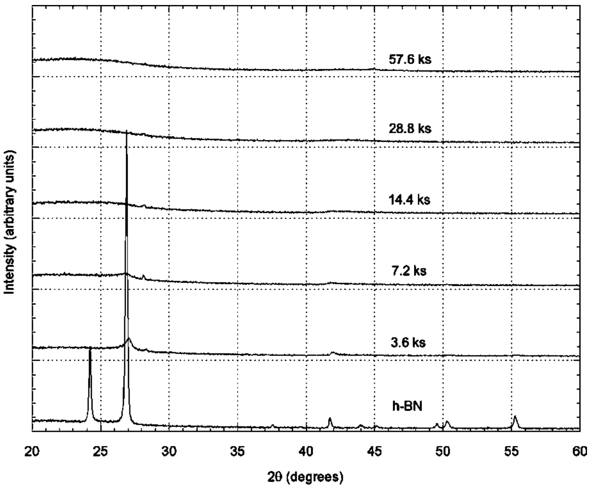

Figure 1 XRD patterns for *h*-BN powder milled in a Spex flat steel vial for the time periods marked on the figure. The lowest curve is from unmilled *h*-BN powder.

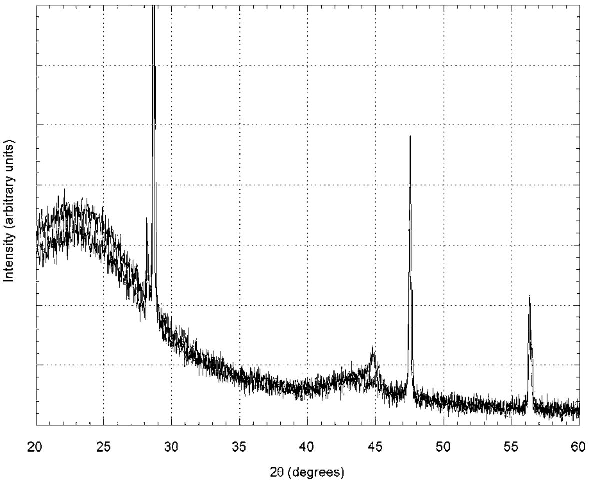

Figure 2 XRD spectra of *h*-BN powder milled 72 ks (lower curve) and 288 ks (upper curve). The three large peaks are from Si powder added to the specimen as an internal standard. The smaller peak at 44.7 ° is thought to be the Fe (110) peak introduced from steel mill vial and media wear debris; note that this peak is more pronounced in the pattern from the powder given a longer milling time.

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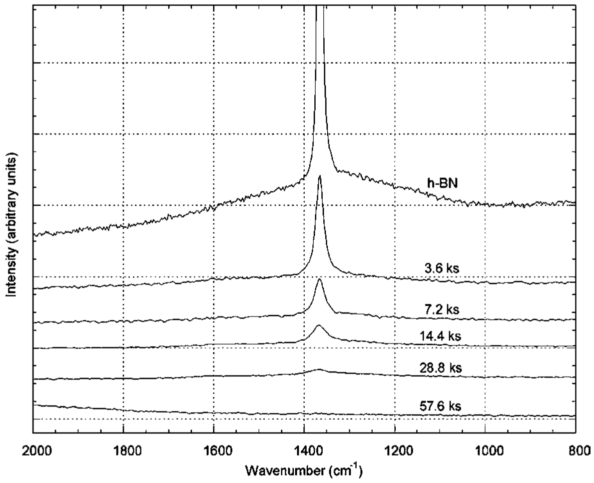

Figure 3 Raman spectra for unmilled *h*-BN powder (top curve) and for BN powder Spex milled for the time intervals marked.

more than 7.2 ks (Fig. 1) indicate that the material was predominantly amorphous.

Longer milling times did not improve the degree of amorphization; the XRD patterns for two specimens of *h*-BN milled for 72 ks and 288 ks (Fig. 2) are nearly identical to those from the powders milled for 14.4 to 57.6 ks. Moreover, very long milling times increase Fe contamination from accumulated mill vial and media wear debris. The peak near 45 ° in Fig. 2 does not correspond to any *h*-BN or *c*-BN peaks but matches the highest intensity Fe peak (110) at 44.67 °. X-ray fluorescence analysis indicated that the sample milled for 288 ks contained 7.4 wt% Fe.

A second measure of the degree of amorphization of the milled powder was provided by Raman spectroscopy performed on powder milled for 3.6, 7.2, 14.4, 28.8, and 57.6 ks. A Bruker model RFS 100/S FT-Raman spectrometer was used with Nd:YAG laser radiation (1064 nm wavelength) for excitation. The single large Raman peak in *h*-BN shown in Fig. 3 results from the strong sp^2 bonding within the atom layers. This technique fails to detect peaks for the weaker π bonds between the layers. The strong Raman peak in unmilled *h*-BN diminished as milling time increased, which supports the conclusion that the powder became more amorphous as milling progressed.

Transmission electron microscopy (TEM) was performed in a Philips CM30 300 kV microscope to view the powders and to perform electron energy loss spectroscopy (EELS) analysis on milled powder. A TEM image obtained from powder milled 57.6 ks (Fig. 4) shows an average particle size estimated to be 10 to 20 nm. The diffuse rings in the selected area diffraction (SAD) pattern suggest a low degree of crystallinity, which is consistent with an amorphous or nearly amorphous material. The lower energy loss portion of the EELS spectrum along with the spectra for *h*-BN and *c*-BN are shown in Fig. 5. The *h*-BN spectrum was obtained from the unmilled powder, and the *c*-BN spectrum was obtained from an EELS spectra database. The milled BN powder displays a peak for the weak *h*-BN π bonding; this peak is absent in *c*-BN. This suggests that the bonding in the milled powder more closely matches the bonding in *h*-BN, but there were differences between the spectra of the milled powder and

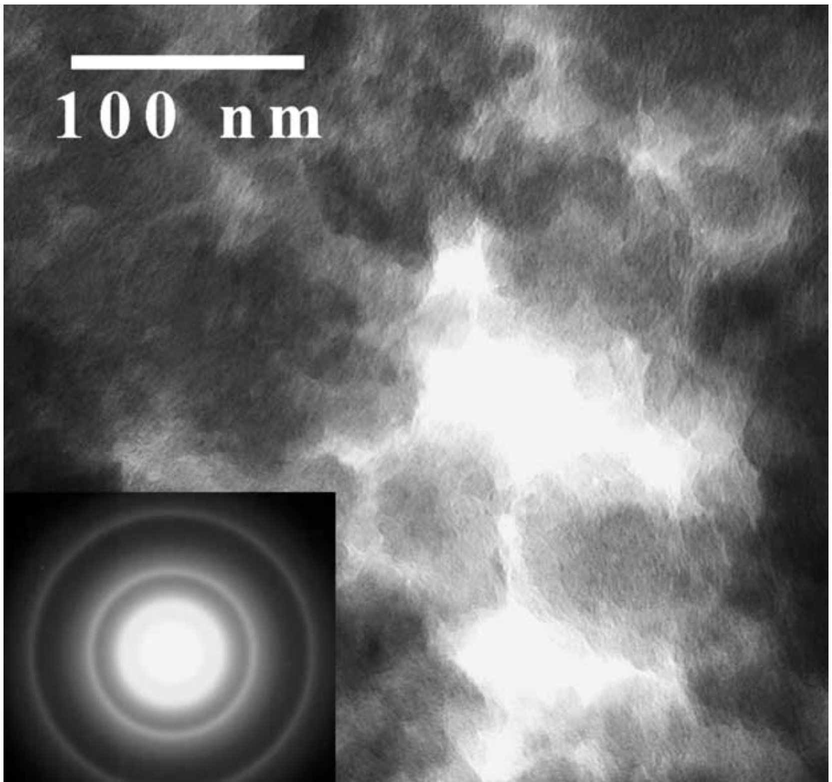

Figure 4 TEM image and selected area diffraction pattern of powder milled 57.6 ks. The specimen was prepared by floating loose powder on a graphite grid. Note that the selected area diffraction pattern shows diffuse rings, but does not appear completely amorphous.

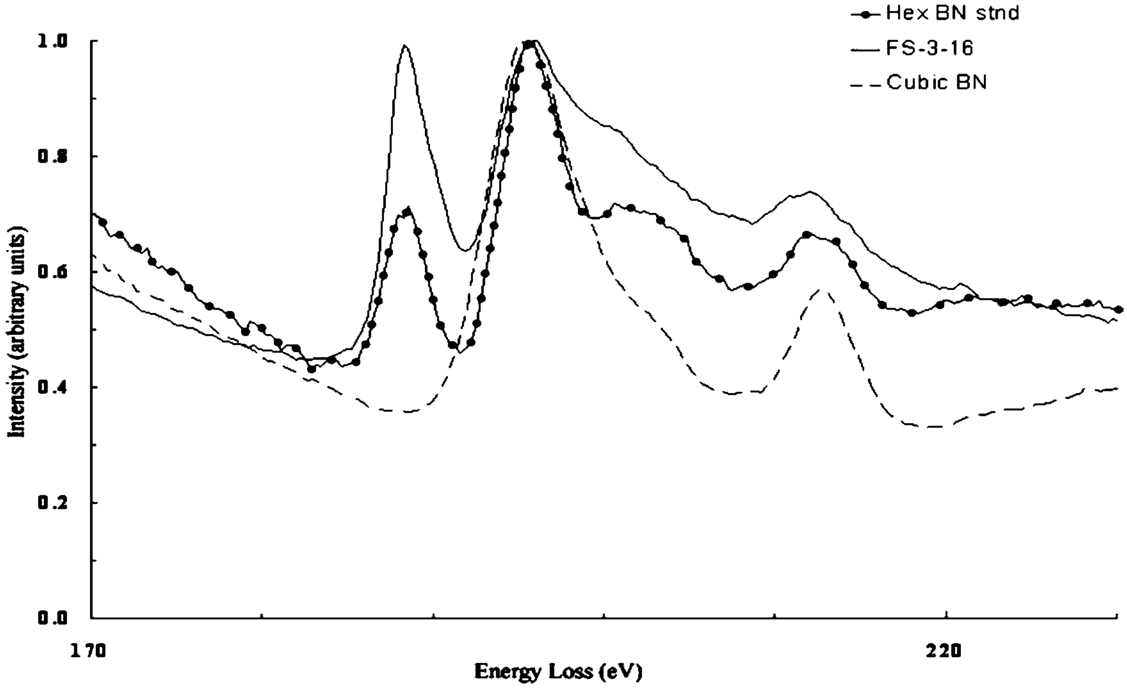

Figure 5 Low energy loss portion of EELS spectra of Spex milled BN (labeled FS-3-16), h-BN, and c-BN. Note that the peak at 188 eV attributed to π bonding is observed in the milled BN and h-BN, but this peak is absent in c-BN.

the unmilled h-BN. This could be due to some of the sp^2 bonds being transformed to sp^3 hybridization, as has been noted in other investigators' EELS analysis of milled BN [1].

The second part of this project was devoted to measuring the stability of the a-BN formed by milling at elevated temperature. A sample milled 57.6 ks was analyzed by differential thermal analysis (DTA) to determine if any exothermic crystallization events occurred during heating. Both the sample and a high-purity powdered alumina standard were contained in alumina crucibles and heated at 0.33 K/s to 1770 K in a Perkin Elmer DTA 7 analyzer. Amorphous material might be expected to crystallize to form the equilibrium crystalline phase. No exothermic crystallization events were recorded, suggesting that either a-BN is stable up to 1770 K or the crystallization kinetics are slow.

Although no thermal transformations were detected with DTA, truly amorphous material should crystallize if held long enough at a sufficiently high temperature, and several heat treatments were performed on a-BN powder followed by XRD, Raman, and TEM analyses to search for a transformation missed by DTA.

A series of heat treatments was performed at temperatures ranging from 1370 to 2220 K to assess the stability of the a-BN. Powders heat treated at 1370 K were sealed in fused-silica tubes back-filled with Ar; heat treatment times were 3.6, 14.4, 57.6, and 720 ks. A heat treatment was also performed at 1770 K in an alumina crucible in flowing Ar. The XRD patterns (Fig. 6) from these five samples showed little indication of devitrification. A small peak at 28.1 ° ($d = 0.318$ nm) is discernible on most of the patterns of milled material

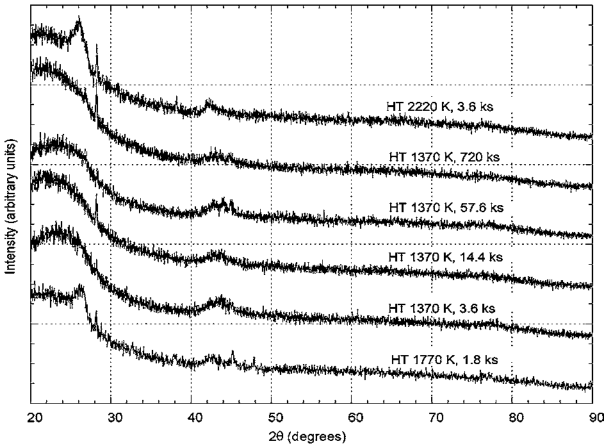

Figure 6 XRD spectra of Spex milled BN powder heat treated under the conditions marked on the curves.

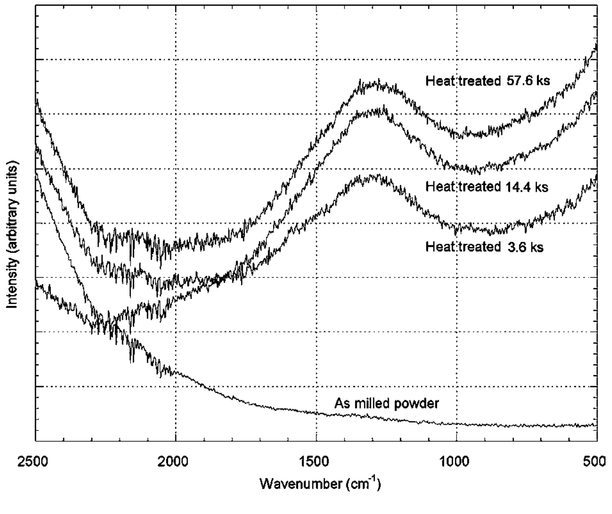

Figure 7 Raman spectra of powder, as milled and heat-treated at 1370 K for the times marked on each curve.

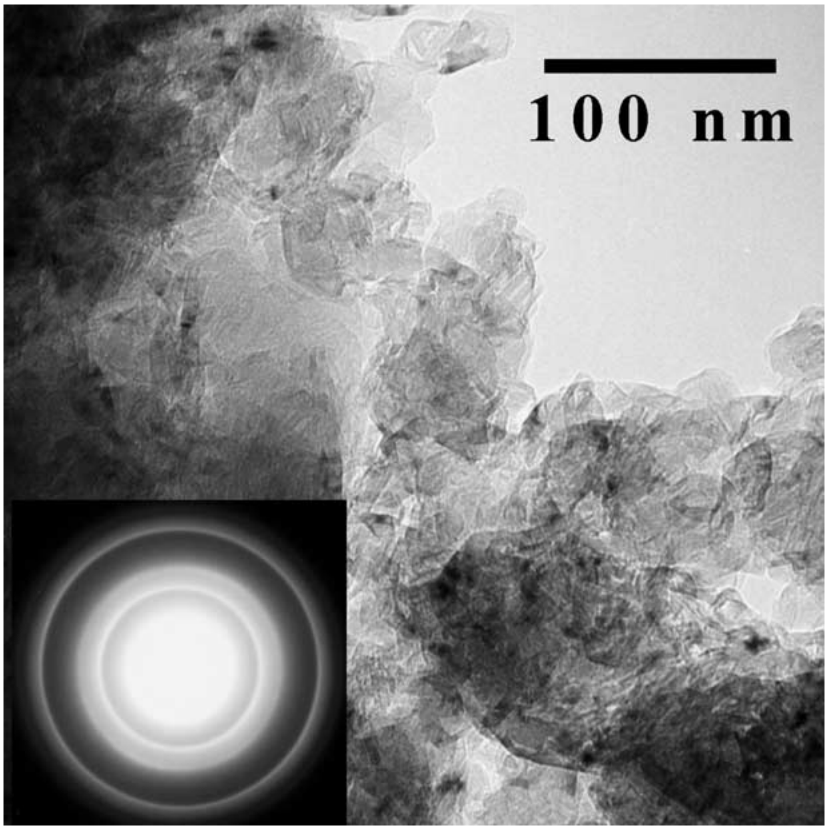

Figure 8 TEM image of powder heat treated at 2220 K for 3.6 ks.

in Figs 1 and 6. The strongest *h*-BN peak lies at 26.8 ° ($d = 0.333$ nm), and the 28.1 ° peak does not index to any polymorph of any of the cataloged binary compounds involving B, N, O, or Fe; its origin remains unknown.

A final heat treatment was performed in an alumina crucible at 2220 K for 3.6 ks in flowing N_2. After the heat treatment, this sample displayed small, crystalline "whiskers" at the crucible rim that may have formed from sublimation and condensation of the BN. The XRD analysis of this powder annealed at 2220 K is the top curve in Fig. 6. This sample appears more crystalline than any of the other heat-treated powders. It has a larger, sharper peak close to the location of the most intense *h*-BN peak. Even after annealing at 2220 K, the sample appears incompletely crystallized. The broadening and reduction in intensity of the peaks in the amorphous powder is probably due to the small particle size, but the absence of larger peaks after this highest temperature heat treatment suggests that *a*-BN is remarkably resistant to devitrification.

Raman spectroscopy was performed on the 3.6, 14.4, and 57.6 ks samples after their 1370 K heat treatments. Fig. 7 shows that even the briefest heat treatment at 1370 K began to reinstate the normal *h*-BN Raman peak at a wavenumber of 1370 cm^{-1}.

TEM analysis was also performed on the powder heat treated at 2220 K (Fig. 8). This image appears more crystalline than the image from the powder before heat treatment (Fig. 4). The powder particles are sharper and better defined, and the rings in the selected area diffraction pattern are less diffuse than those in Fig. 4, indicating a higher degree of crystallinity.

In summary, it was found that *a*-BN powder can be produced by Spex milling at relatively short milling times. XRD, Raman spectroscopy, EELS, and SAD in TEM all indicated that the material was essentially amorphous. The *a*-BN produced was highly resistant to crystallization, even at relatively high temperatures. Heat treatments at temperatures as high as 2220 K resulted in only partial devitrification of the *a*-BN.

Acknowledgments

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