



## Shear amorphization of boron suboxide

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We report for the first time the shear-induced local amorphization of boron suboxide subjected to nanoindentation. The amorphous bands have a width of  $\sim 1\text{--}3$  nm and a length of 200–300 nm along the (0111) crystal plane. We show direct experimental evidence that the amorphous shear bands of boron suboxide are driven from the coalescence of dislocation loops under high shear stresses. These observations provide insights into the microscopic deformation and failure of high-strength and lightweight ceramics. © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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Superhard materials with strong covalent bonds often fail in a brittle manner dominated by normal stresses at room temperature. Lightweight boron suboxide ( $B_6O$ ) is a superhard material with a hardness comparable to boron carbide ( $B_4C$ ) and cubic boron nitride (BN) ceramics [1–5]. The unusual hardness of  $B_6O$  comes from its basic structure, which is composed of icosahedra ( $B_{12}$ ) and two oxygen (O–O) atom chains at the center of the rhombohedron, which is similar to 12-atom icosahedra and the three-atom chain configuration of  $B_4C$  [6–10]. Unlike  $B_4C$  and BN, which have been widely used in industry,  $B_6O$  has not been commercialized so far, partly because of the difficulty in obtaining full densification using conventional sintering methods. Therefore, the basic properties of this ceramic material have not been completely studied [4,11–13]. The potential applications of the  $B_6O$  ceramic in wear and hardfacing parts could be realized by understanding the underlying deformation and failure mechanisms under high contact pressures. In this letter, we report for the first time the microscopic evidence of amorphous  $B_6O$  that was produced by nanoindentation, indicating that the failure of  $B_6O$  is associated with shear amorphization.

$B_6O$  powders were synthesized from the mixture of crystalline boron ( $\beta$ -B) and amorphous boron oxide

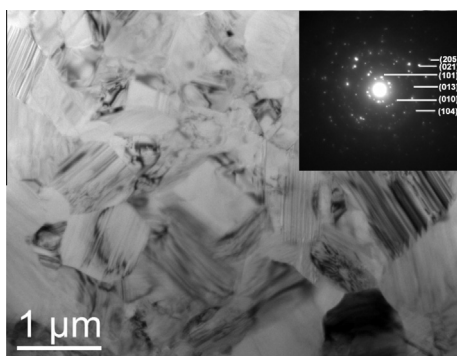
( $B_2O_3$ ) by a solid–liquid reaction. The  $B_6O$  powders were consolidated by the hot-pressing technique at 2173 K, 60 MPa for 1 h. A detailed synthesis procedure can be found in the previous report [14]. The relative density of bulk  $B_6O$  is  $\sim 97.5\%$  ( $2.55\text{ g cm}^{-3}$ ) of theoretical density ( $2.62\text{ g cm}^{-3}$ ). A series of indentation tests were performed on the smoothly polished  $B_6O$  surface at a constant loading force (1 N) and loading rate ( $\sim 14\text{ mN s}^{-1}$ ) using a dynamic ultra-microhardness tester (Shimadzu W201S) equipped with a Berkovich diamond indenter. The average measured hardness value was  $\sim 38$  GPa. Raman spectra were collected using a Renishaw 1000 spectrometer with an excitation wavelength of 633 nm produced by an argon laser source. The beam size of the laser spot is about 1  $\mu\text{m}$ . The transmission electron microscopy (TEM) specimen of the as-sintered  $B_6O$  was sliced from bulk and mechanically ground to  $\sim 150\text{ }\mu\text{m}$ . The surface of the thin specimen was then dimpled to a thickness of about 20  $\mu\text{m}$  and ion-beam milled to obtain electron transparency (Fischione 1010 Model). The cross-sectional TEM specimens of the indented  $B_6O$  samples were prepared by the lift-out technique using a focused ion beam (FIB) milling system (JEOL JIB-4600F) [15]. The cross-sectional indentation samples were subjected to low-voltage ion milling (i.e. 900 V) in a Fischione 1040 Nanomill to remove the damaged layers without altering the surface chemistry before the TEM analysis. The microstructures of the as-prepared and deformed samples were characterized with a JEOL JEM-2100F transmission electron

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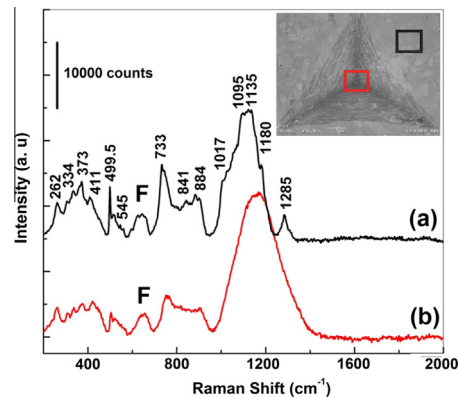
microscope equipped with a Gatan imaging system for electron energy loss spectroscopy.

A typical TEM image of the as-sintered  $B_6O$  ceramic shows fine and tight grained microstructure (Fig. 1). The grain size distribution of  $B_6O$  ranges from 100 nm to 2  $\mu\text{m}$ , with a mean size  $\pm$  SD of about  $400 \pm 190$  nm. Numerous stacking faults and twin bands can be seen in the  $B_6O$  grains. The selected area electron diffraction (SAED) pattern (Fig. 1, inset) reveals roughly equiaxed grains with random orientations separated by high-angle grain boundaries (GBs) (Fig. 1). High-resolution TEM observations (not shown here) display sharp GBs without any amorphous or crystalline interfacial phases.

To explore the possible phase transitions induced by the nanoindentation, Raman spectroscopy was employed to characterize the residual indentation impressions of  $B_6O$ . Figure 2 shows the typical Raman spectra in the range of 200–2000  $\text{cm}^{-1}$  acquired from the pristine and residual indented region of  $B_6O$ . The inset scanning electron microscopy (SEM) image shows the residual indentation at a load of 1 N. A number of characteristic Raman bands from the pristine  $B_6O$  reflect the complex atomic structure of  $B_6O$ . In the low-frequency region, a peak with an uncertain origin is located at 262  $\text{cm}^{-1}$  [16]. The band at 373  $\text{cm}^{-1}$  is associated with the motion of O–O pairs and that at 499.5  $\text{cm}^{-1}$  is related to the symmetric stretching of the O–O pairs [17]. The peak around 545  $\text{cm}^{-1}$  is attributed to the motion of icosahedra boron atoms about oxygen atoms at the ends of the each chain [17,18]. In the high-frequency region, the multiple bands at 734, 838, 882, 1017, 1089, 1134 and 1178  $\text{cm}^{-1}$  have been assigned to intra- and inter-icosahedral vibrations of boron atoms [16–18]. Apart from the vibration modes of  $B_6O$ , the additional peaks at 335, 411 and 516  $\text{cm}^{-1}$  might be associated with oxygen deficiency in  $B_6O$ , and the weak band at 1285  $\text{cm}^{-1}$  is attributed to unreacted boron oxide ( $B_2O_3$ ) [18]. The broad peak between 600 and 700  $\text{cm}^{-1}$  is the result of the strong fluorescence (F) of the 633 nm (red) laser used in this study [17]. Compared with the Raman spectrum of the as-sintered  $B_6O$ , the spectrum obtained from the center of a residual impression shows the obvious changes in the Raman intensity and peak position (Fig. 2). The considerable peak



**Figure 1.** A typical TEM image of polycrystalline  $B_6O$  synthesized at 60 MPa and 2173 K for 1 h. The SAED pattern of  $B_6O$  is shown in the inset.



**Figure 2.** Representative Raman spectra of (a) the  $B_6O$  pristine surface and (b) residual indentation obtained using an argon ion laser with an excitation wavelength of 633 nm. The inset SEM image shows the Berkovich-indentation impression at a load of 1 N.

broadening and red shift of the intra- and inter-icosahedral vibrations indicate that a certain structural disorder associated with the  $B_{12}$  icosahedra is introduced by the nanoindentation experiment. However, no additional  $B_6O$  Raman bands can be found and none have disappeared, which appears to be inconsistent with a previously reported diamond anvil cell (DAC) experiment in which single-crystal rhombohedral  $B_6O$  is observed to transform into an amorphous  $B_2O_3$  and a glassy boron phase under a quasi-static pressure of 90 GPa [19]. Since the nanoindentation contact pressure of 30–40 GPa is significantly lower than that of the DAC experiment, it would appear to be insufficient to cause the global phase transition of  $B_6O$  and, instead, only produces local structural changes accompanied by inelastic deformation driven by shear components.

In order to verify the structural transformation caused by nanoindentation, FIB milling was employed for the preparation of cross-sectional TEM specimens from the residual indentation of  $B_6O$ . The detailed procedure for the lift-out technique using FIB milling has been described in our previous report [15]. The low-magnification bright-field and dark-field scanning transmission electron microscopy (STEM) images of  $B_6O$  beneath the indenter region show several crack regions and deformation shear bands with variations in contrast, which are indicated with black and white arrowheads (Fig. 3(a) and (b)). Moreover, a number of dislocations, which are rarely seen in the as-prepared samples, appear in the vicinity of the deformation bands and microcracks, suggesting that conventional dislocation plasticity is involved in the indentation deformation as well as microcracks and shear bands. The deformation shear bands usually have a width of  $\sim 1$ –3 nm and a length of 200–300 nm. High-resolution STEM reveals the loss of lattice fringes in the bands (Fig. 3(c)). The fast Fourier transform (FFT) pattern taken from the band shows a diffuse halo without any crystalline diffraction spots, which confirms the amorphous nature of the shear band (inset B). By contrast, FFT patterns taken from both sides of the band reveal the parent crystal structure to be  $\langle 10\bar{1}1 \rangle$  rhombohedral  $B_6O$  (inset A and C) (Fig. 3(c)). The angular mismatch between the

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