Dislocation-mediated shear amorphization in boron carbide

Kolan Madhav Reddy1, Dezhou Guo2, Shuangxi Song1, Chun Cheng3, Jihu Han3, Xiaodong Wang1, Qi An2, Mingwei Chen3,4,5*

The failure of superhard materials is often associated with stress-induced amorphization. However, the underlying mechanisms of the structural evolution remain largely unknown. Here, we report the experimental measurements of the onset of shear amorphization in single-crystal boron carbide by nanoindentation and transmission electron microscopy. We verified that rate-dependent loading discontinuity, i.e., pop-in, in nanoindentation load-displacement curves results from the formation of nanosized amorphous bands via shear amorphization. Stochastic analysis of the pop-in events reveals an exceptionally small activation volume, slow nucleation rate, and lower activation energy of the shear amorphization, suggesting that the high-pressure structural transition is activated and initiated by dislocation nucleation. This dislocation-mediated amorphization has important implications in understanding the failure mechanisms of superhard materials at stresses far below their theoretical strengths.

INTRODUCTION

Dislocations not only play an important role in strength and ductility of engineering materials but also are responsible for incipient plasticity of crystalline solids (1). However, for superhard materials with strong covalent bonds, such as a diamond and boron carbide (nominally B4C), dislocation activities and thus dislocation plasticity are not expected under conventional loading conditions at room temperature due to high lattice resistance and barrier energy (2, 3). B4C is an important armor material owing to its exceptional light-weight (~2.5 g/cm3), together with the ultrahigh hardness and high Hugoniot elastic limit (3, 4). The extraordinary physical and mechanical properties of B4C have been attributed to the unique crystal structure, which is composed of 12-atom icosahedra connected by a 3-atom chain in a rhombohedral unit cell (5, 6). However, B4C undergoes an anomalous reduction in shear strength at a critical shock pressure of ~20 to 26 GPa (7–10). Transmission electron microscopy (TEM) has revealed that the shear softening of B4C is associated with localized amorphization (11), which has been confirmed by high-pressure diamond anvil cell and indentation experiments as well as dynamic scratching and laser shocking (12, 13). Quantum mechanics simulations also verify the pressure-induced amorphization in B4C (13–15). However, different amorphization mechanisms have been proposed from carbon cluster formation to three-atom-chain bending and icosahedral cluster breaking. It remains unclear how the localized amorphization and thereby material failure take place in the superhard materials at applied stresses far below the theoretical strength (higher than 39 GPa) predicated by density functional theory (16, 17). In particular, experimental insights into the amorphization mechanisms are still missing.

Nanoindentation has been proven to be a powerful technique to characterize mechanical response of materials because of the ultra-high resolutions in both forces and displacements (18). The discontinuity in the nanoindentation load-displacement curves, referred to as a pop-in, has been widely used to study stress-induced phase transformation, dislocation activation, and shear instability, which occur within a small volume of materials beneath a diamond indenter (18, 19). The transition portions of load-displacement curves from elastic to inelastic have been ubiquitously used to assess the activation volume and barrier energy of dislocation nucleation in crystalline materials and shear band initiation in disordered glasses (18–20). Since the amorphization of B4C only causes a very small volume change of ~4% reduction, the onset of the first-order phase transformation has not been detected by pressure-volume experiments, such as diamond anvil cells (12). However, the localized amorphization of B4C results in the formation of nanosized shear bands (11–17, 21, 22), similar to glassy materials (23). Therefore, the detection and quantitative measurements of the shear band initiation in B4C will provide a unique way to explore the kinetics of amorphization and thus underlying mechanisms.

Here, we use depth-sensitive nanoindentation to probe the structural evolution of single-crystal B4C. The pop-in displacements in load-depth curves are demonstrated to originate from the onset of amorphous shear bands, and the corresponding activation volume and energy are close to those of dislocation nucleation and propagation. TEM characterization provides compelling evidence that the amorphization of B4C is mediated by dislocations, rather than a direct crystal-to-amorphous transition by chemical bond breaking.

RESULTS

Pop-ins in B4C single crystals

The nanoindentation experiments of a single-crystal B4C are schematically illustrated in Fig. 1A, together with possibly activated slip systems in the B4C single crystals (Table 1). Raman spectra taken from the (214), (223), and (104) single crystals are displayed in fig. S1, showing the clear difference in relative intensity of sharp peaks at 482- and 534-cm−1 modes, which are associated with stretching of three-chain atom chains and rigid rotation of icosahedra in B4C (Supplementary Text). The load-displacement curves of the (214)
crystal at a loading rate of 0.125 mN/s are shown in Fig. 1B. When the applied load \( (p) \) is smaller than ~7 mN, the loading-unloading curves are fully overlapped (fig. S2), suggesting that only elastic deformation takes place. When the applied load is increased to 25 mN, a sudden displacement (i.e., pop-in) occurs during loading as marked by a box and highlighted by the inset in Fig. 1B. The transition from elastic to permanent deformation by a pop-in event has a displacement of ~3.5 nm. The pop-in phenomenon is often related to the incipient plasticity by the nucleation and propagation of a dislocation or twin along a specific slip system of crystals \((1, 16)\), or a shear band formation in amorphous materials \((17–19)\). Although the mechanical properties and stress-induced amorphization of B\(_4\)C have been extensively studied using instrumented indentation in the past two decades, the pop-in events in load-displacement curves have not been observed before \((3, 4, 13, 20, 22)\). We noticed that the pop-ins are only visible at lower loading rates (Fig. 1C) and disappear when the loading rate is higher than ~0.125 mN/s. Although the loading rate does not have an obvious effect on the hardness of the single-crystal B\(_4\)C (Fig. 1D), the rate dependence of the pop-in events indicates that the initiation of the stress-induced structural instability may be time dependent and governed by a thermal activation process. Although the displacement resolution of the nanoindentation may also affect the visibility of pop-ins in loading curves, the several-nanometer displacements of pop-ins are one order of magnitude larger than the resolution of our instrument at the loading rate of 1.0 mN/s. Besides the loading rate dependence, the pop-in events also depend on crystallographic orientations of B\(_4\)C single crystals. Similar to the (214) crystal (Fig. 1B), the pop-ins can be well identified in the loading curves of (223) crystals at a slow loading rate of 0.125 mN/s (fig. S3). However, for (104) crystal, the loading and unloading curves smoothly change with displacement, and a pop-in event cannot be seen at the slow loading rate of 0.125 mN/s (fig. S4).

Table 1. Summary of possible slip systems with their Burgers vectors and lattice plane shift in B\(_4\)C.

| Slip system | Burger vector | Lattice plane shift |
|-------------|---------------|---------------------|
| (122)(20T)  | (1T2)         | ~1.7 Å              |
| (303)(212)  | (102)         | ~1.3 Å              |
| (113)(1T0)  | (003)         | <1.0 Å              |
**Microstructural characterization of pop-ins**

To understand the underlying mechanisms of the pop-in displacements, we investigated the microstructure of the deformed regions underneath indenter, which undergo the discrete deformation. Figure 2A is a representative scanning electron microscopy (SEM) image of an indentation impression produced on the (214) crystal at the maximum load of 25 mN and the loading rate of 0.125 mN/s. The characteristics of slip bands are visible on the three faces of the Berkovich impression. No cracks can be observed within and at the corners of the indent region. Raman spectra taken from the indented region show three additional broad peaks at 1340, 1550, and 1810 cm\(^{-1}\) as compared with the pristine single-crystal B\(_4\)C (Fig. 2B). These Raman bands have been identified as the characteristic Raman modes of amorphous B\(_4\)C (a-B\(_4\)C) (3–4, 12–13, 21–22). TEM image taken from the cross-sectioned indented region of fig. S5 displays with a shear band of ~300 nm in length and ~1 to 4 nm in width (Fig. 2C). High-resolution TEM (HRTEM) image (Fig. 2D) further confirms the amorphous nature of the shear band. The diffuse halo ring of the fast Fourier transform pattern (FFT) (the inset b of Fig. 2D) further confirms the amorphous nature of the shear band as compared to the crystalline matrix on either side of [20\(\bar{T}\)] zone axis (the inset a of Fig. 2D). An HRTEM image reveals that the formation of an amorphous shear band is on a (122) plane. A series of HRTEM images obtained along the amorphous band confirmed that the deviation is <2° on either side of crystal plane. The observations of amorphous band width in the range of ~1 to 4 nm are consistent with previous experimental and simulations studies (3, 11–17, 22). The zoom-in lattice images (Fig. 2, E and F) show that the displacement generated by the amorphous band can be described by a pair of dislocation dipoles with the Burgers vector of \(\langle 1\bar{1}2\rangle\) and the relative lattice plane shift of ~1.7 Å as marked by the loop in Fig. 2 (E and F). Simulated TEM images overlaid on experimental images of Fig. 2 (E and F) suggest that the amorphization is along the (122) plane of the rhombohedral B\(_4\)C unit cell. We also characterized the structural evolution of the (223) crystal, which also experiences the pop-in displacements. Similar to the (214) crystal, nanosized amorphous bands with shear displacements can also be observed and the relative lattice plane shift is of ~1.3 Å as shown in figs. S6 and S7 and Table 1. These observations demonstrate that the amorphous band formation is responsible for the discrete pop-in events. The localized amorphization results in shear deformation and appears to be associated with the dislocation formation. In contrast, multiple amorphous bands can be faintly identified from the deformed (104) crystal (fig. S8), indicating that this orientation is not favorable to access shear deformation along the indentation projection by a single shear band as shown schematically in Fig. 1A and Supplementary Text. Upon examination under the same orientation of (1\(\bar{T}\)0) for the (104) crystal (fig. S9), we have noticed that the amorphous bands are apparent and dislocation nucleation can be seen along the (113) plane, suggesting that the indentation geometry is important to activate preferentially slip systems (Table 1). The smooth load-displacement curves of the (104) crystal may be caused by the activation of multiple shear bands, and the elastic-to-plastic transition takes place by continuous deformation, instead of a single pop-in event. In a similar way, a higher loading rate may also promote multiple shear band formation, while a lower loading rate provides sufficient time for a single shear band initiation with a visible pop-in in the load-displacement curves.

---

**Fig. 2. Microstructural characterization of (214) single crystal after nanoindentation testing.** (A) Scanning electron microscopy (SEM) image of nanoindentation impression of B\(_4\)C at the applied load of 25 mN. No cracks can be found at the corners of indent region. (B) Raman spectra taken from pristine B\(_4\)C (black curve) and residual indentation (red curve) of single-crystal B\(_4\)C, a.u., arbitrary units. (C) The cross-sectioned TEM image displaying a shear band with the length of ~300 nm and width of ~1 to 4 nm. (D) A magnified TEM image of shear band confirming amorphous structure along the (122) plane. Fast Fourier transform (FFT) pattern taken from the band shows the amorphous diffuse halo ring pattern (inset b). The inserted FFT pattern acquired from the lattice image corresponds to the [20\(\bar{T}\)] direction of rhombohedral B\(_4\)C (inset a). (E) High-resolution TEM (HRTEM) image displaying the shear displacement, equivalent to dislocation dipoles, at the origin of tip of the amorphous shear band. (F) HRTEM image acquired from the other end of the amorphous shear band revealing the shear displacement at the termination. The simulated images and atomic models are overlaid on the HRTEM images in (E) and (F), showing the consistence with the experimental lattice spacing of the [20\(\bar{T}\)] projection.
shear stresses ($\tau_{\text{critical}}$) under the Berkovich indenter are evaluated from the applied force ($P$) at the initialization of first pop-ins using the following equation (24)

$$\tau_{\text{critical}} = 0.31 \left( \frac{6PE^*}{\pi^2 R^2} \right)^{1/2}$$  

where $R$ is the tip radius of the indenter, and $E^*$ is defined as effective elastic modulus (~350 to 410 GPa). Correspondingly, the distributions of the critical shear stresses for both (214) and (223) crystals are stochastic and fall in a wide range from 23 to 38 GPa for the (214) crystal and 25 to 40 GPa for the (223) crystal (Fig. 3, A and D).

To determine the nucleation rate, activation volume, and activation energy of the first pop-in events from the loading curves, the statistical analysis of instantaneous shear stresses ($\tau$) beneath the indenter is given by Eq. 2 (25)

$$f = 1 - \exp\left(-\frac{\eta kT}{\tau \nu^* \exp\left(\frac{\tau \nu^*}{kT}\right)}\right)$$  

where $\eta$ is the nucleation rate, $\nu^*$ is the activation volume for the nucleation of pop-ins, $T$ is the testing temperature (herein, room temperature), $k$ is the Boltzmann constant, $\tau$ is the loading rate, and $\tau$ is the critical shear stress for the first pop-ins. Before the first pop-ins, the load-displacement curves are fitted to the Hertzian contact solution for determining the radius $R = \left(\frac{P_0}{3.4E^*h^2}\right)^{1/2}$, where $h$ maximum depth, and $E^*$ can be obtained from $E^* = \frac{1 - \nu_m^2}{E_m} + \frac{1 - \nu_i^2}{E_i}$ for elastically anisotropic specimen. Here, $E_m$ and $\nu_m$ are the Young’s modulus and Poisson’s ratio of specimens, and $E_i$ and $\nu_i$ are the Young’s modulus and Poisson’s ratio of the diamond indenter (26).
The cumulative distribution of the critical shear stress at the constant loading rate of 0.125 mN/s for the (214) crystal is shown in Fig. 3B. The activation volume $\upsilon^*$ and nucleation rate $\eta$ can be determined by the linear least-squares method by plotting $\ln \lfloor \ln(1 - f) \rfloor$ versus $\tau$ as shown in Fig. 3C. The activation volume $\upsilon^*$ is directly obtained from the slope of the plot, while $\eta$ is subsequently derived from the intercept. Also, we have estimated $\upsilon^*$ and $\eta$ of the (223) crystal by linear least-squares fitting of critical shear stress ($\tau$) (Fig. 3, E and F). The measured $\upsilon^*$ and $\eta$ for both (214) and (223) crystals are given in Table 2. The deviations of the linear fitting for Fig. 3 (C and F) could be related to the surface roughness variation and chemical and structural fluctuation of samples, which are commonly observed in stochastic indentation tests (24, 26). On the basis of the stochastic data analysis, the activation volumes of the first pop-ins are estimated to be ~2.5 Å$^3$ for the (214) crystal and ~1.8 Å$^3$ for the (223) crystal. Note that the volumes are just about one eighth the size of the B$_{12}$ icosahedron in the B$_4$C unit cell, suggesting that the initiation of the pop-ins and amorphization only requires a part of atoms within a unit cell of B$_4$C for the structural and dynamic transitions. We compared the estimated activation volumes and nucleation rates of the pop-in events of B$_4$C with those of metallic and ceramic crystals and amorphous alloys subjected to the similar loading conditions as shown in Table 2 (18–20, 25, 27). The small activation volumes are similar to those of dislocation nucleation in crystalline materials, but orders of magnitude smaller than that of shear band formation in amorphous alloys. The activation volumes of B$_4$C are too small to explain the first-order phase transition of amorphous transition (24, 25, 27–30). However, the underlying mechanisms of the localized crystal to amorphous transition have not been well understood because of the challenges of conventional microscopic diffraction and scattering techniques in detecting heterogeneous nanoscale transition under extreme loading conditions of high nonhydrostatic pressures and/or fast loading rates. Previous microscopic observations have found that the shear local amorphization often coincides with inherent planes of stacking faults and twins (14, 38), indicating certain correlation between amorphization and crystal defects. In this study, the small activation volume, slow nucleation rate, and lower activation energy derived from the stochastic analysis of the onset of amorphization, divulged by the pop-ins in load-displacement curves, provide kinetic evidence that the shear amorphization of B$_4$C is mediated by dislocation formation, rather than direct phase transition from crystalline to amorphous B$_4$C. We also estimated the activation energy $E_a$ of the first pop-ins using the nucleation rate equation (29), $n = \eta \exp(-\frac{E_a}{kT})$, where $k$ is the Boltzmann’s constant, $T$ is the temperature (herein, room temperature), $E_a$ is the activation energy for dislocation nucleation, $E_a = \Delta H - \tau \upsilon^*$, in which $\Delta H$ is the activation enthalpy, $\tau$ is the shear stress, and $\upsilon^*$ is the activation volume. The experimentally measured $\Delta H$ is 1.674 (± 0.004) eV (Supplementary Text and fig. S12) obtained from best fitting of cumulative load statistics function $f(P)$ using the equation given in the supplementary information of (25). From this analysis, we evaluated the activation energy of $E_a$≈1.6 ± 0.1 eV for both B$_4$C single crystals, which is consistent with the value estimated by electric field pulse experiments on the initialization of B$_4$C amorphization (30, 31) and falls in the range of dislocation nucleation and motion in covalently bonded inorganic materials (32, 33).

**DISCUSSION**

Shear amorphization has been widely observed in complex crystals, such as ice, minerals (e.g., $\alpha$-quartz and coesite), semiconductors (e.g., silicon and germanium), intermetallic (e.g., Ni$_3$Al and Ti$_3$Al), and covalently bonded boron-rich ceramics (B$_4$C, B$_{12}$O$_{25}$, and B$_{12}$P$_2$), and is generally related to shear-induced lattice destabilization (34–39). However, the underlying mechanisms of the localized crystal to amorphous transition have not been well understood because of the challenges of conventional microscopic diffraction and scattering techniques in detecting heterogeneous nanoscale transition under extreme loading conditions of high nonhydrostatic pressures and/or fast loading rates. Previous microscopic observations have found that the shear local amorphization often coincides with inherent planes of stacking faults and twins (14, 38), indicating certain correlation between amorphization and crystal defects. In this study, the small activation volume, slow nucleation rate, and lower activation energy derived from the stochastic analysis of the onset of amorphization, divulged by the pop-ins in load-displacement curves, provide kinetic evidence that the shear amorphization of B$_4$C is mediated by dislocation formation, rather than direct phase transition from crystalline to amorphous structures, as shown in the schematic diagram (Fig. 4). Separate HRTEM observations endow additional evidence to support the novel amorphization mechanisms in ultra-hard covalent materials. Although the underlying mechanisms of the dislocation-mediated amorphization require further theoretical and experimental investigations, it is apparent that the relatively low energy barrier of dislocation nucleation, in comparison with that of
the first-order phase transition, favors the activation of dislocations by nucleating new dislocations or motivating existing dislocations under high nonhydrostatic pressures (40). The high lattice resistance, arising from the strong covalent bonds, may prevent dislocation motion by conventional lattice sliding at room temperature, and instead, the large lattice distortion and symmetry breaking at dislocation cores can initiate amorphization and amorphous band formation under high shear stresses.

In summary, we used the depth-sensitive indentation technique to characterize the onset of shear amorphization in B₄C. Stochastic analysis of the first pop-in events, which correspond to the formation of amorphous shear bands, reveals the kinetic variables of shear amorphization. The measured activation volumes, activation energies, and nucleation rates from two single-crystal B₄C are consistent with those of dislocation nucleation in covalent ceramics and much lower than those of the direct crystal-amorphous transition. This finding provides new insights into the mechanisms of shear amorphization of B₄C. The novel amorphization mechanisms unveiled by this study may be applicable to the failure and damage of other ultrahard and ceramic materials under extreme loading conditions.

MATERIALS AND METHODS

High-quality B₄C single crystals were prepared using a float zone method. The single crystals of (214), (223), and (104) orientations were prepared from different runs and polished to have mirror finish surfaces for the nanoindentation experiments. These orientations have been confirmed to experience the amorphization transition under indentation and high-pressure diamond anvil cell experiments by in situ Raman spectroscopy and postmortem TEM characterization in our previous studies (9, 10, 19, 20). The crystallographic orientations of the single-crystal B₄C samples used this study are calibrated to be within 2° of their designed directions by x-ray diffraction. The Raman spectra taken from the polished (214), (223), and (104) surfaces illustrated in fig. S1 show the crystal orientation dependence of Raman modes. A nanoindenter (MTS G200, Oak Ridge, TN) with a Berkovich diamond indenter tip was used in this study. Before the measurements, the system was calibrated with a standard fused-silica specimen. A series of indentation tests with a spacing of 10 μm between the indents were conducted at loading rates ranging from 0.125 to 1.0 mN/s and a maximum load of 25 mN. The dwell time of 30 s was used before unloading. A Renishaw micro-Raman spectrometer with the excitation laser line at 514 nm was used to characterize the structural evolution beneath indentation. A scanning electron microscope (Helios NanoLab ×50 Dual Beam TM series) and a transmission electron microscope operated at an acceleration voltage of 200 kV (JEOL-ARM 200F) were used to characterize the deformation microstructure of all the single crystals. The cross-sectional TEM specimens of the indents were prepared using a focusing ion beam milling system. HRTEM image simulations were performed by using the Win HREM (HREM Research Inc.). R-Lattice 1.3 was used to calculate the angle between the loading plane and amorphous band plane. For all TEM images, boron carbide was assigned with the rhombohedral crystallographic planes as (hkl) and crystallographic direction [uvw] notations (41).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/8/eabc6714/DC1

REFERENCES AND NOTES

1. A. Gouldstone, K. J. Van Vliet, S. Suresh, Simulation of defect nucleation in a crystal. Nature 411, 656 (2001).
2. R. B. Kaner, J. J. Gilman, S. H. Tolbert, Designing superhard materials. Science 2576, 1268–1269 (2005).
3. V. Dominich, S. Reynaud, R. A. Haber, M. Chhowalla, Boron carbide: Structure, properties, and stability under stress. J. Am. Ceram. Soc. 94, 3605–3628 (2011).
4. K. Madhav Reddy, J. J. Guo, Y. Shinoda, T. Fujita, A. Hirata, J. P. Singh, J. W. McCauley, M. W. Chen, Enhanced mechanical properties of nanocrystalline boron carbide by nanoporosity and interface phases. Nat. Commun. 3, 1052 (2012).
5. F. Mauri, N. Vast, C. J. Pickard, Atomic structure of icosahedral β₄C boron carbide from a first analysis of NMR spectra. Phys. Rev. Lett. 87, 085506 (2001).
6. K. Y. Xie, Q. An, T. Sato, A. J. Breen, S. P. Ringer, W. A. Goddard III, J. M. Cairey, K. J. Hemker, Breaking the icosahedra in boron carbide. Proc. Natl. Acad. Sci. U.S.A. 113, 12012–12016 (2016).
7. D. E. Grady, Shock-wave compression of brittle solids. Mech. Mater. 29, 181–203 (1998).
8. T. J. Holmquist, G. R. Johnson, Characterization and evaluation of boron carbide for plate-impact conditions. J. Appl. Phys. 100, 093525–093525-13 (2006).
9. D. Dankedar, Shock response of boron carbide: ARRL-TR-2456 (Army Research Laboratory), Aberdeen Proving Ground, Aberdeen, MD (2001).
10. D. E. Grady, Dynamic properties of ceramic materials: SAND 94–3266 (Sandia National Laboratories) Albuquerque, NM (1995).
11. M. W. Chen, J. W. McCauley, K. J. Hemker, Shock-induced localized amorphization in boron carbide. Science 299, 1563–1566 (2003).
12. X. Q. Yan, Z. Tang, L. Zhang, J. J. Guo, C. Q. Jin, Y. Zhang, T. Goto, J. W. McCauley, M. W. Chen, Depressurization amorphization of single-crystal boron carbide. Phys. Rev. Lett. 102, 075505 (2009).
13. D. Ge, V. Domnich, T. Juliano, E. A. Stach, Y. Gogotsi, Structural damage in boron carbide under contact loading. Acta Mater. 52, 3921–3927 (2004).
14. S. Zhao, B. Kad, B. A. Remington, J. C. La Salvia, C. E. Wehnchen, K. D. Behler, M. A. Meyers, Directional amorphization of boron carbide subjected to laser shock compression. Proc. Natl. Acad. Sci. U.S.A. 113, 12088–12093 (2016).
15. G. Fanchini, J. W. McCauley, M. Chhowalla, Behavior of disordered boron carbide under stress. Phys. Rev. Lett. 97, 035502 (2006).
16. Q. An, W. A. Goddard III, Atomistic origin of brittle failure of boron carbide from large-scale reactive dynamics simulations: Suggestions toward improve ductility. Phys. Rev. Lett. 115, 105501 (2015).
17. Q. An, W. A. Goddard III, T. Cheng, Atomistic explanation of shear-induced amorphous band formation in boron carbide. Phys. Rev. Lett. 113, 095501 (2014).
18. A. C. Schul, Nanoindentation studies of materials. Mater. Today 9, 32–40 (2006).
19. J. H. Perepezko, S. D. Imhoff, M.-W. Chen, J.-Q. Wang, S. Gonzalez, Nucleation of shear bands in amorphous alloys. Proc. Natl. Acad. Sci. U.S.A. 111, 3938–3942 (2014).
20. D. Pan, A. Inoue, T. Sakurai, M. W. Chen, Experimental characterization of shear transformation zones for plastic flow of bulk metallic glasses. Proc. Natl. Acad. Sci. U.S.A. 105, 14769–14772 (2008).
21. X. Q. Yan, W. J. Li, T. Goto, M. W. Chen, Raman spectroscopy of pressure-induced amorphous boron carbide. Appl. Phy. Lett. 88, 131905 (2006).
22. K. M. Reddy, P. Liu, A. Hirata, T. Fujita, M. W. Chen, Atomic structure of amorphous shear bands in boron carbide. Nat. Commun. 4, 2483 (2013).
23. M. W. Chen, A. Inoue, W. Zhang, T. Sakurai, Extraordinary plasticity of ductile bulk metallic glasses. Phys. Rev. Lett. 96, 245502 (2006).
24. K. L. Johnson, Contact Mechanics (Cambridge Univ. Press, Cambridge, UK, 1995).
25. C. Schuh, A. C. Lund, Application of nucleation theory to the rate dependence of incipient plasticity during nanoindentation. J. Mater. Res. 19, 2152–2158 (2004).
26. W. C. Oliver, G. M. Pharr, Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology. J. Mater. Res. 19, 3–20 (2004).
27. J. K. Mason, A. C. Lund, A. C. Schuh, Determining the activation energy and volume for the onset of plasticity during nanoindentation. Phys. Rev. B 73, 054102 (2006).
28. D. Hull, D. J. Bacon, Introduction to Dislocations, Fourth Edition (Butterworth-Heinemann, Oxford, 2001).
29. G. Schoeck, The activation energy of dislocation movement. Phys. Stat. Sol. B, 499–507 (1965).
30. C. Wood, D. Emin, Conduction mechanism in boron carbide. Phys. Rev. B 29, 4582–4587 (1984).
31. G. Fanchini, V. Gupta, A. B. Mann, M. Chhowalla, In situ monitoring of structural changes in boron carbide under electric fields. J. Am. Ceram. Soc. 91, 2666–2669 (2008).
32. P. K. Sitch, R. Jones, S. Øberg, M. I. Heggie, Ab initio investigation of the dislocation structure and activation energy for dislocation motion in silicon carbide. Phys. Rev B 52, 4951–4955 (1995).
33. C. St. John, The brittle-to-ductile transition in pre-cleaved silicon single crystals. Phil. Mag. 32, 1193–1212 (1975).
34. S. Sharma, S. K. Sikka, Pressure induced amorphization of materials. *Prog. Mater. Sci.* **40**, 1–77 (1996).
35. R. J. Hemley, A. P. Jephcoat, H. K. Mao, L. C. Ming, M. H. Manghnani, Pressure-induced amorphization of crystalline silica. *Nature* **334**, 52–54 (1996).
36. K. M. Reddy, A. Hirata, P. Liu, T. Fujita, T. Goto, M. Chen, Shear amorphization of boron suboxide. *Scripta Mater.* **76**, 9–12 (2014).
37. A. Awasthi, G. Subhash, Deformation behavior and amorphization in icosahedral boron-rich ceramics. *Prog. Mater. Sci.* **112**, 100664 (2020).
38. K. J. Kingma, C. Meade, R. J. Hemley, H.-K. Mao, D. R. Veblen, Microstructural observations of α-quartz amorphization. *Science* **259**, 666–669 (1993).
39. H. J. Fecht, Defect-induced melting and solid-state amorphization. *Nature* **356**, 133–135 (1992).
40. S. Ryu, K. Kang, W. Cai, Predicting the dislocation nucleation rate as a function of temperature and stress. *J. Mater. Res.* **26**, 2335–2354 (2011).
41. H. K. Clarke, J. L. Hoard, The crystal structure of boron carbide. *J. Am. Chem. Soc.* **65**, 2115–2119 (1943).

Acknowledgments
Funding: This work was sponsored by the MOST 973 of China (grant no. 2015CB856800), the National Natural Science Foundation of China (grant nos. 11327902, 51271113, 11704245, 51821001, and 51850410501), and the fusion research program of “World Premier International Research Center (WPI) Initiative” by MEXT, Japan. M.C. was sponsored by the Whiting School of Engineering, the Johns Hopkins University, and the NSF (NSF NSF-DMR-1804320). Author contributions: M.C. conceived and supervised this study. K.M.R. conducted nanoindentation measurements, TEM characterization, and stochastic analysis. S.S. contributed to the nanoindentation measurements. C.C., J.H., and X.W. contributed to the TEM sample preparation and characterization. D.G. and Q.A. contributed to the data analysis. K.M.R. and M.C. wrote the manuscript. All the authors discussed the results and commented on the manuscript. Competing interests: The authors declare that they have no competing interests.
Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 7 May 2020
Accepted 23 December 2020
Published 17 February 2021
10.1126/sciadv.abc6714

Citation: K. M. Reddy, D. Guo, S. Song, C. Cheng, J. Han, X. Wang, Q. An, M. Chen, Dislocation-mediated shear amorphization in boron carbide. *Sci. Adv.* **7**, eabc6714 (2021).
Dislocation-mediated shear amorphization in boron carbide
Kolan Madhav Reddy, Dezhou Guo, Shuangxi Song, Chun Cheng, Jiuhui Han, Xiaodong Wang, Qi An and Mingwei Chen

Sci Adv 7 (8), eabc6714.
DOI: 10.1126/sciadv.eabc6714