

Supplemental Information

Silicon-Stabilized Three-Dimensional Covalent Networks in High Entropy Diborides

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Experimental Methods

Materials

Acetone (Thermo Fisher 99.5%), boron powder (Alfa Aesar 325 mesh 98%), chromium powder (Strem Chemicals Inc. 99%), diamond suspension – 3 micron (LECO 811-997-016), diamond suspension – 1 micron (LECO 810-998-016), epoxy resin (LECO 811-563-101), hardener (LECO 812-518), isopropyl alcohol (VWR 99.5%), microid diamond compound extender (LECO 811-003), niobium (Beantown Chemical Inc., 99.99%, 325 mesh), silicon (Strem Chemicals Inc. 99%), tantalum (Beantown Chemical Inc., 99.95%), titanium (Alfa Aesar, 99.40%, 100 mesh).

Sample Preparation

Powders of boron, chromium, niobium, silicon, tantalum, and titanium were stoichiometrically weighed out (typical loading values are listed in **Table S1** and **Table S2**) and ground in an agate mortar and pestle with acetone. After the sample had dried, the resulting mixture was pressed into a 10 mm diameter pellet and placed into an alumina boat. The alumina boat was then placed into a Lindberg Blue tube furnace capable of reaching 1000°C. A titanium rod was positioned upstream in the furnace to act as an oxygen getter at high temperatures. Throughout the heating process, a constant flow of argon was used to maintain an inert atmosphere for the duration of the heating cycle. The heating cycle started with an initial 6-hour room temperature purge, then heating to 1000°C at a rate of 5°C/min and holding temperature for 24-hours, followed by cooling back to room temperature at a rate of 5°C/min. After the conclusion of the heat cycle, the pellet was placed in an Edmund Bühler GmbH MAM 1 arc melter along with a zirconium slug to act an oxygen getter at high temperatures. The chamber was vacuumed and refilled with argon to ambient pressure; this purging cycle was repeated three times. The zirconium slug was initially arced, the argon plasma was then placed onto the unreacted pellet, the flame would go in circular motions

around the pellet to uniformly heat the sample. The pellet would then be removed from the arc melter and flipped, repeating the arc melting process until the pellet was melted into an ingot. The ingot was then hit with a tool steel high-impact mortar and pestle to break the sample into smaller pieces. One piece was then transferred to a synthetic sapphire mortar and pestle with acetone to grind the sample into a fine powder to analyze for pXRD. Another piece was then placed into a mold where it would be placed into epoxy and allowed to cure for 24-hours. After the epoxy had cured, the sample was polished using a LECO PX 300 down to 1200 grit.

Sample Characterization Instrumentation

Sample characterization was performed using powder X-ray diffraction (Rigaku Miniflex 6T), scanning electron microscopy (Regulus 8100 Scanning Electron Microscope), energy-dispersive X-ray spectroscopy (Octane Elect EDS), Fourier Transformed Infrared Spectrophotometry (Shimadzu IRTracer-100), Nanoindentation (Anton Paar Hit 300), Vickers indenter (Wilson Tukon 1202).

Table S1. Typical Mass $\text{Cr}_{0.2}\text{Nb}_{0.2}\text{Si}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{B}_2$

Element	mmol	Mass (mg)
B	8	86.48
Cr	0.8	41.60
Nb	0.8	74.33
Si	0.8	22.47
Ta	0.8	144.76
Ti	0.8	38.29

Table S2. Typical Mass $\text{Cr}_{0.25}\text{Nb}_{0.25}\text{Ta}_{0.25}\text{Ti}_{0.25}\text{B}_2$

Element	mmol	Mass (mg)
B	8	86.48
Cr	1.0	52.00
Nb	1.0	92.91
Ta	1.0	180.95
Ti	1.0	47.87

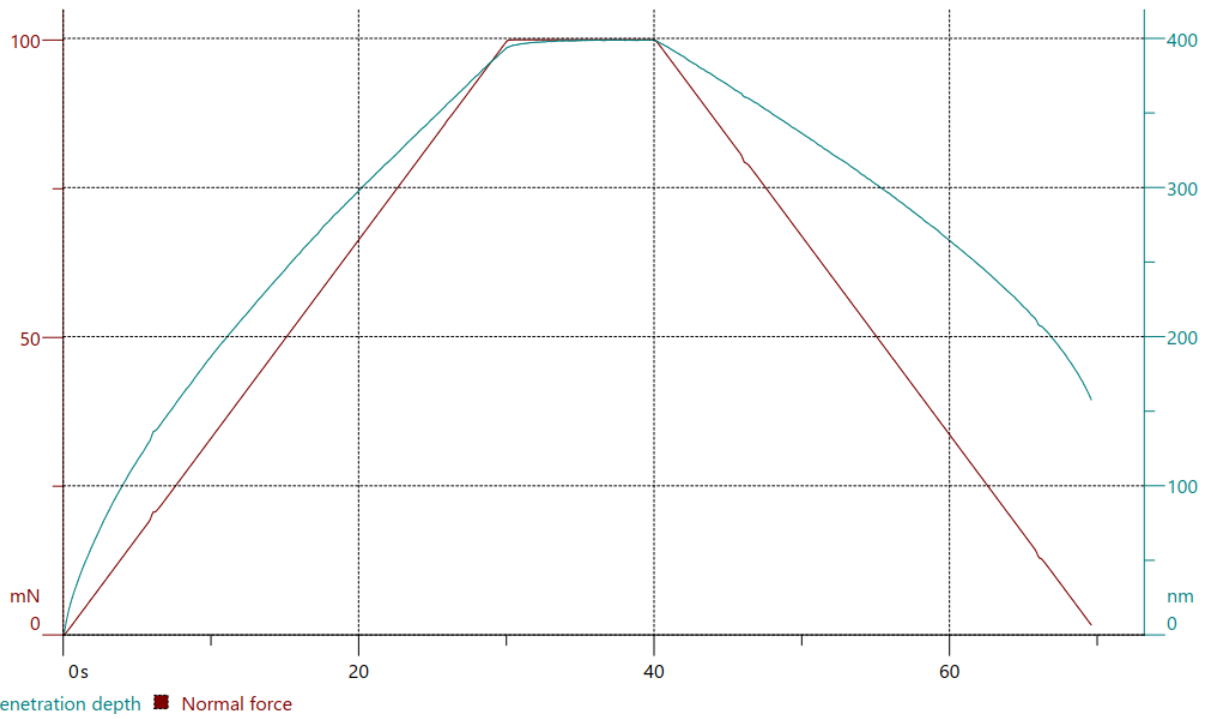


Figure S1. Example nanoindentation plot of indentation depth in regard to normal force occurring on the sample.

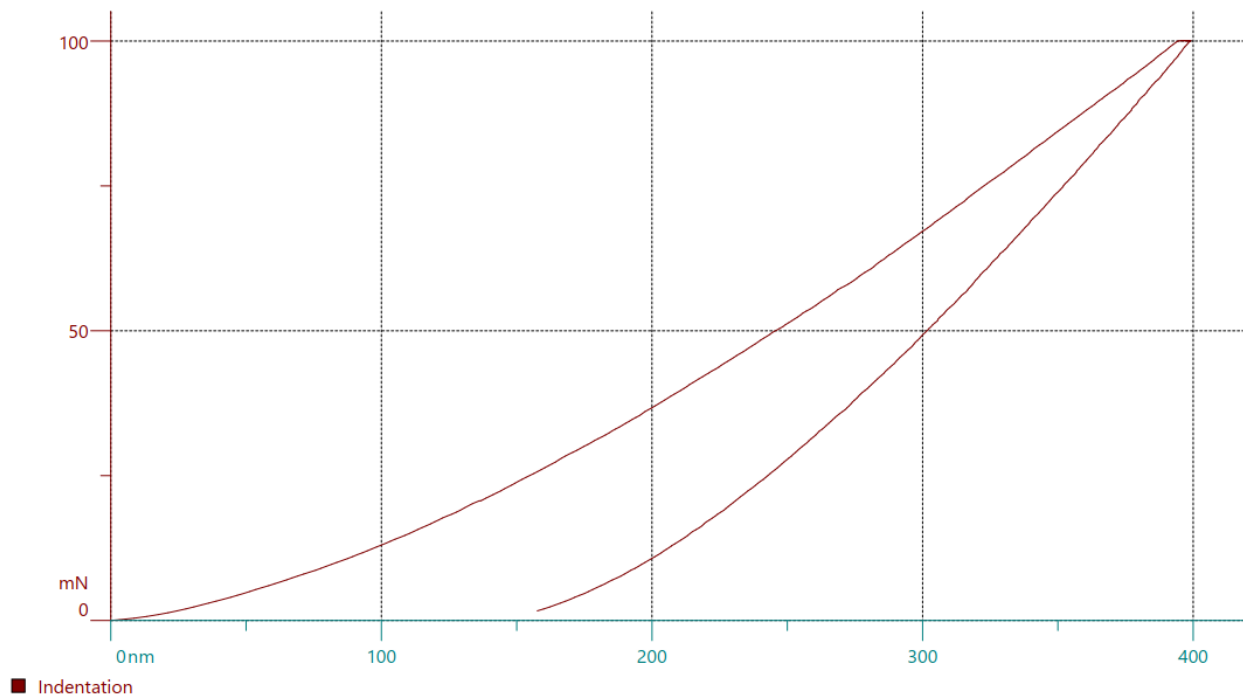


Figure S2. Example nanoindentation plot for indentation versus penetration depth.

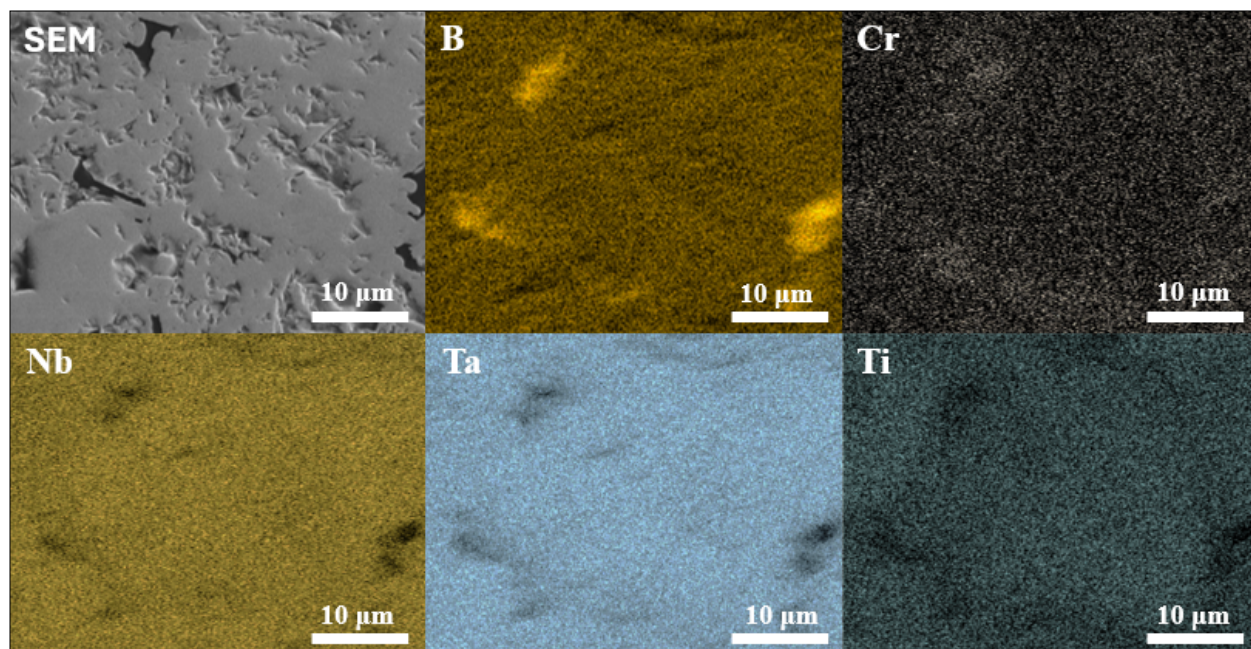


Figure S3. SEM-EDS image for the $\text{Cr}_{0.25}\text{Nb}_{0.25}\text{Ta}_{0.25}\text{Ti}_{0.25}\text{B}_2$ MEB showing uniform distribution of elements across the surface of the ingot.

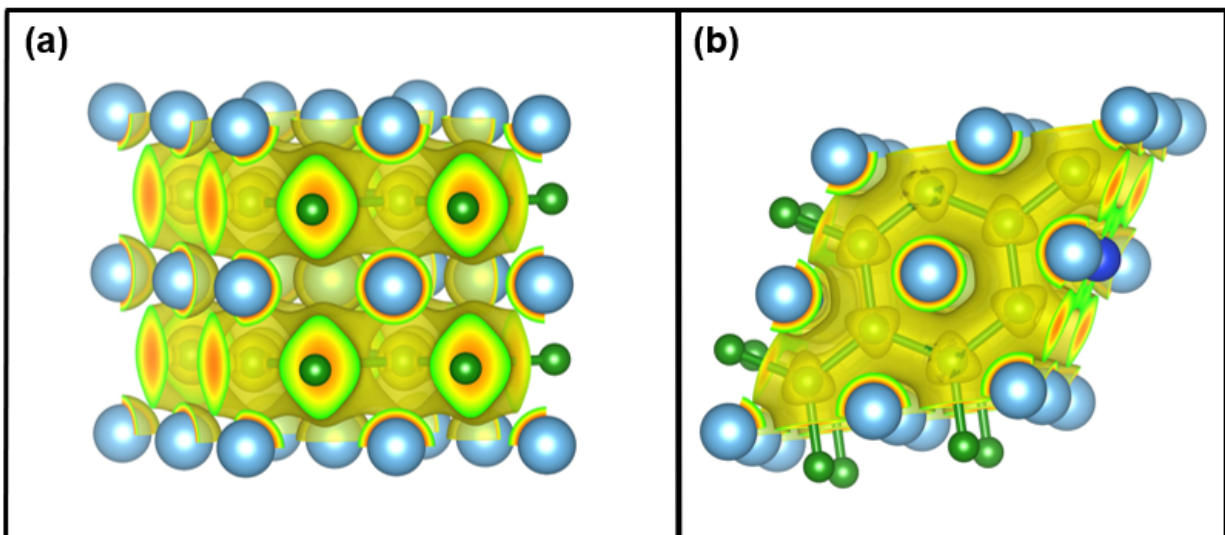


Figure S4. (a) ELF isosurfaces on TiB₂, showing largely isolated and weakly directional electron density around titanium. (b) ELF isosurfaces ‘top-down’ on the silicon-substituted TiB₂, showing the covalent network of the borophene layer.