# **Supplementary Information**

## High pressures pathway toward boron-based nanostructured solids

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### MATERIALS AND METHODS

Synthesis of the nanoscaled precursors. Before heating, all powders were handled into an argon-filled glovebox. Anhydrous HfCl<sub>4</sub> (Alfa Aesar, 99.9%), CaCl<sub>2</sub> (Alfa Aesar, 99.9%) and NaBH<sub>4</sub> (Alfa Aesar, 98%) were used as received. Prior to synthesis, LiCl and KCl (Aldrich) were mixed at the eutectic composition LiCl:KCl = 45:55 wt% and finely ground in a mortar. The resulting mixture was evacuated at 200 °C for 4 days and transferred into the glovebox. Before heating, anhydrous metal chlorides, sodium borohydride and the eutectic salt mixture LiCl:KCl (2.5 g) were finely ground together with a Retsch MM400 ballmiller (airtight vials of 50 mL, one steel ball of 62.3 g and a diameter of 23 mm) for 2 min at 20 Hz. The mixture was transferred into a glassy carbon crucible which was then heated under argon flow in a tube oven at 10 °C min<sup>-1</sup>. For HfB<sub>2</sub>, 1 mmol of hafnium (IV) chloride and 4 mmol of sodium borohydride were used. The reaction medium was heated at 900 °C for 4 h. For CaB<sub>6</sub>, 1 mmol of calcium (II) chloride and 8 mmol of sodium borohydride were used. The reaction medium was heated at 800 °C for 4 h. After cooling, the metal boride powders were recovered by dissolution of the frozen eutectic in deionized water and four washing-centrifugation cycles (in 10 mL polycarbonate centrifugation tubes, at 16500 rpm for 20 min), then dried under vacuum at 60 °C overnight.

#### Characterizations.

The precursors and products were characterized with a Bruker D8 X-ray diffractometer operating in the Bragg-Brentano reflection mode equipped with a nickel filter to select the Cu-K<sub> $\alpha$ </sub> radiation. The data were collected in the 2 $\theta$  = 10-80 ° range with 0.05 ° steps. For samples recovered after HP-HT treatment, crystalline silicon low-background sample holders from Bruker were used for XRD analysis.

The morphology and the average particle size of the samples were analysed by **transmission electron microscopy (TEM)** using a Tecnai spirit G2 apparatus (LaB<sub>6</sub>, operating at 120 kV). HRTEM analyses were performed on a JEOL JEM 2011 (LaB<sub>6</sub>, operating at 200 kV) apparatus at the Microscopy Centre of Institute of Materials of Paris Centre (IMPC), Sorbonne Universités-UPMC, Paris. **The STEM-HAADF and STEM-DF** observations were performed on a JEOL 2100 F operating at 200 kV and equipped with aberration correction on the electronic probe at the Institut de Physique et Chimie de la Matière de Strasbourg.

**XRD and high resolution (S)TEM** data were indexed along the ICSD reference cards 30422, 196516, 417031 and 23241 for HfB<sub>2</sub>, CaB<sub>6</sub>,  $\beta$ -HfB<sub>2</sub>O<sub>5</sub> and CaB<sub>2</sub>O<sub>4</sub> (IV), respectively. Le Bail refinements of XRD data were performed on JANA2006 software (Petrícek, V.; Dušek, M.; Palatinus, L. Crystallographic Computing System JANA2006: General Features. *Zeitschrift fur Krist.* **2014**, *229* (5), 345–352). All samples for (S)TEM were prepared by evaporating a drop of diluted suspension in ethanol on a carbon-coated copper grid. For infrared spectroscopy, a Perkin-Elmer spectrum 400 FT-IR apparatus equipped with ATR FT-IR was used.

For X-ray photoelectron spectroscopy (XPS), the spectra were recorded on an Omicron Technology apparatus at the IMPC. It was equipped with a hemispheric analyzer (SPECS) and an aluminum cathode with an Al K $\alpha$  monochromator. The analysis of the data was performed on CasaXPS software. The spectra were calibrated according to the C 1s signal at 285.0 eV. Shirley background type was chosen in Hf 4f region and linear background type in B 1s and O 1s regions. Binding energy and full width at half maximum (BE, eV; FWHM, eV) of contributions are (i) in the Hf 4f region : Hf-B (4f<sub>7/2</sub>)(14.3, 0.9), (4f<sub>5/2</sub>)(16.0, 0.9) and Hf<sup>(IV)</sup> (4f<sub>7/2</sub>)(17.4, 1.4) (4f<sub>5/2</sub>)(19.1, 1.4) (ii) in the B 1s region: B-Hf (186.6, 0.9), B<sup>(0)</sup> (188.0, 1.5), B-O (189.7, 1.5), BO<sub>3</sub> (192.3, 1.6) and (iii) in the O 1s region: (531.9, 2.3). In the Hf 4f region, constraints were imposed between contributions due the  $4f_{7/2}$ - $4f_{5/2}$  spin-orbit splitting: BE( $4f_{5/2}$ ) = BE( $4f_{7/2}$ ) + 1.7 eV ; Area( $4f_{5/2}$ ) = 0.75 Area( $4f_{7/2}$ ).

#### FIGURES



**Figure S1.** Fourier Transform Infrared spectra of (a) HfB<sub>2</sub>/amorphous boron and (b) CaB<sub>6</sub>/amorphous boron nanocomposites after exposure to air during seven days.



**Figure S2.** UHV-XPS spectra of the initial  $HfB_2$  nanocomposite in the Hf  $4f_{7/2}$ , B 1s and O 1s regions. Incident photon energy : 1500 eV.

The composition of the superficial layer of the initial material was investigated using X-ray photoelectron spectroscopy under ultra-high vacuum (**Figure S2**). In the B 1s region, the signal reveals four distinct environments for boron. The most intense contribution is detected at a binding energy of 187.9 eV. It corresponds to elemental boron. The two peaks at higher binding energies of 190.0 and 192.4 eV are attributed to oxygen-bonded boron species. In comparison to the literature, they correspond to partially oxidized boron with one and two neighboring oxygen atoms, respectively.<sup>1</sup> These three species are attributed to the amorphous matrix, whereas the fourth one, detected at 186.6 eV, is attributed to boron included in HfB<sub>2</sub> nanocrystals.<sup>2</sup> The relatively low intensity of this peak is due to the metal boride being included in the amorphous matrix, *ca*. 3 nm deep. Indeed, B 1s electrons emitted deeply are partly reabsorbed by the material according to an exponential law. The depth of XPS analysis in each region can be evaluated by calculating the inelastic mean free path (IMFP) of electrons extracted with a given kinetic energy from a given material.<sup>3</sup> As the superficial layer is mainly composed of boron and oxygen, it is

approximated to boron oxide for the calculations (considering only boron yields similar values). For incident photon energy of 1500 eV, the IMFP is 3.7 nm. It is thus expected that electrons emitted from HfB<sub>2</sub> are only partly detected. In the Hf 4f region, two distinct environments of hafnium are distinguished, each one being composed of two contributions due to the spin-orbit splitting of 1.7 eV between  $4f_{7/2}$  and  $4f_{5/2}$ . The Hf  $4f_{7/2}$  peak at 14.3 eV is attributed to hafnium at oxidation state (0)<sup>4</sup> and involved in HfB<sub>2</sub> in our case. The Hf  $4f_{7/2}$  peak at 17.4 eV corresponds to Hf<sup>(IV)</sup>.<sup>4,5</sup> It is attributed to oxidized hafnium in the superficial layer. A single contribution is detected in the O 1s region, at 531.9 eV. This is larger than the usual binding energy reported for oxygen in HfO<sub>2</sub> (530.2 eV)<sup>5</sup> and smaller than for B-O groups in B<sub>2</sub>O<sub>3</sub> (533.2 eV).<sup>6</sup> It corresponds probably to hydroxyl groups Hf-OH reported at 531.7 eV <sup>5</sup> together with oxygen from B-O and O-B-O groups.

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**Figure S3.** (a) XRD powder patterns of the initial CaB<sub>6</sub>-based precursor and of the CaB<sub>6</sub>/CaB<sub>2</sub>O<sub>4</sub>-(IV) nanocomposite obtained after treatment at 5 GPa and 1200 °C. For legibility sake, only main CaB<sub>2</sub>O<sub>4</sub>-(IV) peaks are indexed. CaB<sub>6</sub> peaks are highlighted as black triangles. (b) and (c) HRTEM images of the initial CaB<sub>6</sub>-based precursor and corresponding FFTs of the black-squared zones, indexed along the CaB<sub>6</sub> structure. Scheme describing the initial material nanocomposite consisting in CaB<sub>6</sub> nanocrystals dispersed in an amorphous matrix composed of partly oxidized boron. ICSD reference cards are 196516 and 23241 for CaB<sub>6</sub> and CaB<sub>2</sub>O<sub>4</sub> (IV), respectively. Refined cell parameters of CaB<sub>6</sub> and CaB<sub>2</sub>O<sub>4</sub>-(IV) were close to the values reported: a = 4.1565(6) Å for CaB<sub>6</sub> prior to any HP-HT treatment; a = 4.180(3) Å for CaB<sub>6</sub> and a = 9.0231(12) Å for CaB<sub>2</sub>O<sub>4</sub> in the post-HP-HT samples.



**Figure S4.** Transmission electron microscopy of the CaB<sub>6</sub>/CaB<sub>2</sub>O<sub>4</sub>–(IV) nanocomposite obtained after HP-HT treatment: (a) TEM image showing the CaB<sub>6</sub> nanoparticles, (b) HRTEM image with FFT of the squared region and (c) corresponding CaB<sub>2</sub>O<sub>4</sub>–(IV) image Fourier-filtered from the (002) reflection, showing the extent of CaB<sub>2</sub>O<sub>4</sub>–(IV) matrix crystallization. Scheme of the nanocomposite obtained after HP-HT treatment, consisting in CaB<sub>6</sub> nanocrystals dispersed in a CaB<sub>2</sub>O<sub>4</sub>–(IV) matrix.