**Method**

**Experimental**

HfC (<1.25 μm, Sigma Aldrich), Mo₂C (-325 mesh, 99.5%, Alfa Aesar), TiC (-325 mesh, 99.5%, Alfa Aesar), TaC (<1 μm), B₄C (1-7 μm, Alfa Aesar), and SiC (whiskers) were mixed with a molar ratio of 2:1:2:1:2:2. The powder mixture was homogenized via ball milling for 2 hours, and the weight ratio between the powder and stainless-steel ball was 1:5. Pulsed current processing (PCP) was conducted using an SPS-530ET (Dr. Sinter Spark Plasma Sintering System, Fuji electronic industrial co., ltd., Japan) at 1650 °C with a heating rate of 100 °C/min, which was held for 2 minutes. The sintering atmosphere was kept as a vacuum, and a uniaxial pressure of 60 MPa was applied during the process.

The sample surface was polished by following the standard metallurgical sample preparation procedures and then sent for microstructure characterization using a Scanning Electron Microscope JSM-IT300 (JEOL, Tokyo, Japan). Compositional mapping analysis was performed using the energy dispersive spectrometer (EDS) mounted on JSM-IT300 and a wavelength dispersive spectrometer (WDS) that is mounted on a Field Emission Scanning Electron Microscope (Zeiss, Merlin). The high-entropy ceramic (HEC) composite was crushed into powder form and analysed using transmission electron microscopy (FEI Tecnai G2F20, FEI Company, USA). X-ray diffraction (XRD) was conducted using an X-ray diffractometer (Empyrean, PANalytical, United Kingdom) and Cu-Kα radiation with a wavelength of 0.154 nm. The XRD patterns were analysed by the PANalytical X’Pert HighScore Plus software created by Empyrean.

The oxidation resistance test was conducted in two different ways. One is heating the sample to 900 °C and keeping it isolated for 50 hours under an air atmosphere in a differential scanning calorimeter (STA 449 F3 Jupiter®, NETZSCH, Germany), while the other is exposing the sintered HECs composite to a liquefied petroleum gas (LPG) torch for 20 seconds and recording mass change and phase evolution using XRD. The wear resistance was tested using a tribometer (Universal Tribometer, Rtec Instruments, US) with the ball-on-disk mode with a testing load of 10 N, a sliding distance of 120 m and a sliding speed of 100 rpm under room temperature. Nanoindentation was performed using an MTS NanoIndenter XP by recording the force-displacement curve of the indenter. The maximum load applied on the sample was 20 mN.
Phase composition analysis of the HEC composite

Table S1 Densities and lattice parameters of the hexagonal metal diborides

<table>
<thead>
<tr>
<th>Diborides</th>
<th>Density (g/cm³)</th>
<th>Lattice parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>c</td>
</tr>
<tr>
<td>HfB₂</td>
<td>10.5</td>
<td>0.3150</td>
</tr>
<tr>
<td>MoB₂</td>
<td>7.97</td>
<td>0.305</td>
</tr>
<tr>
<td>TaB₂</td>
<td>12.53</td>
<td>0.3076</td>
</tr>
<tr>
<td>TiB₂</td>
<td>4.52</td>
<td>0.3026</td>
</tr>
</tbody>
</table>

The formation of ceramic composite of HEC phase with SiC was concluded from the experimental results including microstructure and phase composition analysis using SEM, XRD and TEM. According to the X-ray diffractogram (Figure 2, in the main manuscript), the synthesized HEC phase displays hexagonal crystal structure with a lattice parameter of a=0.307nm and c=0.330nm. The lattice structure and lattice constants of metal diborides listed in Table S1 show similarity to the HEC phase. The metal diborides show vast difference in their density (Table S1), which should result in presence of multiple phases with different contrast in the backscattered electron microstructure; due to the sensitivity of the backscattered electrons to the atomic number. In case of HEC, the microstructure of HEC composite shows two distinct phases (Fig. 1 in the main manuscript) one is SiC detected by EDS and the second phase has a homogeneous phase containing constituent elements (Hf, Mo, Ta, Ti, C and B). Therefore, we have concluded the formation of a high-entropy phase in the HEC composite, instead of diboride composites.

Crystal structure search

XtalOpt\(^5\) version r11.0 together with the Vienna ab initio simulation package (VASP)\(^6\) version 5.4.1 05Feb16 was used to perform density function theory (DFT) based crystal structure searches. The empirical formula used in XtalOpt was B\(_x\)(Hf\(_x\)Mo\(_x\)Ta\(_x\)Ti\(_x\))C\(_{8(1-x)}\). Here x denotes the boron content in the (002) plane (the hexagonal grid) of the HEC were x = 1 corresponds to all boron and x = 0 all carbon. The number of formula units (FU) was fixed to 2 for all crystal structure searches. Unit cell parameters was set so to not constrain the crystal structure search with minimum and maximum length of the lattice parameters set to 3 and 12 Å, respectively. The limits in angle was keep at the default values (60 to 120 degrees) and the minimum and maximum volume per FU was set to 50 and 150 Å\(^3\).

For the DFT calculations five optimization steps per structure was used. First the atomic positions were relaxed while keeping the lattice parameters fixed (ISIF = 2). In the second step both the atomic positions and the lattice parameters were relaxed while keeping the volume fixed (ISIF = 4). For the third step both the atomic positions and the lattice parameters were relaxed while allowing for a volume change (ISIF = 3). For the two last step the ISIF parameter was kept at 3 but the accuracy of the calculations was increased by changing the parameters EDIFF, EDIFFG, PREC and the number of k-points used by VASP.

For all optimization steps the following pseudopotentials was used

- PAW_PBE Hf_sv_GW 16Jan2015
- PAW_PBE Mo_sv_GW 05Dec2013
- PAW_PBE Ta_sv_GW 23Mar2010
The search settings in XtalOpt was set to, 60 initial structures with a pool size of 30 and 30 continuous structures. Crossover was kept at the default settings while the stripe settings were changed to have a strain stdev range of 0.5 to 1.0 with the number of waves in axis 1 and 2 set to 2. The permustrain settings were change to a maximum strain stdev of 1.0 and number of exchanges was set to 5. Crystal structure searches were performed with two different boron contents \( x = 1.0 \) and \( x = 0.875 \). For each \( x \) the search was allowed to evolve for 14 generations (around 600 structures) which was enough to achieve a good convergence.

**Density functional theory calculations**

To determine lattice parameters and formation enthalpies for the high-entropy ceramic, DFT calculations were performed. Due to its disordered nature the HEC was modelled using special quasirandom structures (SQS). SQS based on the theoretical predicted HEC crystal structure was created using the alloy theoretic automated toolkit (ATAT)\(^7\) with a pair range of 5.5 Å (mcsqs -2=5.5) and specified supercell sizes (mcsqs -rc). The supercell sizes used were 2x2x2 (24 atoms), 4x4x4 (192 atoms) and 6x6x6 (648 atoms) repetitions of the theoretically predicted crystal structure. Each structure was created with different boron content, \( x = 1.0, 0.875, 0.75, 0.625, 0.5, 0.375, 0.25, 0.125 \) and 0.0. The difference between boron and carbon content for varying \( x \) is defined according to the base FU, \( B_2x(Hfo.25Mo0.25Ta0.25Ti0.25)C_{2(1-x)}. \)

DFT calculations were performed using high accuracy (PREC = Accurate) with a plane wave basis set energy cutoff equal to 600 eV (ENCUT = 600). All calculations were spin polarized (ISPIN = 2) without any symmetry (ISYM = 0). For the electronic self-consistent (SC) calculations a Methfessel-Paxton smearing of order 1 was used (ISMEAR = 1) with the smearing width set to 0.05 eV (SIGMA = 0.05). The convergence criteria for the SC loop was set to 10-5 eV (EDIFF = 1.0E-5) and the accuracy in the forces was increased by specifying (ADDGRID = .TRUE). All structures were fully relaxed, both atomic positions and lattice parameters (ISIF = 3), using the conjugate-gradient algorithm (IBRION = 2) until the forces acting on the structure was smaller than 0.01 eV/Å (EDIFFG = -1.0E-2). For the small 2x2x2 SQS a gamma centred k-point grid of 4x4x4 was used, for the larger 4x4x4 SQS the amount of k-points was reduced to 2x2x2. For the large 6x6x6 SQS only the gamma point was used. Due to the large amount of computational resources and time required to fully relax the large 6x6x6 SQS, relaxations of these were only performed for boron contents of \( x = 1.0 \) and \( x = 0.875 \).

Formation enthalpies, \( H_f \), without the zero-point energy, at 0 K was calculated using the following equation:\(^8\)

\[
H_f = \left( E - \sum_{i=1}^{N} n_i E_i \right) / M_{FU} 
\]

(S1)

Here \( E \) is the DFT calculated total energy for a structure with \( N \) number of different atomic types. \( n_i \) is the number of atoms of type \( i \) and \( E_i \) is the energy per atom of this type. \( M_{FU} \) is the number of formula units in the SQS, here \( M_{FU} = 8, 64 \) and 216 for SQS of size 2x2x2, 4x4x4 and 6x6x6, respectively. \( E_i \) was calculated with DFT using the setup described above and the following structures.

- **Hf**, bulk Hafnium, hexagonal close-packed unit cell, 2 atoms per cell.
- **Mo**, bulk Molybdenum, body-centered cubic unit cell, 1 atom per cell.
- **Ta**, bulk α-Tantalum, body-centered cubic unit cell, 1 atom per cell.
- **Ti**, bulk Titanium, hexagonal close-packed unit cell, 2 atoms per cell.
- **B**, bulk α-R Boron, rhombohedral unit cell, 12 atoms per cell.
- **C**, bulk Graphite, hexagonal close-packed unit cell, 4 atoms per cell.

XRD patterns for the relaxed SQS was simulated using the *Mercury* - Crystal Structure Visualization software\(^9\) and the structures were visualized using VESTA\(^10\).

**Results**

**Crystal structure search**

Crystal structure searches performed using XtalOpt and VASP yielded structures very similar to the theoretical one predicted from the experimental XRD data (see main paper). Fig. S1 shows the result from the crystal structure search using \(x = 1.0\). Here it is clear that the search has converged after 7 generations with the subsequent generations giving structures with very similar energies. The structure with absolute lowest energy was found after 11 generations and is shown in Fig. S1b-d. This structure has alternating layers of metal and boron atoms, were the boron atoms form a hexagonal grid. The red dashed lines in in Fig. S1c, d outlines the hexagonal close-packed (HCP) unit cell determined from experimental XRD measurements (see Fig. 3 in the main paper).

![Fig. S1 Results from crystal structure search with \(x = 1.0\). (a) The evolution of the formation enthalpy per generation, here the most stable structure is found after generation 7. (b), (c) and (d) The most stable structure found during the search (in generation 11). Here the green spheres represent B, blue Ti, purple Mo, brown Ta and yellow Hf. The dashed red lines indicate the theoretically predicted unit cell (see Fig. 3d in the main paper).](image)

The crystal structure search with \(x = 0.875\) yielded very similar results, see Fig. S2. Predicting a structure with alternating metal and nonmetal atoms (boron and carbon). Comparing the formation enthalpies, \(H_f\), for the different crystal structure searches Fig. S1a and Fig. S2a we see that for \(x = 1.0\) the formation enthalpy is lower. A closer look at the predicted lowest energy structure for \(x = 0.875\) (Fig. S2b-d) shows that the addition of carbon in the hexagonal grid produces distortions in the lattice which raises the formation enthalpy.
Fig. S2 Results from crystal structure search with $x = 0.875$. (a) The evolution of the formation enthalpy per generation, here the most stable structure is found after generation 8. (b), (c) and (d) The most stable structure found during the search (in generation 14). Here the green spheres represent $B$, blue Ti, purple Mo, brown Ta and yellow Hf. The dashed red lines indicate the theoretically predicted unit cell (see Fig. 3d in the main paper).

Crystal structure searches with $x < 0.875$ failed to find structures similar to the one predicted from experiments (alternating layers of metal and nonmetal atoms).
Density functional theory calculations

The lattice parameters and the formation enthalpy for the experimental precursors (all except SiCw) used to synthesize the HEC were calculated using DFT. For the calculation of the formation enthalpy Eq. (S1) was used with $M_{FU} = 1$ for all precursors.

Table S2 The calculated formation enthalpy, $H_f$, for the precursors used in the experiment, the lattice parameters, $a$, $b$, $c$ and the volume of the unit cell, $V_{DFT}$, obtained after full relaxation using DFT. Also reported is the experimentally determined unit cell volume of the precursors, $V_{exp}$.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Component</th>
<th>Crystal structure</th>
<th>$H_f$ (eV)</th>
<th>$a$ (nm)</th>
<th>$b$ (nm)</th>
<th>$c$ (nm)</th>
<th>$V_{DFT}$ (nm$^3$)</th>
<th>$V_{exp}$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfC</td>
<td>Face-centered cubic</td>
<td>-1.826</td>
<td>0.4652</td>
<td>0.4652</td>
<td>0.4652</td>
<td>0.0252</td>
<td>0.0250</td>
<td></td>
</tr>
<tr>
<td>TaC</td>
<td>Face-centered cubic</td>
<td>-1.164</td>
<td>0.4477</td>
<td>0.4477</td>
<td>0.4477</td>
<td>0.0224</td>
<td>0.0221</td>
<td></td>
</tr>
<tr>
<td>TiC</td>
<td>Face-centered cubic</td>
<td>-1.661</td>
<td>0.4327</td>
<td>0.4327</td>
<td>0.4327</td>
<td>0.0202</td>
<td>0.0202</td>
<td></td>
</tr>
<tr>
<td>Mo$_2$C</td>
<td>Hexagonal close-packed</td>
<td>-0.280</td>
<td>0.3059</td>
<td>0.3059</td>
<td>0.4658</td>
<td>0.0377</td>
<td>0.0368</td>
<td></td>
</tr>
<tr>
<td>B$_4$C</td>
<td>Rhombohedral</td>
<td>-0.449</td>
<td>0.5185</td>
<td>0.5185</td>
<td>0.5185</td>
<td>0.1112</td>
<td>0.1095</td>
<td></td>
</tr>
</tbody>
</table>

The DFT calculated formation enthalpies at 0 K in Table S2 show that HfC has the lowest formation enthalpy followed by TiC, TaC, B$_4$C and Mo$_2$C. Thus, replacing HfC and possible TiC with different ultrahigh temperature ceramics with higher formation enthalpies might make the HEC easier to synthesize. The unit cell volume of the precursors obtained after full relaxation using DFT agrees very well with the experimentally determined volumes, $V_{exp}$.

DFT calculations on SQS of different sizes 2x2x2, 4x4x4 and 6x6x6 show that a 4x4x4 or larger SQS is required in order to correctly model the disorder present in the high-entropy system (see Fig. 4 in the main paper). However, very large computational resources and time is required in order to fully relax the large 6x6x6 SQS. Thus, SQS of size 4x4x4 (and 2x2x2) were chosen in order to investigate the effect of different boron content, x, in the hexagonal grid of the HEC. The DFT results from the fully relaxed 4x4x4 SQS can be found in Table S3 and Fig. S3. Here the formation enthalpy at 0 K is calculated using Eq. (S1) and the volume of the unit cell is scaled by the number of formula units in the SQS.

Table S3 The calculated formation enthalpy, $H_f$, for the 4x4x4 SQS HEC for varying boron content x. Also reported are the lattice parameter $a/4$, $b/4$, $c/4$, $α$, $β$, $γ$ and the volume of the unit cell $V/64$ obtained after full relaxation using DFT.

<table>
<thead>
<tr>
<th>HEC, 4x4x4 SQS</th>
<th>B con. $x$</th>
<th>$H_f$ (eV)</th>
<th>$a/4$ (nm)</th>
<th>$b/4$ (nm)</th>
<th>$c/4$ (nm)</th>
<th>$α$ (deg.)</th>
<th>$β$ (deg.)</th>
<th>$γ$ (deg.)</th>
<th>$V/64$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-2.291</td>
<td>3.082</td>
<td>3.083</td>
<td>3.325</td>
<td>90.00</td>
<td>90.00</td>
<td>120.0</td>
<td>0.02737</td>
<td></td>
</tr>
<tr>
<td>0.875</td>
<td>-1.697</td>
<td>3.036</td>
<td>3.047</td>
<td>3.389</td>
<td>90.10</td>
<td>89.95</td>
<td>119.8</td>
<td>0.02720</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>-1.154</td>
<td>3.060</td>
<td>3.002</td>
<td>3.450</td>
<td>89.50</td>
<td>90.98</td>
<td>120.3</td>
<td>0.02736</td>
<td></td>
</tr>
<tr>
<td>0.625</td>
<td>-0.649</td>
<td>2.994</td>
<td>2.993</td>
<td>3.557</td>
<td>89.99</td>
<td>91.32</td>
<td>120.2</td>
<td>0.02753</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>-0.256</td>
<td>3.102</td>
<td>3.034</td>
<td>3.553</td>
<td>91.46</td>
<td>88.20</td>
<td>121.7</td>
<td>0.02842</td>
<td></td>
</tr>
<tr>
<td>0.375</td>
<td>0.618</td>
<td>3.070</td>
<td>2.900</td>
<td>3.704</td>
<td>90.33</td>
<td>92.19</td>
<td>117.7</td>
<td>0.02915</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>0.419</td>
<td>2.887</td>
<td>3.293</td>
<td>3.586</td>
<td>87.27</td>
<td>89.93</td>
<td>119.0</td>
<td>0.02976</td>
<td></td>
</tr>
<tr>
<td>0.125</td>
<td>1.234</td>
<td>3.227</td>
<td>3.445</td>
<td>3.221</td>
<td>94.73</td>
<td>95.00</td>
<td>120.9</td>
<td>0.03026</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.954</td>
<td>3.281</td>
<td>3.570</td>
<td>3.136</td>
<td>81.86</td>
<td>88.30</td>
<td>120.3</td>
<td>0.03117</td>
<td></td>
</tr>
</tbody>
</table>

From Fig. S3a and Table S3 it is clear that the formation enthalpy increases linearly as a function of the boron content, $x$. The most energetically favorable structure at 0 K is found to be the one with highest boron content, $x = 1.0$. Comparing the formation enthalpy of the HEC with that of the
precursors it is found that for a boron content smaller than ~0.875 the HEC has a higher formation enthalpy than HfC, the precursor with the lowest formation enthalpy.

According to the phase stability at 0 K it would be energetically favorable to create HEC with a boron content, x, roughly 0.8 to 0.9 using these precursors. However, one should note that the DFT calculated formation enthalpy is at 0 K and without including the zero-point energy. Thus, including vibration energy and temperature effects might change the formation enthalpies.

![Graphs showing phase stability and unit cell volume as a function of boron content](image)

**Fig. S3** Effect of varying boron content, x, in the HEC. (a) The phase stability at 0 K as a function of x, open circles represent DFT calculated formation enthalpies using Eq. (S1). The black dashed line is a linear fit to the DFT data and the red dashed line is the formation enthalpy for the most stable precursor (HfC). (b) The calculated unit cell volume per FU for the fully optimized 2x2x2 and 4x4x4 SQS, here the dashed line is a parabolic fit to the five last datapoints.

The effect of different boron content, x, on the crystal structure of the HEC can be seen in Table S3. For the lattice parameters a, b, c and α, β, γ in Table S3 it is clear that the higher the carbon content is (lower value of x) the more distorted the lattice parameters become. This effect can also be seen in the volume of the unit cell which shows a parabolic behavior for a boron content x ≥ 0.5. For x smaller than 0.5 the volume increases linear as a function of x. The smallest volume, 0.0272 nm³, is found in the parabolic region for a value of x = 0.875. For this boron content the volume of the fully relaxed SQS best matches the experimentally determined volume of 0.0269 nm³.

XRD patterns were simulated for the fully relaxed 4x4x4 SQS with different boron content, x. It is shown in the main paper (Fig. 4) that the 4x4x4 SQS with x = 1.0 has an XRD pattern that closely match the experimentally measured pattern. The simulated XRD pattern for all the investigated values of x is shown in Fig. S4. Here it is clear that the XRD pattern for the two highest boron contents (x = 1.0 and x = 0.875) are very similar. For these two values of x the intensity and positions of the three highest peaks are very similar. For the higher angle reflections of x = 0.875 there is a slight shift in the peak positions and some peak splitting is observed. The peak shift can be explained by the change in the lattice parameters caused by the presence of carbon, see Table S3. Peak splitting can be explained by a decrease in the symmetry of the atomic positions in the SQS. The symmetry is reduced since the presence of carbon in HEC causes local distortions of the atomic positions.
Fig. S4 The simulated XRD pattern for the fully relaxed 4x4x4 SQS with different boron content, $x$. As the carbon content increases ($x$ decreases) the simulated XRD pattern diverges more from the experimentally determined one.

Fig. S4 shows that a further increase of carbon (lower values of $x$) cause more shifts and splitting of the peaks. This points to even more distortions of the lattice parameters and further reduction in symmetry of the atomic positions as the carbon content in the HEC increases. As $x$ decreases below 0.5 the pattern becomes unrecognizable compared to the experimentally determined XRD pattern. One thing to note is that although the size of the SQS used here are relatively large (4x4x4, 192 atoms) there will still be some unrealistic long-range ordering not found in the experimentally synthesized HEC due to the periodicity of the SQS. This will affect the shifting and splitting of the peaks in the simulated XRD pattern.

The reduction in symmetry of the atomic positions and subsequently the distortion of the lattice parameters can be explained by the difference in metal-boron and metal-carbon binding. The DFT calculated metal-boron and metal-carbon bond lengths for borides and carbides with same metals as the precursors yield bond lengths of Hf-B = 2.42 Å, Hf-C = 2.33 Å, Ta-B = 2.40 Å, Ta-C = 2.24 Å, Mo-B = 2.32 Å, Mo-C = 2.20 Å, Ti-B = 2.35 Å and Ti-C = 2.16 Å. For all metals the metal-carbon bond length is shorter than the metal-boron bond length, pointing to the fact that the metal-carbon bonds are stronger than the metal-boron bonds for these metals. This will cause the carbon atoms in the hexagonal grid to move closer to the metal atoms, equivalently the metal atoms will move closer to the carbon atoms, thus distorting the structure.

The DFT calculations thus show that increasing the carbon content in the hexagonal grid of the HEC leads to a decrease in phase stability at 0 K. This is due to the fact that replacing boron atoms with carbon atoms increases the lattice distortion, which will increase the mechanical properties of the HEC due to the strain strengthening mechanism.
References