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Synthesis and Characterization of High-Purity, High-Entropy Diboride Ceramic Powders by a Liquid Phase Method

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Abstract: A nano-dual-phase powder with ultra-fine grain size was synthesized by the liquid precursor method at 1200 °C. A series of single-phase high-entropy ceramic powders ((Ti, Zr, Hf, Nb)B₂, (Ti, Zr, Hf, Nb, Ta)B₂, (Ti, Zr, Hf, Nb, Mo)B₂, (Ti, Zr, Hf, Nb, Ta, Mo)B₂) with high purity (C content less than 0.9 wt% and O content less than 0.7 wt%) and ultrafine (average grain sizes of 340–570 nm) were successfully synthesized at 1800 °C. The sample of (TiZrHfNbTa)B₂ exhibited a hexagonal close-packed (HCP) structure, and the metal elements were uniformly distributed at the nanoscale, microscale, and macroscale. This method did not apply to the preparation of all high-entropy ceramic powders and was unfavorable for the formation of single-phase high-entropy borides when the size difference factor exceeded 3.9%. The present work provides a guide for the development of ceramic-based composites through precursor impregnation pyrolysis.

Keywords: liquid-phase precursor method; high-entropy diboride powders; solid solutions; microstructure; pyrolysis mechanism



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1. Introduction

High-entropy transition metal diborides belonging to the hexagonal crystal system are a polymeric solid solution with an AlB₂ structure [1], where the metal atom layer and boron layer are arranged alternately in the c-axis direction and the transition metal atoms are randomly arranged in the metal layer [2]. Meanwhile, boron atoms are bonded by covalent bonds and a mixture of ionic and covalent bonds between metal and boron atoms [3]. The excellent properties, such as high melting point (>3000 K), high hardness, good chemical stability, and high temperature stability [4–7], attribute to the strong force between the chemical bonds. Therefore, it has good application prospects in aerospace, cutting tools, microelectronics, and nuclear reactors [8–10].

Yan Zhang et al. [11] synthesized a high-entropy ceramic (Hf, Zr, Ta, Cr, Ti)B₂ with high hardness (more than 29 GPa) and high toughness (more than 4.63 MPa m^{1/2}) due to over 99% densification. In 2023, Steven M. Smith II et al. [12] obtained (Cr, Hf, Ta, Ti, Zr)B₂ and (Hf, Ta, Ti, V, Zr)B₂ ceramics for the first time with densities close to 100% by pressureless sintering. Secondary phases were present in (Hf, Ta, Ti, W, Zr)B₂ and (Hf, Mo, Ti, W, Zr)B₂ ceramics, which did not attain full density. Generally, the HEB materials were difficult to densify due to a low self-diffusion rate and the presence of impurities [13]. Therefore, the synthesis of high-entropy metal diboride powders is essential for excellent-performance ceramics, with current research predominantly focused on transition metals from groups IVB, VB, and VIB [14,15]. In 2016, Joshua Gild et al. [16] made the pioneering effort to prepare seven quinary boride ceramic bulk materials, including (Hf, Zr, Ta, Nb,

Ti)B₂, (Hf, Zr, Ta, Mo, Ti)B₂, (Hf, Zr, Mo, Nb, Ti)B₂, (Hf, Mo, Ta, Nb, Ti)B₂, (Mo, Zr, Ta, Nb, Ti)B₂, (Hf, Zr, W, Mo, Ti)B₂, and (Hf, Zr, Ta, Cr, Ti)B₂. XRD results show that all systems, except (Mo, Zr, Ta, Nb, Ti)B₂, form a single solid solution of ceramic. However, the majority of the systems have varied degrees of elemental inhomogeneity, according to the EDS examination of ceramics. This is primarily due to the ultra-high melting point and strong covalent bonding characteristics of borides, which make it challenging for them to form uniform solid solutions. In 2019, Tallarita G et al. [17] mixed equimolar amounts of Ti, Hf, Nb, Ta, and Mo metal powders with amorphous boron powder and used self-propagating high-temperature synthesis (SHS) to prepare (Hf, Mo, Ta, Nb, Ti)B₂ ceramic powders. However, the powders obtained by this method exhibited low sintering density, poor mechanical properties, and a noticeable enrichment of Ti elements. Wei-Min Guo et al. synthesized (Hf, Zr, Ta, Cr, Ti)B₂, (Hf, Mo, Zr, Nb, Ti)B₂, and (Hf, Mo, Ta, Nb, Ti)B₂ boride high-entropy ceramic powders using metal oxide and amorphous boron powders as raw materials by boron-thermal reduction at 1600 °C for 24 h [18]. However, XRD characterization results showed the presence of certain oxide impurities, including m-(Zr, Hf)O₂ and t-ZrO₂, in the powders. Hence, there is an urgent need to synthesize high-purity, high-entropy metal diboride powders to further promote the development of high-entropy boride ceramics. Yan Zhang et al. [11], using B, ZrO₂, HfO₂, Ta₂O₅, Nb₂O₅, and TiO₂ powders as raw materials, produced a nano-dual-phase powder by molten salt-assisted borothermal reductions at 1100 °C. The as-synthesised powder has a specific surface area of 22.971 m²/g, according to the BET measurement result, implying good sinterability. Dong Zhijun et al. [19] used precursor polyboron nitride (PBN) as the boron source and an organic precursor of HfC to synthesize HfB₂ ceramic powders with particle sizes of about 200 nm through a liquid-phase route at 1500 °C. (Hf, Nb, Cr, Ta, Mo)B₂ ceramic powder with an average particle size of 62.09 nm was obtained by the sol-gel method at a relatively low temperature of 1650 °C. Molten salt and sol-gel methods contribute to the synthesis of low-temperature fine grains, but the processability of these methods can be inferior. The liquid-phase precursor method offers distinct advantages in producing high-purity, ultrafine, and uniformly distributed ceramic powders [20,21]. Meanwhile, the method exhibits good process performance, which contributes to the formation of high-performance ceramic fibers and ceramic composites [22,23].

In this study, we utilized the liquid-phase precursor method to synthesize a series of high-purity, high-entropy metal diboride powders. The relationship between the size difference factor of the system and the physical phase structure of the product is also investigated. The effect of the ratio of boron to carbon to metal sources on the purity and phase structure of the product was investigated using (Ti, Zr, Hf, Nb, Ta)B₂. We then delved deeper into the mechanism of precursor decomposition, providing the morphology, microstructure, and compositional homogeneity of the powder, as well as the oxygen content.

2. Experimental

2.1. Materials and Preparation

The general flow chart for synthesizing high-entropy boride (HEB) powder is shown in Figure 1. In this work, metal alkoxides (MA, M = Ti, Zr, Hf, Nb, Ta, Mo, W) were used as the initial metal sources. TiA (titanium n-propoxide, Ti(OC₃H₇)₄, purity > 99 wt%, in n-propanol) and ZrA (zirconium n-propoxide, Zr(OC₃H₇)₄, purity > 72 wt%, in n-propanol) were purchased from Heruidong Co., Ltd., Shandong, China. HfA, NbA, WA, MoA, and TaA were prepared by the corresponding metal chloride; for instance, TaA was synthesized by the reaction of TaCl₅ and n-propanol, using triethylamine (Et₃N) as a precipitant with a TaCl₅/ n-propanol /Et₃N molar ratio of 1/5/5 and glycol dimethyl ether as a solvent. The precipitate was removed by filtration to obtain a clear solution. Acetylacetone (Hacac) was added to MAs at room temperature with a mole ratio of MA:Hacac = 1:1 to obtain stable solutions of metal acetylacetonate alkoxides (MAAs). Afterwards, controlled co-hydrolysis and polycondensation reactions were achieved by the dropwise addition of deionized water with a molar ratio of MAAs: H₂O = 1:1, followed by distillation to obtain

metal polymers. Borate ester (BE, self-made in our laboratory) and allyl-functional novolac (AN) resin (self-made in our laboratory) acted as sources of boron and carbon, which were respectively dissolved in normal propyl alcohol and added to the solution of metal polymers. The proportion of the molarities of the metal source, the molarities of the boron source, and the mass of the carbon source (M: B: C) were studied to obtain high-purity, high-entropy borides. The mixture was continually stirred at 25 °C for 2 h to obtain a homogenous solution. The solvent was partially removed to obtain the HEB precursor by rotary evaporation. Subsequently, precursors were heated at 100 °C, 140 °C, 180 °C, 200 °C, 220 °C, and 250 °C each for an hour. The obtained powders were heated in an alumina tube furnace to remove substances released at 400 °C for 2 h in an argon atmosphere. Afterwards, the above samples were pyrolyzed to undergo a boro/carbothermal reduction reaction with a heating rate of 10 °C/min at 600 °C, 800 °C, 1000 °C, 1200 °C, 1400 °C, 1600 °C, and 1800 °C for 4 h to obtain ceramic powders in a graphite furnace.

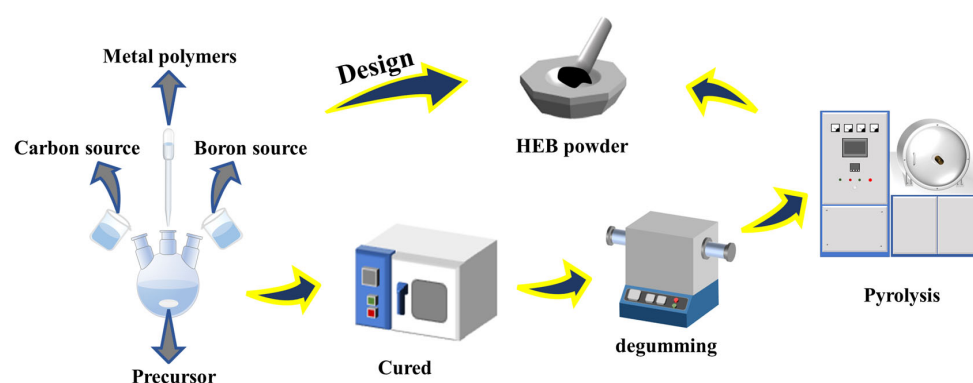


Figure 1. Schematic diagram of the synthesis procedure for liquid polymer and ceramic powders.

2.2. Characterization

Thermogravimetry Analysis (TGA, STA 449F5) was used to analyze the transformation process of polymer to ceramic. X-ray diffraction (XRD, PANalytical Empyrean, Almelo, The Netherlands) was carried out to investigate the crystal structure of HEB powders with Cu K α radiation at 40 KV and 40 mA. The diffraction patterns were scanned from 10° to 90° of 2 θ in a step-scan mode at a step of 0.026° and a scanning speed of 4°/min. Scanning electron microscopy (SEM, SU8020, Hitachi Limited, Tokyo, Japan) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM2100 F, Tokyo, Japan), both outfitted with energy dispersive spectroscopy (EDS), were used to examine the morphologies of HEB powders. The oxygen and carbon content of the HEB powders were respectively determined by an Oxygen /Nitrogen Analyzer (TC-600C, Leco, St. Joseph, MO, USA) and a Carbon/Sulphur Analyzer (CS844, Leco, St. Joseph, MO, USA). The contents of boron and other metal elements in the powders were measured Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, IRIS Intrepid II, Thermal, Acton, MA, USA). The software Jade 6.5 was used to calculate the lattice parameter and crystal plane spacing.

3. Results and Discussion

3.1. Factor Analysis of Size Difference

HEBs are a type of multi-component solid solution with a single-phase structure. The lattice parameter of the transition metal boride has a great influence on the formation of single-phase solid solutions. Therefore, before conducting the synthesis experiments, we calculated the size difference factor δ to assess the structural compatibility of the boride components [24]. A smaller δ value indicates a closer structural match, while a larger value suggests greater divergence. The formula for calculating δ in high-entropy borides is as follows [24]:

$$\delta = \sqrt{\sum_{i=1}^n \frac{n_i}{2} \left[\left(1 - \frac{a_i}{a}\right)^2 + \left(1 - \frac{c_i}{c}\right)^2 \right]} \quad (1)$$

In this equation, n represents the total number of components constituting the high-entropy boride, n_i is the molar fraction of the MeB_2 component for each constituent, and a_i and c_i are the numerical values of the lattice parameters a and c for the corresponding hexagonal boride. $\bar{a}$ and $\bar{c}$ denote the average values of a and c , respectively, for the binary borides comprising the high-entropy material. Typically, a smaller size difference factor δ implies a closer structural resemblance among the components, facilitating the formation of high-entropy materials. We calculated the δ values for the high-entropy transition metal borides to be synthesized in this experiment based on reported boride lattice parameter values, and the results are presented in Table 1. Table 1 reveals that the size difference factors for various 4–6 component high-entropy borides fall within the range of 2.811% to 4.168%. The lattice parameters of $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Ta}, \text{W})\text{B}_2$ and $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Mo}, \text{W})\text{B}_2$ are the average values of the lattice parameters of the five binary borides, and these specific values are listed in Table S1.

Table 1. δ values and unit cell parameters of six kinds of high-entropy boride.

Composition	δ (%)	Lattice Parameter (Å)
$(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb})\text{B}_2$	2.925	$a = b = 0.3113$, $c = 0.3374$
$(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta})\text{B}_2$	2.811	$a = b = 0.3105$, $c = 0.3356$
$(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Mo})\text{B}_2$	3.315	$a = b = 0.3090$, $c = 0.3363$
$(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta}, \text{Mo})\text{B}_2$	3.078	$a = b = 0.3087$, $c = 0.3341$
$(\text{Ti}, \text{Zr}, \text{Hf}, \text{Ta}, \text{W})\text{B}_2$	3.901	$a = b = 0.3084$, $c = 0.3310$ [25]
$(\text{Ti}, \text{Zr}, \text{Hf}, \text{Mo}, \text{W})\text{B}_2$	4.168	$a = b = 0.3073$, $c = 0.3292$ [25]

To investigate the correlation between the size difference factor (δ) and the phase composition of the samples, we performed XRD analysis on six different high-entropy borides. The results are presented in Figure 2. From the graph, it is evident that $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb})\text{B}_2$, $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta})\text{B}_2$, $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Mo})\text{B}_2$, and $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta}, \text{Mo})\text{B}_2$ all exhibit a single-phase structure, with their respective lattice parameters listed in Table 1. In contrast, $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Ta}, \text{W})\text{B}_2$ and $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Mo}, \text{W})\text{B}_2$ show variations. In the XRD patterns of $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Ta}, \text{W})\text{B}_2$ and $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Mo}, \text{W})\text{B}_2$ systems, in addition to the high-entropy phase, impurity phases such as $(\text{Mo}, \text{W})_2\text{B}_5$, W_2B_5 , and minor amounts of $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Mo}, \text{W})\text{C}$ and B_4C were observed. Notably, these non-single-phase $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Ta}, \text{W})\text{B}_2$ and $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Mo}, \text{W})\text{B}_2$ systems corresponded to higher δ values. Hence, it is less likely to form single-phase, high-entropy borides when δ exceeds 3.9%. In the upcoming experiments, our focus will be on $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta})\text{B}_2$, which boasts the smallest δ value.

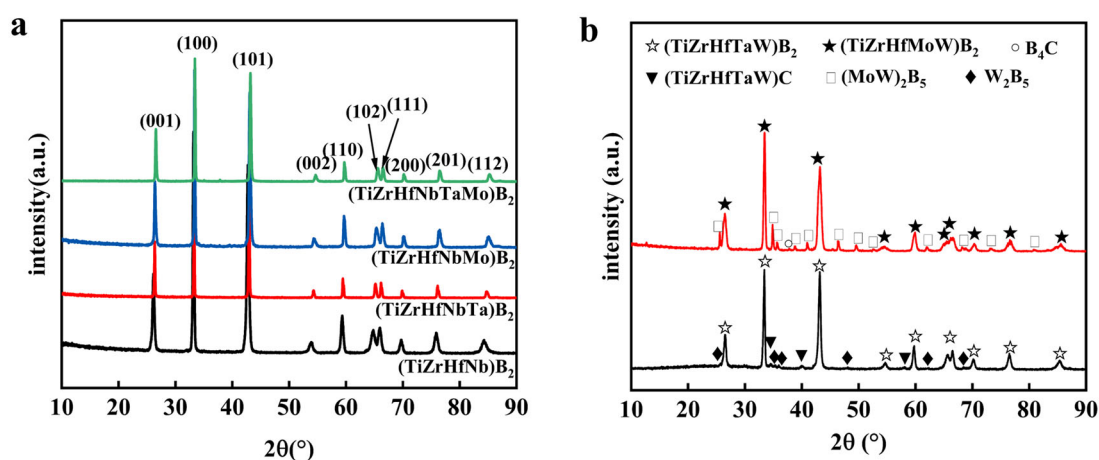


Figure 2. XRD patterns of the as-synthesized powders: (a) $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb})\text{B}_2$, $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta})\text{B}_2$, $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Mo})\text{B}_2$, and $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta}, \text{Mo})\text{B}_2$. (b) $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Ta}, \text{W})\text{B}_2$ and $(\text{Ti}, \text{Zr}, \text{Hf}, \text{Mo}, \text{W})\text{B}_2$.

In the process of preparing high-entropy borides through the liquid precursor method, the quantities of boron and carbon sources play a vital role in determining the phase

structure and purity of the final product. Therefore, the amounts of boron and carbon sources are investigated to find the optimal synthesis recipe. The specific ratios of the raw materials are listed in Table 2. This table includes metal-to-boron molar ratios of 1:8, 1:10, and 1:16, as well as metal-to-carbon mass ratios of 1:30 and 1:40. To examine the phase structure of the final products, XRD tests were performed on products synthesized with different ratios. Figure 3 reveals that the optimal composition, yielding a single-phase boride structure, is achieved with a metal-to-boron-to-carbon ratio of 1:16:30. When the metal-to-boron ratio falls below 1:16, it results in the presence of corresponding metal carbide phases. When the ratio of metal and carbon is greater than 1:30 and the boron source is moderate, the impurity phase of B_4C is detected. The elemental contents of the as-synthesized powder at the optimum ratio are listed in Table 3, illustrating that the proportions of metal elements in the powder are nearly 1:1:1:1:1, and the metal-to-boron ratio is close to 1:2, with lower contents of carbon and oxygen. Excessive boron and oxygen elements indicate that boron oxide impurities are likely to be present in the sample. Hence, 1:16:30 (M: B: C) represents the best synthesis proportion, and exploring the quantities of boron and carbon sources is of great significance.

Table 2. Raw material composition and corresponding Phase structure of (Ti, Zr, Hf, Nb, Ta) B_2 .

Samples	M:B:C	Phase Structure
1#	1:8:30	(Ti, Zr, Hf, Nb, Ta) B_2 , (Ti, Zr, Hf, Nb, Ta)C
2#	1:8:40	(Ti, Zr, Hf, Nb, Ta) B_2 , (Ti, Zr, Hf, Nb, Ta)C
3#	1:10:30	(Ti, Zr, Hf, Nb, Ta) B_2 , (Ti, Zr, Hf, Nb, Ta)C
4#	1:10:40	(Ti, Zr, Hf, Nb, Ta) B_2 , (Ti, Zr, Hf, Nb, Ta)C
5#	1:16:30	(Ti, Zr, Hf, Nb, Ta) B_2
6#	1:16:40	(Ti, Zr, Hf, Nb, Ta) B_2 , B_4C

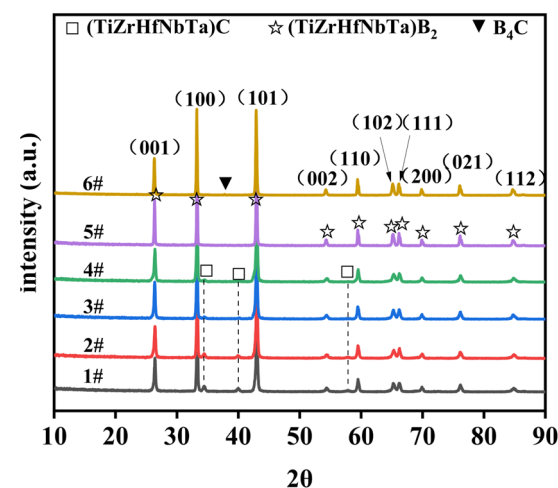


Figure 3. XRD patterns of the different proportions of (Ti, Zr, Hf, Nb, Ta) B_2 powders. 1#–6# represent ceramic powders pyrolyzed at 1800 with different contents of boron and carbon sources, and these specific proportions can be found in Table 2.

Table 3. Element content analysis of four kinds of powders prepared at 1800 °C.

Empirical Formula	Ti	Zr	Hf	Nb	Ta	Mo	B	C	O
(Ti _{0.25} Zr _{0.26} Hf _{0.27} Nb _{0.26})B _{2.7} C _{0.09} O _{0.01}	9.1	17.9	36.3	18.2	/	/	22.2	0.8	0.4
(Ti _{0.2} Zr _{0.21} Hf _{0.22} Nb _{0.21} Ta _{0.21})B _{2.1} C _{0.08} O _{0.01}	6.6	13	26.7	13.6	26.00	/	15.7	0.7	0.7
(Ti _{0.2} Zr _{0.21} Hf _{0.2} Nb _{0.2} Mo _{0.2})B _{2.1} C _{0.1} O _{0.01}	6.7	13.2	25.3	/	25.4	13.7	15.9	0.8	0.6
(Ti _{0.17} Zr _{0.17} Hf _{0.17} Nb _{0.17} Ta _{0.17} Mo _{0.18})B _{2.49} C _{0.19} O _{0.01}	5.8	11.3	22.1	11.5	22.3	11.9	16.4	0.9	0.7

3.2. Thermogravimetric Analysis of Precursors

To gain a deeper insight into the pyrolysis process of high-entropy boride (HEB) precursors, we conducted a study on the pyrolysis process of the cured products using thermogravimetric analysis (TG). As depicted in Figure 4, the TG-DTG curves reveal a pyrolysis process comprising three distinct phases. The first part, extending from room temperature to 237 °C, is associated with a weight loss of approximately 7.37 wt%. This initial weight loss is primarily attributed to the removal of hydroxyl groups present in the sample and a small amount of adsorbed water vapor. The second part occurs within the temperature range of 237 °C to 680 °C and results in a weight loss of about 27.52 wt%. This phase signifies the transformation from organic to inorganic materials, involving the breakdown of organic-inorganic molecular chains and the substantial departure of organic groups. The final phase is linked to the boron-carbon thermal reduction process, potentially leading to the release of CO, CO₂, and B₂O₃ [26]. This phase is marked by a substantial weight reduction of 31.24 wt%. During this stage, metals gradually form borides, laying the groundwork for the ultimate formation of a single-phase high-entropy boride. These discoveries hold significant importance for comprehending and refining the preparation process for high-entropy borides.

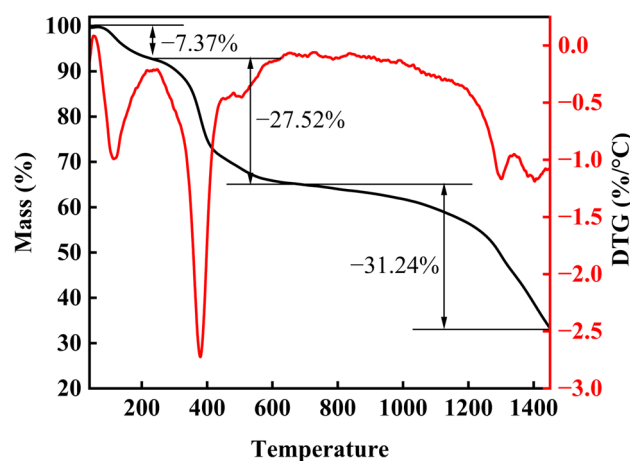


Figure 4. TG-DTG describes the pyrolysis process of the (Ti, Zr, Hf, Nb, Ta)B₂ curing sample.

3.3. Analysis of the Pyrolysis Process of Precursors

We conducted further research into the transformation of the (Ti, Zr, Hf, Nb, Ta)B₂ precursor from a polymer to ceramics using X-ray diffraction (XRD). Figure 5 illustrates the results of this investigation, showing the evolution of phases at different heat treatment temperatures. Samples treated at 600 °C are predominantly composed of oxide phases, including (Nb, Ta)₂O₅, (Zr, Hf, Ti)₆(Nb, Ta)₂O₁₇, (Ti, Zr, Hf)O₂, and (Nb, Ta)O₂. As the annealing temperature increases to 800 °C, (Nb, Ta)₂O₅ and (Ti, Zr, Hf)O₂ gradually transform into (Ti, Nb, Ta)O₄. When the temperature is further raised to 1000 °C, oxide phases such as m-(Zr, Hf)O₂ undergo a reaction with B and C elements, resulting in a two-phase structure primarily consisting of (Zr, Hf)B₂ and (Ti, Nb, Ta)B₂. It is noteworthy that the diffraction peaks of (Zr, Hf)B₂ are observed to the left of the diffraction peaks of (Ti, Nb, Ta)B₂ due to the larger atomic radii of Zr and Hf. Simultaneously, the diffraction peak intensity of (Zr, Hf)B₂ is lower than that of (Ti, Nb, Ta)B₂, indicating a relatively lower content of (Zr, Hf)B₂ due to the continued presence of some Zr and Hf elements in oxide form. As the heat treatment progresses from 1200 °C to 1600 °C, the powder maintains a two-phase structure, and the diffraction peaks intensity of (Zr, Hf)B₂ gradually approaches that of (Ti, Nb, Ta)B₂. This suggests the nearly complete transformation of metal oxides into borides. Figure 4 shows that there is still a mass loss after 1200 °C, primarily due to TG being conducted in an Ar atmosphere, which slows down the volatilization of excess boron oxide. The pyrolysis process, carried out in a vacuum, has almost entirely volatilized the boron oxide by 1200 °C. Ultimately, through element diffusion, (Zr, Hf)B₂ and (Ti, Nb,

Ta) B_2 form a single-phase solid solution, (Ti, Zr, Hf, Nb, Ta) B_2 , in the heated samples at 1800 °C.

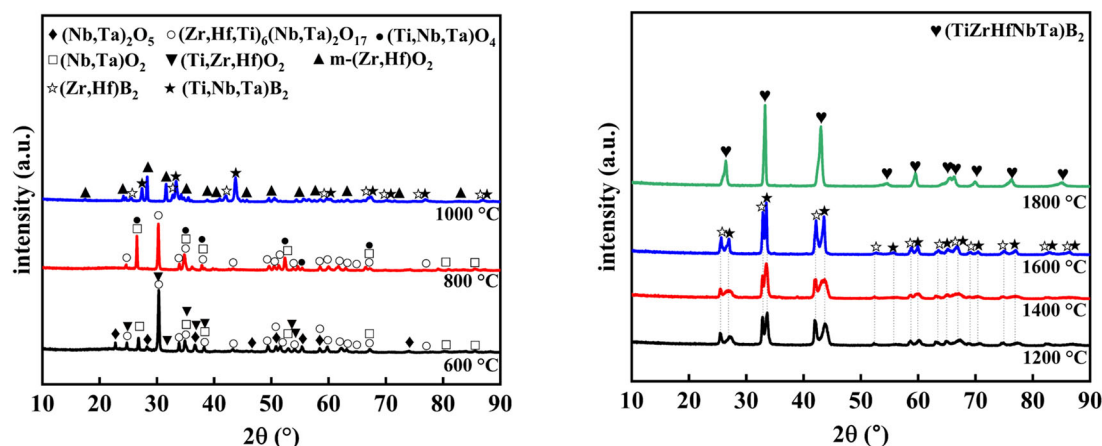


Figure 5. XRD patterns of (Ti, Zr, Hf, Nb, Ta) B_2 powders obtained at 600–1800 °C.

3.4. Micro/Nanostructure of (Ti, Zr, Hf, Nb, Ta) B_2 Powders

As depicted in Figure 6, we conducted a scanning electron microscopy (SEM) study to examine the morphology of (Ti, Zr, Hf, Nb, Ta) B_2 ceramics obtained at different temperatures ranging from 600 °C to 1800 °C. The morphological changes in the powders between 600 °C and 800 °C are relatively minor, primarily consisting of particles and a filament network. According to XRD results, the particles mainly consist of metallic oxides enveloped within an amorphous layer formed by the interaction of carbon and boron. The formation of filament materials is likely due to a high-temperature softening process followed by cooling and drawing, presumed to be caused by an excess of boron esters. At 1000 °C, the filament materials disappear, suggesting substantial decomposition of the boron esters at this stage. A small number of crystalline particles are enveloped within a mixture of amorphous boron oxide and carbon. According to XRD results, these particles are composed of oxides and a small amount of borides. The amorphous materials cannot be observed around the powders obtained at 1200 °C to 1400 °C. However, there are two types of particles in these powders, with the larger particles likely being the first-formed boride crystals. The powders at 1800 °C exhibit significantly increased particle size compared to those at 1600 °C, accompanied by some degree of sintering. Figure 7 demonstrates the image of SEM and particle size distributions of (Ti, Zr, Hf, Nb) B_2 , (Ti, Zr, Hf, Nb, Ta) B_2 , (Ti, Zr, Hf, Nb, Mo) B_2 , and (Ti, Zr, Hf, Nb, Ta, Mo) B_2 , which show that the ceramic samples prepared by the liquid precursor method have a particle size of approximately 340–570 nm. Figure 8 is the SEM and EDS image of the (Ti, Zr, Hf, Nb, Ta) B_2 heat treat at 1800 °C, which revealed a uniform distribution of metallic elements at the micrometer scale with no evidence of metallic element enrichment.

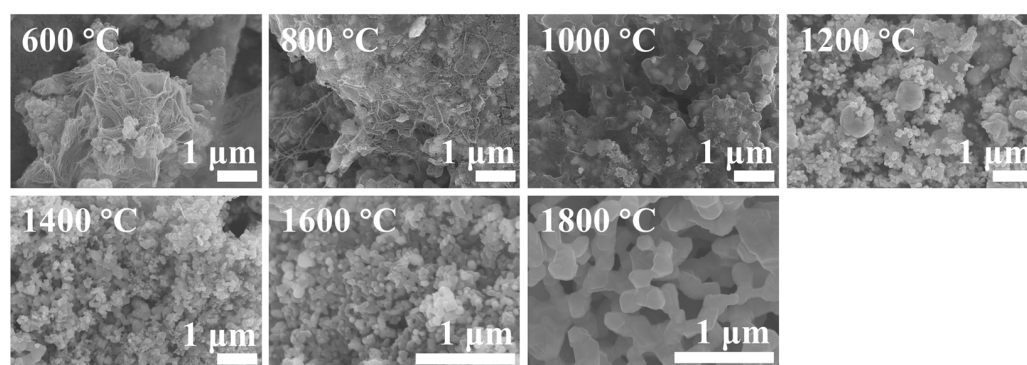


Figure 6. The SEM image (Ti, Zr, Hf, Nb, Ta) B_2 powers obtained at different temperatures.

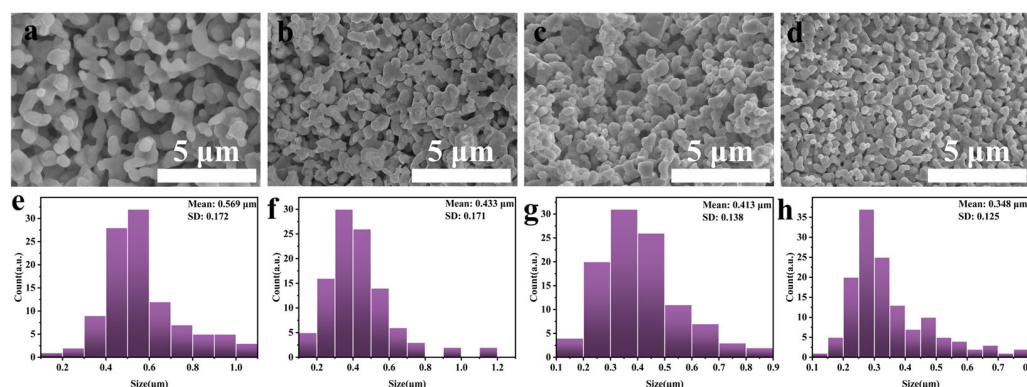


Figure 7. The image of the SEM and particle size distribution of ceramic powder obtained at 1800 °C. (a,e) (Ti, Zr, Hf, Nb)B₂, (b,f) (Ti, Zr, Hf, Nb, Ta)B₂, (c,g) (Ti, Zr, Hf, Nb, Mo)B₂, (d,h) (Ti, Zr, Hf, Nb, Ta, Mo)B₂.

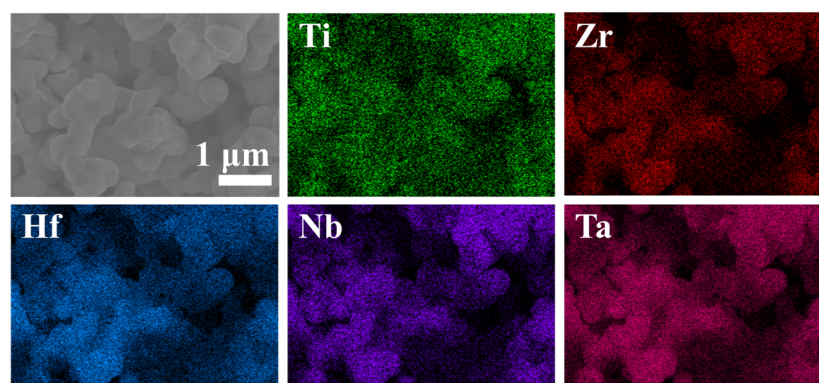


Figure 8. The SEM and EDS images of the (Ti, Zr, Hf, Nb, Ta)B₂ heat-treat at 1800 °C.

To explore the nanoscale crystal structure and compositional uniformity, we conducted further research using Transmission Electron Microscopy (TEM) on (Ti, Zr, Hf, Nb, Ta)B₂ powder obtained at 1800 °C. Figure 9a presents a TEM image of the synthesized (Ti, Zr, Hf, Nb, Ta)B₂ powder, revealing numerous independent nanoscale particles in the synthesized material. Dark regions indicate areas of greater sample thickness. In Figure 9b, a Selected Area Electron Diffraction (SAED) pattern is shown for the synthesized powder along the [0, −1, −1] axis. The well-organized and symmetric arrangement of diffraction spots clearly indicates that the synthesized powder possesses a single-crystal hexagonal structure. High-resolution TEM (HR-TEM) images in Figure 9c,d demonstrate the periodic lattice structure of the synthesized (Ti, Zr, Hf, Nb, Ta)B₂ powder, with a lattice spacing of 0.2097 nm for the (101) crystal plane, closely matching the calculated value (2.1038 Å) from the XRD spectrum. Further analysis through the Energy-Dispersive X-ray Spectroscopy (EDS) in Figure 10 reveals the even distribution of all metallic elements at the nanoscale, without evidence of clustering or depletion. However, a small amount of amorphous boron oxide is present around the ceramic particles, which is consistent with the ICP test results.

3.5. Speculation on the Pyrolysis Mechanism of Precursors

Based on the above analysis, we hypothesize the decomposition mechanism of the (Ti, Zr, Hf, Nb, Ta)B₂ liquid precursor as depicted in Figure 11. During the heat treatment process below 800 °C, the liquid precursor primarily undergoes an organic-to-inorganic transformation, leading to the formation of various metal oxide solid solutions and amorphous carbon and boron oxides. When the decomposition temperature falls within the range of 1000 °C to 1400 °C, the main process involves a carbon-boron thermal reduction reaction, resulting in a two-phase structure primarily composed of (Zr, Hf)B₂ and (Ti, Nb, Ta)B₂. As the decomposition temperature increases from 1600 °C to 1800 °C, the

process primarily entails phase solid solution, ultimately culminating in the formation of the hexagonal (Ti, Zr, Hf, Nb, Ta)B₂ single-phase solid solution.

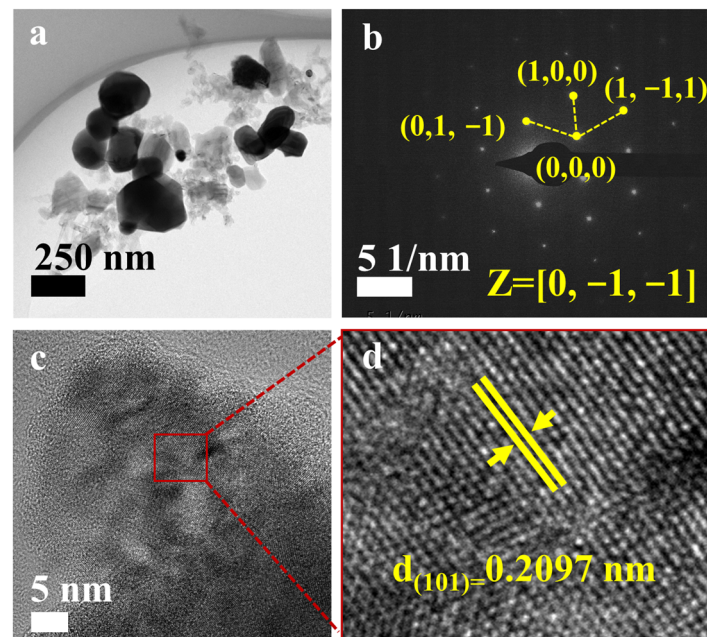


Figure 9. TEM analysis of the as-synthesized (Ti, Zr, Hf, Nb, Ta)B₂ powders at 1800 °C: (a) TEM image; (b) SAED pattern; (c) HR-TEM micrographs; (d) the enlarged HR-TEM micrographs.

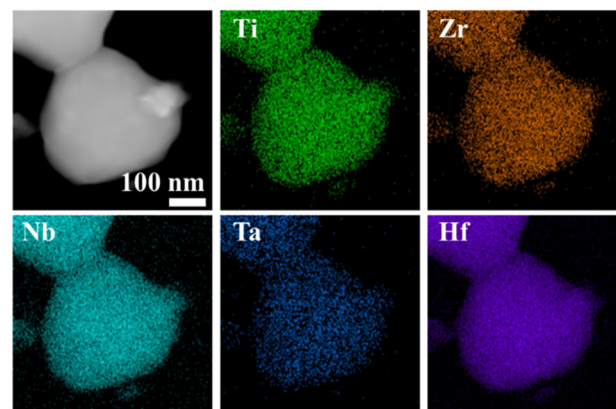


Figure 10. TEM image and the corresponding EDS maps of (Ti, Zr, Hf, Nb, Ta)B₂ powders obtained at 1800 °C.

As a new class of ultrahigh-temperature ceramics with many attractive physicochemical properties (such as high melting point, high hardness and chemical inertness, and good electrical and thermal conductivity), high-entropy diborides can be potential candidates for high-temperature thermal protection materials in extreme environments and electrode materials. The high-purity, high-entropy boride powders in this work can be processed to obtain ceramic blocks and coating materials, which are expected to be applied to parts such as nose cones and wings of aircraft. As shown in Figure S1, we prepared high-entropy boride blocks by hot pressing and ceramic spheres by spray drying using experimentally prepared high-entropy diboride powder. This research lays the foundation for the preparation of ceramic blocks, ceramic matrix composites, and high-temperature resistant coatings.

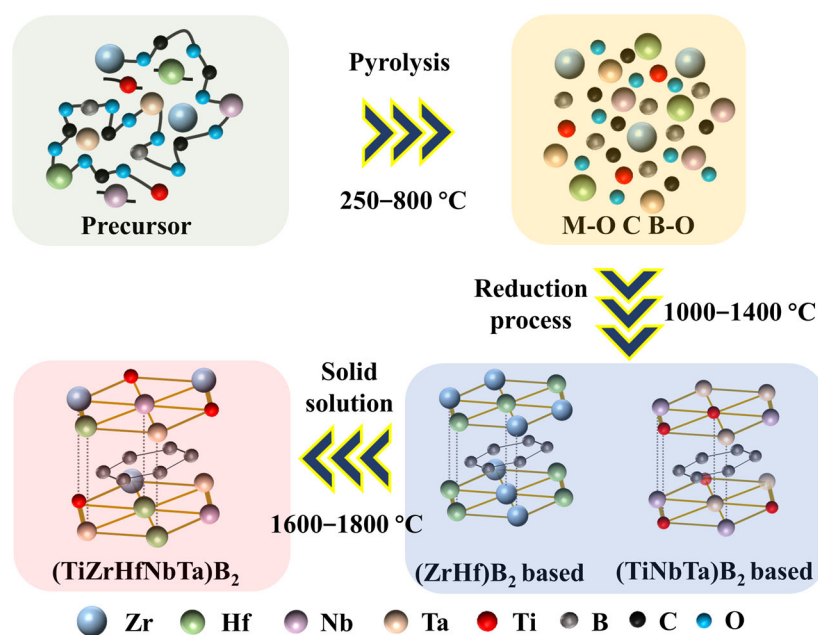


Figure 11. A schematic illustration showing the main process for forming single-phase (Ti, Zr, Hf, Nb, Ta) B_2 high-entropy boron ceramic.

4. Conclusions

In summary, we have successfully synthesized four high-purity nanoscale powders using the liquid precursor method, all of which exhibit δ values below 3.9%. In the case of the two powders with an δ value exceeding 3.9%, a secondary phase, mainly composed of W_2B_5 and $(W, Mo)_2B_5$, was observed. Additionally, we conducted a detailed study of the decomposition process of the (Ti, Zr, Hf, Nb, Ta) B_2 precursors. It was observed that the precursor had already completely formed a two-boride phase, primarily composed of (Zr, Hf) B_2 and (Ti, Nb, Ta) B_2 , at 1200 °C. Single-phase high-entropy borides with hexagonal structure are formed by solid solution at 1800 °C, with cell parameters $a = b = 0.3105$ nm and $c = 0.3356$ nm. The samples prepared by the liquid precursor method have a particle size of approximately 340–570 nm. They exhibit a high degree of compositional homogeneity, from the nanoscale to the microscale.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma16237431/s1>, Figure S1: (a) the image of ceramic blocks prepared by hot pressing at 1900 °C, (b) image of ceramic spheres prepared by spray drying based on (Ti, Zr, Hf, Nb, Ta) B_2 powders prepared in this work; Table S1: The lattice parameter of $(Ti_{0.2}Zr_{0.2}Hf_{0.2}Ta_{0.2}W_{0.2})B_2$ and $(Ti_{0.2}Zr_{0.2}Hf_{0.2}Mo_{0.2}W_{0.2})B_2$.

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References

- Feng, L.; Monteverde, F.; Fahrenholtz, W.G.; Hilmas, G.E. Superhard high-entropy AlB_2 -type diboride ceramics. *Scr. Mater.* **2021**, *199*, 113855. [\[CrossRef\]](#)
- Monteverde, F.; Saraga, F. Entropy stabilized single-phase (Hf, Nb, Ta, Ti, Zr) B_2 solid solution powders obtained via carbo/boro-thermal reduction. *J. Alloys Compd.* **2020**, *824*, 153930–153940. [\[CrossRef\]](#)
- Wang, Y.P.; Gan, G.Y.; Wang, W.; Yang, Y.; Tang, B.Y. Ab Initio Prediction of Mechanical and Electronic Properties of Ultrahigh Temperature High-Entropy Ceramics $(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ta}_{0.2}\text{Mo}_{0.2}\text{Ti}_{0.2})\text{B}_2$ (M. = Nb, Mo, Cr). *Phys. Status Solidi B Basic Res.* **2018**, *255*, 1800011. [\[CrossRef\]](#)
- Zou, Q.; Gu, H.; Li, Y.; Li, Z.; Liang, P.; Luo, Y. Characterization and analysis of high-entropy boride ceramics sintered at low temperature. *J. Am. Ceram. Soc.* **2023**, *106*, 2764–2772. [\[CrossRef\]](#)
- Wen, Z.; Meng, H.; Jiang, S.; Tang, Z.; Liu, Y.; Chu, Y. Non-equimolar (Hf,Zr,Ta,W) B_2 high-entropy diborides enable superior oxidation resistance. *Sci. China Mater.* **2023**, *66*, 3213–3222. [\[CrossRef\]](#)
- Zhang, Y.; Sun, S.; Guo, W.; Xu, L.; Zhang, W.; Lin, H.T. Optimal preparation of high-entropy boride-silicon carbide ceramics. *J. Adv. Ceram.* **2020**, *10*, 173–180. [\[CrossRef\]](#)
- Storr, B.; Kodali, D.; Chakrabarty, K.; Baker, P.A.; Rangari, V.; Catledge, S.A. Single-Step Synthesis Process for High-Entropy Transition Metal Boride Powders Using Microwave Plasma. *Ceramics* **2021**, *4*, 257–264. [\[CrossRef\]](#)
- Guo, R.-F.; Mao, H.-R.; Shen, P. Ultra-fast high-temperature synthesis and densification of high-entropy diborides and diboride-carbide ceramics. *J. Eur. Ceram. Soc.* **2023**, *43*, 5763–5773. [\[CrossRef\]](#)
- Xiang, H.; Xing, Y.; Dai, F.; Wang, H.; Su, L.; Miao, L.; Zhang, G.; Wang, Y.; Qi, X.; Yao, L.; et al. High-entropy ceramics: Present status, challenges, and a look forward. *J. Adv. Ceram.* **2021**, *10*, 385–441. [\[CrossRef\]](#)
- Golla, B.R.; Mukhopadhyay, A.; Basu, B.; Thimmappa, S.K. Review on ultra-high temperature boride ceramics. *Prog. Mater. Sci.* **2020**, *111*, 100651. [\[CrossRef\]](#)
- Guo, R.R.; Li, Z.J.; Li, L.; Liu, Y.; Zheng, R.X.; Ma, C.L. Microstructures and oxidation mechanisms of $(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.2})\text{B}_2$ high-entropy ceramic. *J. Eur. Ceram. Soc.* **2022**, *42*, 2127–2134. [\[CrossRef\]](#)
- Smith, S.M.; Fahrenholtz, W.G.; Hilmas, G.E. Pressureless sintering of high-entropy boride ceramics. *J. Eur. Ceram. Soc.* **2023**, *43*, 5168–5173. [\[CrossRef\]](#)
- Yuan, J.H.; Guo, W.M.; Liu, Y.; Sun, S.K.; Duan, X.M.; Jia, D.C.; Lin, H.T. Hardness and toughness improvement of SiC-based ceramics with the addition of $(\text{Hf}_{0.2}\text{Mo}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.2})\text{B}_2$. *J. Am. Ceram. Soc.* **2021**, *105*, 1629–1634. [\[CrossRef\]](#)
- Razumov, N.; Makhmutov, T.; Kim, A.; Popovich, A. Structure and Properties of High-Entropy Boride Ceramics Synthesized by Mechanical Alloying and Spark Plasma Sintering. *Materials* **2023**, *16*, 6744. [\[CrossRef\]](#) [\[PubMed\]](#)
- Dube, T.C.; Zhang, J. Underpinning the relationship between synthesis and properties of high entropy ceramics: A comprehensive review on borides, carbides and oxides. *J. Eur. Ceram. Soc.* **2023**, *44*, 1335–1350. [\[CrossRef\]](#)
- Gild, J.; Zhang, Y.; Harrington, T. High-Entropy Metal Diborides: A New Class of High-Entropy Materials and a New Type of Ultrahigh Temperature Ceramics. *Sci. Rep.* **2016**, *6*, 37946. [\[CrossRef\]](#) [\[PubMed\]](#)
- Tallarita, G.; Licheri, R.; Garroni, S.; Orrù, R.; Cao, G. Novel processing route for the fabrication of bulk high-entropy metal diborides. *Scr. Mater.* **2019**, *158*, 100–104. [\[CrossRef\]](#)
- Zhang, Y.; Guo, W.; Jiang, Z.; Zhu, Q.; Sun, S.; You, Y.; Plucknett, K.; Lin, H.T. Dense high-entropy boride ceramics with ultra-high hardness. *Scr. Mater.* **2019**, *164*, 135–139. [\[CrossRef\]](#)
- Gong, J.; Zhu, H.; Xie, Q.; Zhang, C.; Lin, Y.; Liu, W.; Zhou, S.; Dong, Z. Synthesis and Ceramization of liquid HfB_2 . *China Ceram.* **2018**, *54*, 34–40.
- Sun, Y.; Ye, L.; Zhang, Y.; Chen, F.; Han, W.; Qiu, W.; Zhao, T. Synthesis of high entropy carbide ceramics via polymer precursor route. *Ceram. Int.* **2022**, *48*, 15939–15945. [\[CrossRef\]](#)
- Wen, Q.; Qu, F.; Yu, Z.; Graczyk-Zajac, M.; Xiong, X.; Riedel, R. Si-based polymer-derived ceramics for energy conversion and storage. *J. Adv. Ceram.* **2022**, *11*, 197–246. [\[CrossRef\]](#)
- Liu, R.; Liu, X.; Wang, Y.; Miao, H.; Song, C.; Qi, G.; Wan, F. Laser ablation behavior and mechanism of Cf/SiC–ZrC ultra-high temperature ceramic matrix composite prepared by PIP method. *Ceram. Int.* **2021**, *47*, 23610–23619. [\[CrossRef\]](#)
- Gai, K.; Guan, B.; Liang, L.; Li, J.; Wang, Q.; Zhao, T. Continuous aluminum oxide-mullite-hafniumoxide composite ceramic fibers with high strength and thermal stability by melt-spinning from polymer precursors. *J. Eur. Ceram. Soc.* **2022**, *42*, 5911–5921. [\[CrossRef\]](#)
- Yang, Y.; Bi, J.; Sun, K.; Qiao, L.; Liang, G.; Wang, H.; Yuan, J.; Chen, Y. The effect of chemical element on hardness in high-entropy transition metal diboride ceramics. *J. Eur. Ceram. Soc.* **2023**, *43*, 5774–5781. [\[CrossRef\]](#)
- Fahrenholtz, W.G.; Wuchina, E.J.; Lee, W.E.; Zhou, Y. *Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications*; John Wiley & Sons: New York, NY, USA, 2014.
- Ji, H.; Yang, M.; Li, M.; Ji, G.; Fan, H.; Sun, X. Low-temperature synthesis of ZrB_2 nano-powders using a sorbitol modified sol-gel processing route. *Adv. Powder Technol.* **2014**, *25*, 910–915. [\[CrossRef\]](#)

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