

Local structure in high-entropy transition metal diborides

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ABSTRACT

Studies on high-entropy materials often speculate about the effects of lattice distortion and disorder on characteristics such as hardness, thermal expansion, and electronic properties. Notwithstanding the ongoing race to discover new compositions, investigations of the local structure at the atomic level remain sparse at best. Additionally, assessments of the homogeneity of the distribution of metals within the lattice sites are often restricted to techniques such as energy dispersive spectroscopy which might lead to an inaccurate picture of the bulk material. Herein, we report an extensive and systematic study of a class of emerging high-entropy ceramics that uses a combination of high-resolution synchrotron powder diffraction and extended X-ray absorption fine structure analysis. Our data are consistent with a random distribution of atoms with local strain around the *d*-metals sites, which describes the bulk structure of these materials. Moreover, a linear trend is observed between the average structure and the first-neighbour distances, regardless the number (from 3 to 5) and type (Ti, Zr, Nb, Hf, Ta, Mo, W) of metals that constitute the high-entropy ceramic, which suggests that any description of properties for such materials need to go beyond the simple dichotomy of long-range order and local structure.

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1. Introduction

High-entropy materials (HEMs) are a class of compounds whose formation is fostered owing to their enhanced molar configurational entropy. Whilst generally exhibiting a high degree of lattice symmetry, widespread chemical disorder is achieved employing multiple elements of similar valence/charge and slightly dissimilar sizes. Since the discovery of HE alloys in 2004 [1–5], the HEM label has been extended to the most recent ceramic counterparts. However, an important distinction stands between HE alloys and ceramics (*e.g.* oxides, carbides, diborides). While the former are characterized by a relatively simple lattice, often described by a single atomic site occupied by several elements with equal atomic fractions, the latter present two or more sublattices: one for the non-substituted element (*e.g.* O, C, N, and B) and one or more for the metal species, such as group IV–V–VI transition metals (TMs) that are object of the present work. Consequently, only the metal-sublattice is chemically disordered while, at the same time, the remaining anionic sublattice is configurationally or-

dered. Whether the label “high-entropy” ceramics is appropriate or not to describe these multi-elemental mixtures of borides, carbides, nitrides, or oxides is a matter of open debate. Recently proposed terms “compositionally-complex”, “entropy-stabilized”, or “HE metal-sublattice” -ceramics seem to be more suitable to address the key feature of higher configurational entropy associated with the mixing of different constituents in only a fraction of the lattice [6–8]. Having different sizes, the TMs should distort at least one sublattice without, however, disrupting the formation of a crystalline structure. These lattice distortions may lead to unrivalled properties, many of which can be highly beneficial for particular applications.

In this scenario, HE ceramics (HECs) form a wide class of compounds, within the extended family of ultrahigh temperature ceramics (UHTCs), which are proposed for applications ranging from thermal/environmental barriers, catalysts for water splitting [9], and electrodes in lithium-ion batteries [10], in addition to hard and wear-resistant coatings for nuclear materials in the next generation fusion power plants. In recent years a frantic race has been on to increase the number of HEMs which has led to the synthesis of several novel compounds, while only a limited number of studies have tried to improve their mechanistic understanding, ranging from the grade of disorder, to internal strain and intrinsic

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properties [11]. Investigations of the homogeneous distribution of metals in the sublattice sites remain sparse at best, with computational studies suggesting segregation of some species at the grain boundaries, e.g. in ZrB_2 [12]. Dai *et al.* predicted only minor lattice distortions in $\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2}\text{B}_2$ as compared to its carbide counterpart [13] and mainly occurring through the displacement of boron atoms. In a recent study, our group investigated several compositions of 5-elements transition-metal diborides and established a method to combine synchrotron adiation X-ray powder diffraction (XRPD) profile analysis with electron microscopy. We concluded that the microstrain refined by high-resolution diffraction is directly related to chemical fluctuations on the transition metals sublattice [14]. As a result, microstrain can be used as observable to measure the extent of chemical homogeneity in these materials and the obtainment of a genuine solid solution. Rost *et al.* studied the chemical homogeneity at the long- and short-ranges in HE oxides in the purely covalent (Mg,Co,Ni,Cu,Zn)O cubic system employing electron-microscopy, XRPD, and extended X-ray absorption fine structure (EXAFS), concluding that distortions occur through disorder in the oxygen sublattice [15,16]. In this context, the term "entropy-stabilised" was appropriately adopted because the relevant contribution of the configurational entropy to stabilise the five-cation rocksalt type oxide was proven. For the totality of other so-called HECs (including those in the present study), the stabilisation effect of the increased mixing entropy has not yet been established experimentally. Fracchia *et al.* have used pre-edge XAS analysis to study the occupational disorder in the two metal-sublattices of an eight-cation inverse-spinel solid solution [17]. Jiang *et al.* have studied HE chalcogenides conducting high-angle annular dark field (HAADF) and atomic X-ray energy dispersive spectroscopy (EDS) analysis using scanning transmission electron microscopy (STEM) at different length-scales, demonstrating homogeneous distribution of all elements from the micrometer to nanometer scale [18]. However, despite the macroscopic existence of lattice strains showed by XRD, their type and spatial distributions was found unclear. Atom probe tomography (APT) was used by Chellai *et al.* to investigate HE oxide nano-powders, confirming that the cations are distributed homogeneously at the atomic level [19]. Cheng *et al.*, using high-energy XRD and pair-distribution function (PDF) analysis, showed the existence of lattice distortion in the crystalline framework of (Ce, La, Pr, Sm, Y) O_2 , revealing an unexpected flexibility in the structure and properties of HE oxides at high-pressure [20]. In this context, studies on the disorder of HE diborides are still at an early stage. After the first report in 2016 by Gild *et al.*, who showed a strategy to synthesize several 5-elements HE-diborides with single-phase hexagonal AlB_2 -type lattice [21], other investigations have typically focused on the synthesis and optimization of new compositions and the assessment of their mechanical properties [22–26], while fundamental studies have been limited to the understanding of defects [27].

To fill this gap in knowledge, we designed an extensive and systematic experimental campaign using high-resolution synchrotron-radiation XRPD and EXAFS analysis to combine the study of the long-range structure with additional insights into the local order and chemical environment on HE-UHTCs. Our analysis disclosed the random distribution of metals with local strain of the boron atoms around the *d*-metals.

2. Methods

A palette of 9 different combinations with 3, 4, or 5 coexisting TMs was selected to produce a diverse collection of compositions. All samples were designed to have both Zr and Ti owing to their established affinity in forming homogeneous solid solutions and to allow the continuous comparison between one large

Table 1

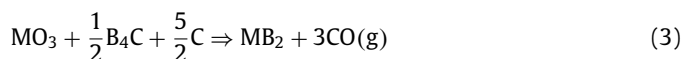
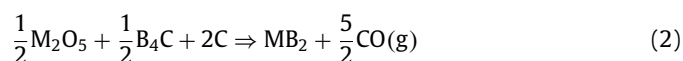
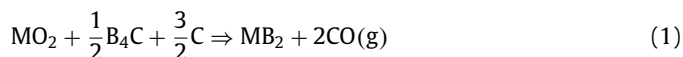
List of designed combinations used to synthesize the diboride solid-solution (DSS) powders. Investigated X-ray absorption edges and energies (E_0) are also reported at the bottom.

ID	molar composition in MB_2						
	Ti	Zr	Hf	Ta	Nb	Mo	W
X-1	1/3	1/3	1/3	-	-	-	-
X-2	1/3	1/3	-	1/3	-	-	-
X-3	1/4	1/4	1/4	-	1/4	-	-
X-4	1/4	1/4	-	1/4	1/4	-	-
X-5	1/4	1/4	-	1/4	-	1/4	-
X-6	1/4	1/4	1/4	-	-	-	1/4
X-7	1/5	1/5	-	-	1/5	1/5	-
X-8	1/5	1/5	-	-	-	1/5	1/5
X-9	1/5	1/5	-	1/5	1/5	1/5	-
edge	K	K	L ₃	L ₃	K	K	L ₃
E_0 (eV)	4996	17998	9561	9881	18986	20000	10207

and one small *d*-metal across the entire series. Combinations having both Hf and Ta in the same starting compositions were intentionally avoided due to superposition of XAFS spectra with similar absorption edges. The complete set of synthesized samples is summarized in Table 1.

Synthesis of samples

Hafnium oxide (HfO_2 , 99%, -325 mesh; Alfa Aesar), zirconium oxide (ZrO_2 , 99%, SC101, mean size 0.8 μm , MEL Chemicals), titanium oxide (TiO_2 , 99.9%, P25, mean size 20 nm, Degussa), tantalum oxide (Ta_2O_5 , 99.85%, - 325 mesh, Alfa Aesar), niobium oxide (Nb_2O_5 , 99.9%, - 325 mesh, Sigma-Aldrich), molybdenum oxide (MoO_3 , 99.9%, 6 μm , US Research Nanomaterials, Houston, TX), tungsten oxide (WO_3 , 99.9%, ~80 nm, Inframat Advanced Materials, Manchester, CT), carbon black (C, BP120, 30 m^2/g , Cabot), and boron carbide (B_4C , purity 96.8%, 0.6 ~1.2 μm , H.C. Starck) were used as starting materials. Purity and particle sizes are from the producers datasheets. Different compositions (cf. Table 1) were designed using different metal (Me) oxides to produce single-phase diboride solid solution (DSS) powders, according to reactions 1–3:



Where M is Ti, Zr, or Hf; Ta or Nb; and W or Mo respectively in reaction 1, 2, and 3. The designed combinations of metal oxides were weighed to obtain equiatomic amount of TMs in the final DSS powders. Carbon black (C) was added in stoichiometric amounts according to reactions 1–3, while about 13 wt% excess B_4C was added to all batches to compensate for loss of B during synthesis [28]. The raw powders of the starting metal oxides mixtures were homogenized with the reducing agents $\text{B}_4\text{C} + \text{C}$ (necessary for the boro-carbothermal reduction reaction) using a high-energy planetary mill (HEPM, Fritsch Pulverisette 6 - Germany) with anhydrous ethyl alcohol as the solvent. The milling jar and milling balls (3 mm diameter) were Y-stabilized zirconia.

The milling cycle consisted of six 15 min-steps at 400 rpm alternated with five 10 min-breaks of cooling, thus bringing the total processing time to 90 min. After milling, the mixtures were dried overnight in a ventilated oven at 343 K and then sieved (150 μm mesh size). The synthesis of the single-phase DSS powders was

conducted in two separate thermal cycles. The first cycle consisted in the boro-carbo thermal reduction (BCTR): pellets (20 mm diameter and about 2 g) for each unreacted X-*n* starting mixture listed in Table 1 were obtained using a uniaxial press and applying a pressure up to 3.5 MPa, followed by a cold isostatic pressing up to 200 MPa. Prior to BCTR, the pellets were first housed in closed graphite-paper boxes which, in turn, were placed inside a lid-free graphite-crucible. The boxes were randomly pierced to allow for volatile products of the BCTR to be pumped away. BCTR was conducted in a special high temperature furnace (LHTG 200–300/24-1G, Carbolite Gero, Germany) under dynamic vacuum (~30–70 Pa). The temperature was raised to 1973 K with a heating rate of about 70 K/min and isothermally held for 120 min. The as-treated products were pulverized using Y-stabilized zirconia mortar and pestle and sieved using a 250 μm mesh size grid, and then re-pressed in a pellet shape. The second and final thermal cycle was conducted in the same special furnace under dynamic vacuum. The temperature is raised to 2373 K with a heating rate of about 70 K/min and isothermally held for 60 min. Then, similarly to the first cycle, the furnace is let to cool down naturally. For the X-8 composition, a second thermal step was performed using a spark plasma sintering (SPS) furnace and applying a pressure up to 50 MPa (more details are reported in the Supporting Information). A field emission scanning electron microscope (FESEM, ZEISS Sigma Germany) equipped with an EDS detector (INCA Energy 300, Oxford Instruments - UK) was used to screen the chemical composition of the obtained specimens. A part of each heat-treated X-*n* pellet was pulverized for subsequent structural analysis.

Structural analysis

Synchrotron radiation XRPD data were collected in Debye-Scherrer geometry on the high-resolution MCX beamline at the Elettra synchrotron light-source (Trieste, Italy) for $\lambda=0.7293$ Å (17 keV). A borosilicate capillary (0.3 mm diameter) was filled with sample powder and the diffraction pattern was acquired at room temperature on the 4-circle Huber goniometer by spinning the capillary at 300 rpm. Patterns were then analyzed by means of either Rietveld or Le Bail refinement assuming the AlB_2 -type structural model (space group $P6/mmm$) in order to extract the lattice parameters. The instrument profile (typically Gaussian for this beamline) was calculated using a silicon standard (NIST SRM 640c) by refining the peaks shape with the pseudo-Voigt (PV) function available in the GSAS-II suite [29]. Profile extra-broadening (from the sample) was evaluated using the uniaxial approximation for microstrain and crystalline domain size. K-edge and L_3 -edge (cf. Table 1) XAS spectra were collected, at room temperature, on the XAFS beamline at Elettra [30]. A monochromatic beam was obtained using the double silicon crystal monochromator. The Si-111 reflection was employed for the lower energy range (i.e. Ti, Ta, Hf, W), whilst the 311 reflection was used for Nb, Zr, and Mo. The spectra were recorded in transmission mode, at room temperature, on pelletized specimens (13 mm diameter) composed by weighted mixtures of boron nitride and finely powdered sample, in order to obtain suitable absorption amplitude. The energy calibration for all samples was attained by simultaneously recording reference spectra of either a metallic foil or an oxide pellet, depending on the investigated element. Spectra of ZrB_2 , TaB_2 , HfB_2 , and TiB_2 were also collected as reference. Subsequent data processing and analysis was performed using the Demeter suite of programs [31]. From two to three spectra were collected per each edge of each samples to increase the signal to noise ratio. The spectra were aligned, merged and normalized using the program Athena [31]. A suitable atomic background was used above the absorption edge to extract the EXAFS signal. The latter was Fourier transformed using a sine-window in a k -range variable within 2–18 Å⁻¹ (depending

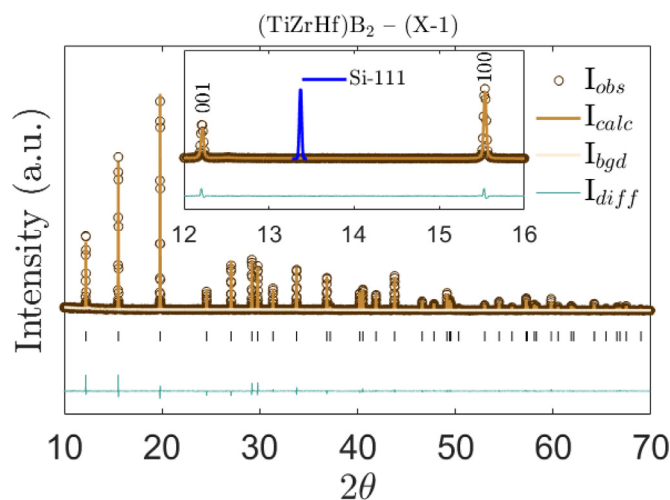


Fig. 1. High-resolution synchrotron XRPD pattern and Rietveld refinement of DSS X-1. Inset: magnification on the 001 and 100 perpendicular reflections, showing no apparent broadening compared to the instrumental resolution (Si-111 reflection displayed in blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

on the edge and quality of the data). For more details about the refinement of the EXAFS data see Appendix A. Summarizing, first the XRPD data were analysed in order to confirm that the samples were single phase and the patterns refined to obtain the initial model for the subsequent EXAFS analysis. Hence, for each X-*n* composition, XAFS data were fitted globally (i.e. using a multiedge approach) starting from the XRPD refined model and using all the available spectra.

3. Results and discussion

Figure 1 shows the Rietveld refined data of sample X-1. Remaining samples are reported in the Supporting Information (see Fig. S-1 and S-8). For all samples the most intense peaks are indexed to the space group $P6/mmm$. The only exception relevant to note is given by sample X-6 (cf. Fig. S-5), where a W_2B_5 -type impurity phase (s.g. $P6_3/mmc$) was refined with content of 4 wt% (more information about this inclusion are given in the Supporting Information), however its effect on the EXAFS spectra was considered negligible at this level of detail. A simple comparison between these patterns and the silicon standard does not show apparent peak broadening. Detailed profile analysis highlighted negligible domain size-broadening, whilst a small microstrain broadening can be observed in some of the compositions, yet fairly small if compared to previously reported values, obtained with the same level of resolution [24,32]. Samples X-4 and X-5 had a slight asymmetry in the profile and were Le Bail-refined with two phases with quasi-identical lattice parameters. However, for the sake of simplicity, they will be hereafter considered as single phases. The obtainment of genuine single phases with negligible microstrain broadening is indicative of a great extent of homogenisation in these DSS powders (see also [14]), with a high level of structural order, at least for the *d*-metals sublattice, which accounts for most of the scattered intensity. The full list of refined structural and microstrain parameters is reported in Table S-I.

In the $P6/mmm$ unit cell, the two sublattices are determined by the chemically disordered TMs, randomly occupying the $1a$ Wyck-off position in (000), and by the boron atoms, located at the $2d$ ($\frac{1}{3}\frac{2}{3}\frac{1}{2}$) sites. The B- sp^2 orbitals form strong σ -type bonds on the (002) planes, while a mixture of ionic and π -covalent bonds characterizes the weaker TM-B interaction [33]. As a consequence, one would expect that the coexistence of several distinct metals on the

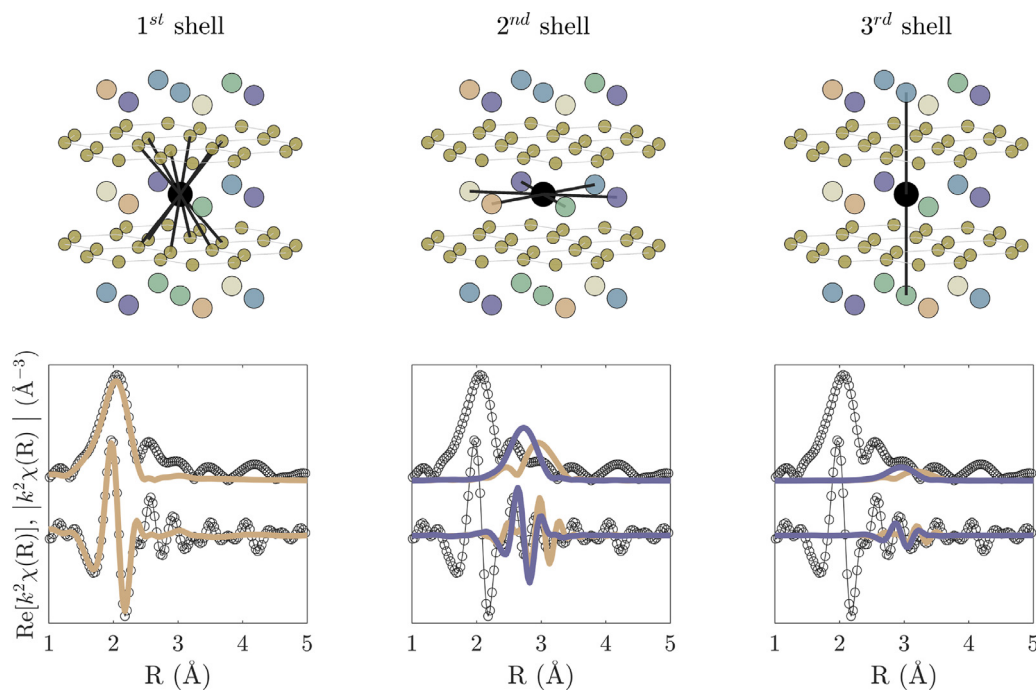


Fig. 2. Visual representation of the first three coordination shells (top) from the perspective of the central *d*-metal (black sphere) in a quaternary random diboride. Below each figure are real data (magnitude and real component, black symbols) for one sample superimposed to modelled components (solid lines) simulating the effect of an L_3 - and K -edge central ions (respectively orange and blue solid lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

same lattice sites would generate some internal strain in the structure, which should be accommodated more easily through the deformation of the M-B or M-M bonds, rather than by distorting the (supposedly-rigid) 2D sp^2 covalent boron layers. Fig. 2 (top panels) shows the structure of a generic quaternary diboride, displaying the first three nearest-neighbour shells with respect to the central metal. Considering a single *d*-metal in the $1a$ site as central atom, the first neighbours are the 12 equidistant boron atoms (r_1 -distance), to which the metal itself is coordinated. The B-atoms form two hexagonal rings (one from the above 2D plane and one from below). The second shell is characterized by 6 random TMs (r_2); while the third shell involves two equivalent TMs aligned respectively to the top and bottom layers (r_3).

A direct observation at the normalized X-ray absorption profiles in the near-edge (XANES) region (cfr. Fig. S-9) does not reveal substantial shift for the same metals in different compounds, suggesting that the oxidation state is constantly maintained for all metals, regardless the composition. EXAFS data fitting was used to determine the local structural parameters around the metals (see Appendix A for an exhaustive description). Simulated partial spectra for the first (left), second (middle), and third shells (right) are displayed for reference in Fig. 2 (bottom panels). Each shell produces a well defined partial signal in the EXAFS spectra, which depends not only on the particular shell but also on the edge-type of the metals forming that particular scattering-path, as shown, in different colours, for K - and L_3 -contributions to the EXAFS spectra. While a single-shell approach was initially attempted to model the 1st shell, it was soon abandoned due to the partial convolutions occurring between the first three shells, which increases the error. These overlaps generated several challenges in the fitting procedure when more than one transition metal coexisted in the same lattice site. In particular, the 2nd shell should be taken into account in order to optimize the fitting of the 1st shell, while the incorporation of the 3rd shell also improves the fitting of the 2nd one. To this end, for each shell the path degeneracy (N) was replaced

to the effective value $N_e = N_i/n$, with N_i the i^{th} -shell path degeneracy and n the number of metals composing the HE-DSS. At the same time, for each composition all spectra at any *d*-metal edge were simultaneously refined in order to use all the available information from complementary data-sets related to the same chemical mixture. For this reason, second- and third-shell parameters were cross-related on different spectra (e.g. for a fixed X-*n* composition, $r_2(\text{TiZr})$ is refined to be the same in both Ti-XAFS and Zr-XAFS spectra). Fig. 3 shows the global fitting results for the complete set of samples. For each of the spectra, the fitted absorption edge, E_0 , remained within $\Delta E_0 = \pm 10$ eV, with values consistently similar for the same metals. Table 2 reports the first-shell distances obtained from the global fitting, compared to the values calculated from the XRPD refinements. The EXAFS r_1 fitted values are evenly distributed around the average refined parameter obtained via XRPD. However, r_1 was different for each metal, highlighting local strain, presumably due to the different sizes of the metals. To better visualize the effect of the local strain, Fig. 4 displays r_1 as plotted against the XRPD refined values. Overall, each metal follows a linear trend with the average lattice parameters, which indicates that the local structure of one metal is affected by the choices of the other metals and the resulting average structure. By assuming r_1 as the sum of the metallic radius of the central *d*-atom and the covalent radius of boron and taking into account the lattice spacings of the pure MeB_2 compositions, the 1st-neighbour distances were tentatively ranked as follows: $r_{1,W} \approx r_{1,Mo} < r_{1,Ti} \approx r_{1,Ta} \approx r_{1,Nb} < r_{1,Hf} \approx r_{1,Zr}$, a figure that is consistent with the data. Moreover, a clear trend can be observed by comparing the two ubiquitous metals, Ti and Zr. The average variation calculated from the difference in the r_1 -values of these two metals, i.e. $r_{1,Zr} - r_{1,Ti}$, is 0.044(8) Å and is consistent across all compositions, notwithstanding the linear increase with the lattice volume. In contrast, a maximum difference of about 0.07 Å was measured when both Zr and W (the largest and smallest metals in this study) were present at the same time, suggesting

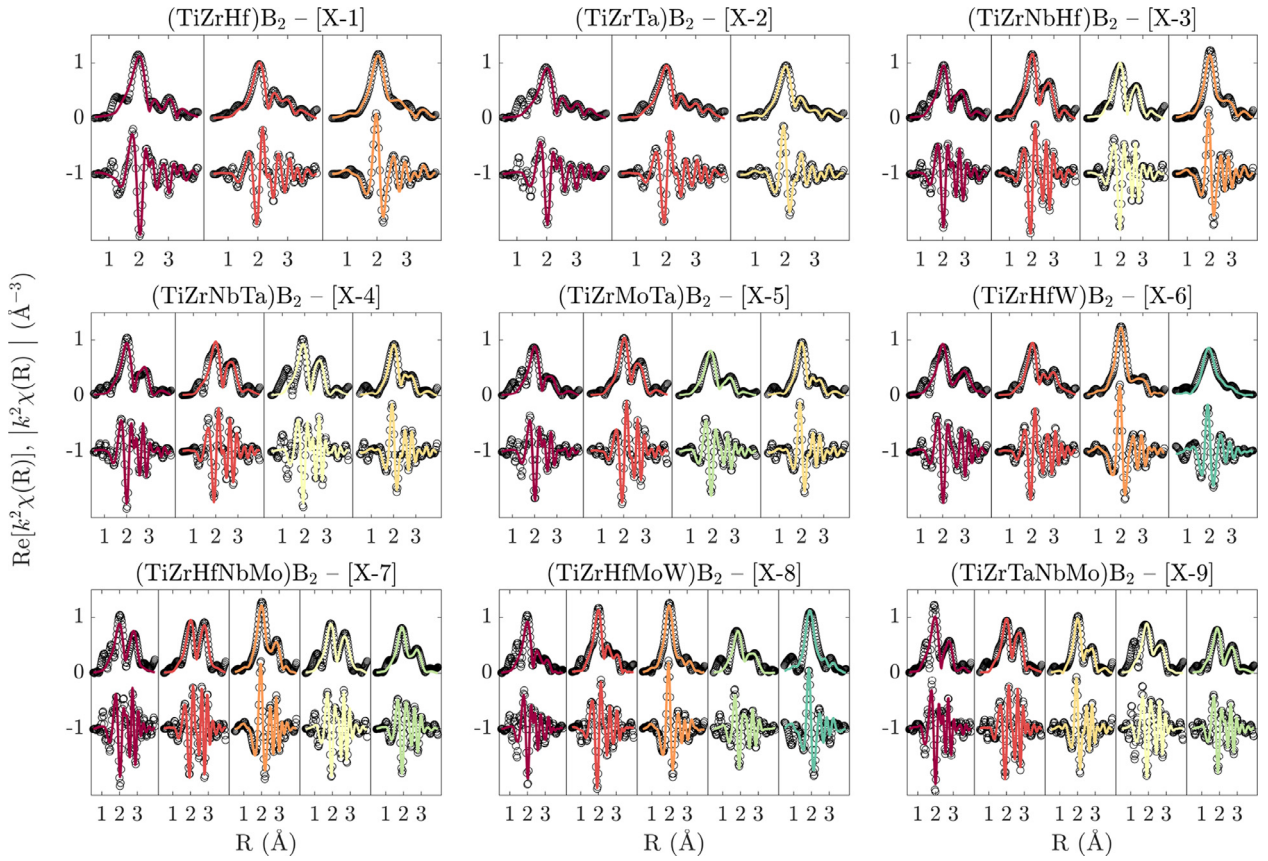


Fig. 3. EXAFS spectra (black symbols), reported as $k^2\chi(R)$ for all investigated compositions, with the same order of appearance of the metals displayed in the chemical equation above and global fits (solid lines) reported using similar colour for the equivalent metal. The real components are arbitrarily shifted by -1 below the module.

Table 2

Summary of first-shell distances ($r_{1,i}$) as refined from XRPD (i.e. $\langle r_1 \rangle$) and EXAFS analysis (reported values are in Å and errors between parentheses).

ID	XRPD $\langle r_1 \rangle_{xrd}$	r_1 -XAFS						
		Ti-B	Zr-B	Hf-B	Nb-B	Mo-B	Ta-B	W-B
X-1	2.486	2.46(01)	2.50(01)	2.49(01)	-	-	-	-
X-2	2.453	2.43(02)	2.47(01)	-	-	-	2.44(01)	-
X-3	2.474	2.46(01)	2.50(01)	2.47(01)	2.48(01)	-	-	-
X-4	2.450	2.43(01)	2.47(01)	-	2.45(01)	-	2.45(01)	-
X-5	2.439	2.43(01)	2.47(01)	-	-	2.44(01)	2.43(01)	-
X-6	2.469	2.45(02)	2.49(01)	2.47(01)	-	-	-	2.43(01)
X-7	2.462	2.45(02)	2.48(01)	2.46(01)	2.46(01)	2.47(01)	-	-
X-8	2.442	2.43(02)	2.48(01)	2.45(01)	-	2.43(02)	-	2.40(01)
X-9	2.437	2.40(03)	2.46(02)	-	2.44(01)	2.44(02)	2.43(02)	-

that the highest level of internal strain might be achieved for these compositions. As for the remaining metals (Hf, Nb, Mo, and Ta), they had less strained 1st shells, with r_1 values close to the average refined parameters.

A further correlation between Ti and Zr atoms becomes apparent after considering the relative displacement for r_1 , expressed as

$$\epsilon_i = \frac{\sqrt{|r_{1,i}^2 - \langle r_1 \rangle_{xrd}^2|}}{\langle r_1 \rangle_{xrd}}, \quad i = (\text{Ti, Zr}) \quad (4)$$

where $r_{1,i}$ is the XAFS value fitted for $M^i - B$ ($M^i = \text{Ti or Zr}$) and $\langle r_1 \rangle_{xrd}$ is the average XRPD-refined parameter for that specific composition. Fig. 5 show a regular trend occurring between ϵ_{Ti} and ϵ_{Zr} which stops obeying a linear law when the composition of the system incorporates more than four distinct TMs.

To give additional indication of the internal strain, we calculated a “strain-free” (sf) displacement, defined as

$$\epsilon_i^{sf} = \frac{\sqrt{|r_{1,i}^2 - (r_{1,i}^{sf})^2|}}{r_{1,i}^{sf}}, \quad i = (\text{Ti, Zr}) \quad (5)$$

which measures the magnitude of the $M^i - B$ bond-length variation in the as-synthesized DSS compared to the value measured for the single-element diboride.

An average “strain-free” value of r_1 (hereafter $\langle r_1^{sf} \rangle$) can also be calculated for the relative DSS composition using the rule-of-mixture from the tabulated lattice parameters of the single-element diborides (cfr. Table S-VI and [34–36]). Fig. 6 reports the average XAFS-calculated value of r_1 (i.e. $\langle r_1 \rangle_{xafs}$) with XRPD-refined and “strain-free” values, both showing a linear trend. The contributions of ϵ_{Ti}^{sf} and ϵ_{Zr}^{sf} were summed up and normalized to $\sum_i \epsilon_i^{sf}$ in order to plot the relative strain contribution originating from Ti

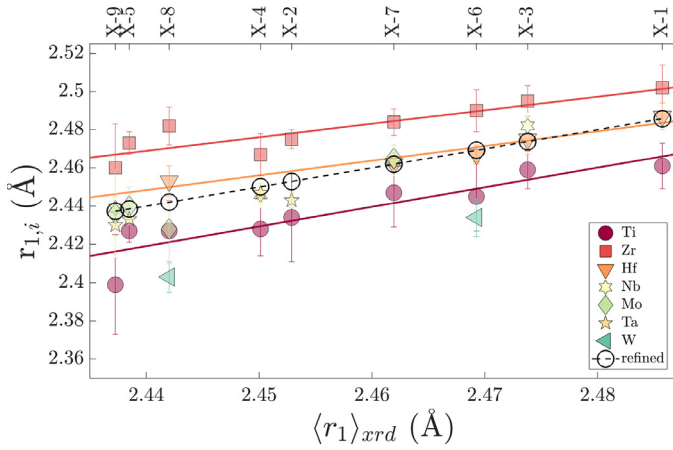


Fig. 4. EXAFS first-shell globally fitted distances (r_1) reported as compared to the average distance refined by XRPD. The average distance is also reported (dashed line with crosses) for comparison. Solid lines are a linear fit to the data for $r_{1,Ti}$, $r_{1,Zr}$, and $r_{1,Hf}$.

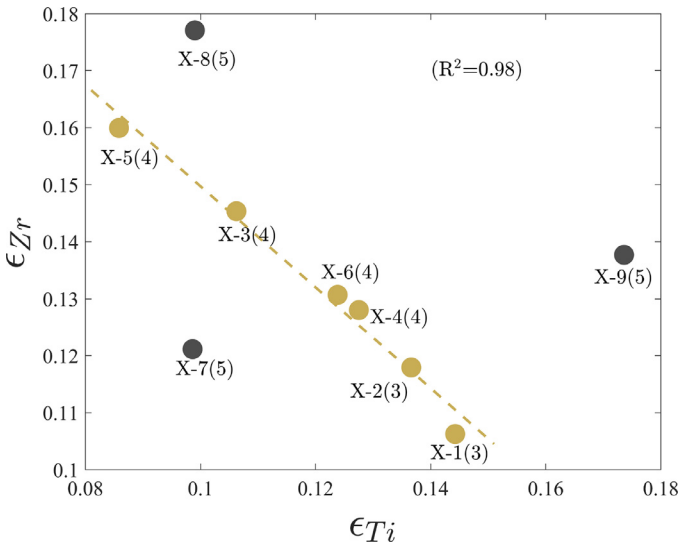


Fig. 5. ϵ_{Ti} and ϵ_{Zr} as calculated using Eq. 4. Relative number of metals is reported between parentheses for each composition. Displayed correlation index R^2 is relative to ϵ_i values with only 3 and 4 TMs (highlighted in orange).

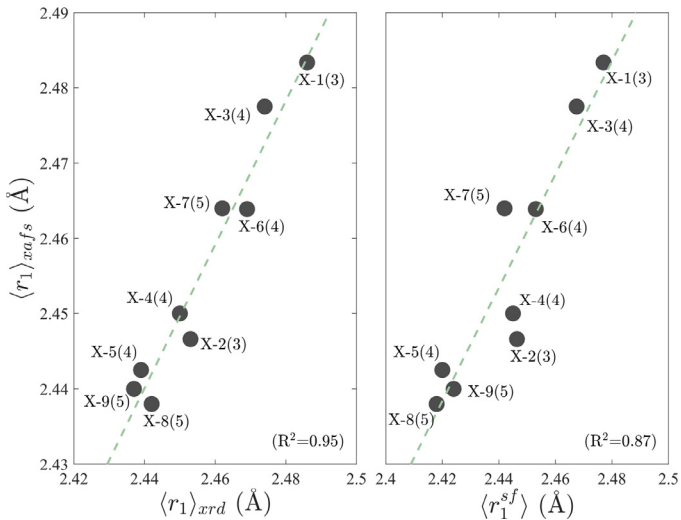


Fig. 6. Linear dependence of the average r_1 parameter as calculated from EXAFS (i.e. $\langle r_1 \rangle_{xafs}$), diffraction (i.e. $\langle r_1 \rangle_{xrd}$), and "strain-free" (i.e. $\langle r_1 \rangle_{sf}$). Relative number of metals is reported between parentheses for each composition.

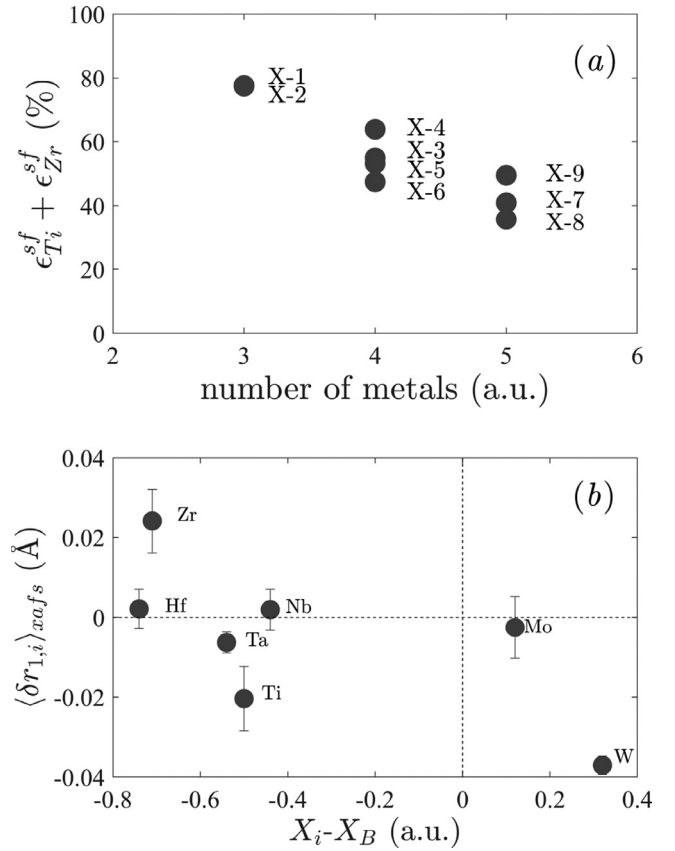


Fig. 7. (a) Chart of Ti and Zr "strain-free" ratio (expressed as $\epsilon_{Ti}^{sf} + \epsilon_{Zr}^{sf}$) decreasing with the diboride complexity and reaching lower values when W and Mo are being employed. (b) Relation between the average calculated displacement ($\langle \delta r_1 \rangle$; standard deviation as error-bars) and calculated electronegativity (χ_i) variation for each transition metal.

and Zr versus the increasing complexity of the composition (see chart in Fig. 7(a) and paragraph 3.1).

2nd shell distortions (i.e. relative to the in-plane TM-TM distances) are significantly less accurate due to the high level of correlation occurring between so many parameters in a relatively small range of distances. Moreover, 2nd and 3rd shells values should be more sensitive to chemical inhomogeneities, although these were initially dismissed for these samples by assessing negligible levels of microstrain. However, overall deviations of r_2 from the average refined values appear to be smaller compared to r_1 (cfr. Tables S-II and S-III). This result is in line with smaller equatorial microstrain values, typically half or less than the axial ones (see Table S-I). The smaller equatorial microstrain should be expected for the layered AlB₂ structure where the strongest sp^2 B-B covalent bonds have more influence on the in-plane spacing of metals better than the weaker M-M bonds. The calculated mean variation of r_2 for Ti-Zr gives an average value of 0.02(1) Å. At the same time r_3 fitted values (cfr. Tables S-IV and S-V) also display slight fluctuation around the refined c -axes. The comparison of the high-resolution XRPD results with the EXAFS analysis can offer a picture of the overall structure at long and short ranges. On the one hand, the calculated uniaxial microstrains, in first approximation originating from the TMs-sublattice, are limited to very low values, affecting only the 3rd or 4th figures in the lattice parameters. On the other hand, the EXAFS first-shell distances display variations of at least an order of magnitude higher than the average lattice. As such, the TM-sublattice appears less prone to accommodate internal strains in the out-of-plane direction as compared to the B-sublattice. The latter, whilst chemically homogeneous, expe-

riences local distortions (i.e. structural disorder) but with a much lower effect on entropy than the chemical variations occurring on the TM-layer. This is in fair agreement with DFT results obtained by Feltrin *et al.* on $(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{V}_{0.25})\text{B}_2$ [37]. These distortions were enhanced in proximity of particular metals. Titanium and tungsten, for example, act as centers of contraction for the neighbouring borons, while zirconium shows an opposite effect. Building upon these considerations, the non-perfect 2D arrangement of the B-layers will inevitably impact on the electronic and vibrational bands of the solid, with the potential of altering the electrical, mechanical, and thermal properties, compared to single-element diborides.

3.1. Further insights and outlook

This study highlighted three interesting consequences of the high-entropy effect on boride ceramics:

1. the short-range structure differs from the average one, at least for the first-shell and the B-sublattice;
2. formation of homogeneous and equimolar solid solutions is possible;
3. the simultaneous substitution of different metals in one sublattice has direct impact on the local structure of both sublattices.

While all these points have been the subject of speculation, the complementary information offered by high-resolution XRPD and EXAFS techniques allowed us to address them comprehensively. In particular, the second aspect appears to be deeply dependent on the designed composition and processing history, as observed for example in the case of samples containing W (see Supporting Information). Additionally, the third observation implies that the local order is an implicit function of the average structure, and *vice versa*. As such, while a different combination of TMs influences the average structure (i.e. cell parameters), at the same time and for the same TMs the local structure is also modified from the one relative to another combination, following a linear trend (cfr. Fig. 2).

The enhanced complexity of these systems depends not only on the different masses or atomic-sizes, but also on other parameters such as valence electron concentration (VEC), mixing entropy (ΔS_{mix}), or electronegativity. In our investigation, when more than 4 different TMs occupy the 1a site (i.e. samples X-7, X-8, and X-9), the linear trend observed for the strains in Ti and Zr is lost. However, the comparison between $r_{1,i}$ (for Ti and Zr) and r_1^{sf} using Eq. 5 can offer an explanation, highlighting a strong correlation between $\epsilon_{1,\text{Ti}}$ and $\epsilon_{1,\text{Zr}}$ as long as $\epsilon_{1,\text{Ti}}^{\text{sf}} + \epsilon_{1,\text{Zr}}^{\text{sf}}$ prevails over the sum of the remaining $\epsilon_{1,i}^{\text{sf}}$ with $i \neq \text{Ti, Zr}$ (cfr. Fig. 6).

Gu *et al.* performed an extensive computational study on a large series of binary and ternary TM diborides [38] sustaining that a VEC-based descriptor is capable of capturing the overall properties. At the same time, the relative electronegativity, among the constituents of the compounds, also plays a crucial role in capturing the effects of relative charge redistribution (even in separate compounds with the same overall VEC) and therefore in determining property trends. Sangiovanni *et al.* recently proposed an approach for realizing HE refractory carbides with unique combination of hardness and fracture resistance at high temperature via tailoring the VEC [39]. Among several properties, hardness can be used as benchmark to shed more light between the complexity of a systems and their properties. In this regard, Feng *et al.* [40] along with other authors [41–43] showed that HE diboride ceramics may be a new class of super-hard materials, and even ultra-incompressible [44]. According to Csanadi *et al.*, the generally observed enhanced hardness obtained from the rule-of-mixture, may be explained through the well-established solid solution strengthening theory [45]. Hardness is affected by many factors, including different slip systems and cross-slip which govern the plastic

deformation and therefore the resulting hardness. Hence, whether the local strains arising from random and homogeneous but complex multi-element systems, not necessarily equimolar, can manifest at the bulk scale through measurable effects is a matter of open discussion. The increase in chemical disorder (i.e., increased ΔS_{mix}) may change the dominant slip systems, thereby resulting in variation of ductility and hardness.

Mass and size disorder acting as an impedance and scattering the energy of dislocation groups was also suggested by Sarker *et al.* for the HE carbides [46]. The so-called “entropic” strengthening effect has been considered by Diplo *et al.* [47] whereby different elements with varying sizes induce local strain in the lattice that may impede dislocation nucleation and/or motion. Zhao *et al.* commented on the importance of lattice strain on hardness [36]: they showed that TM-B bonds in W-substituted Mo diborides is strengthened by increasing electron charge transfer from W to Mo. In addition, the same authors suggested that local symmetry reduction is another key factor to hinder dislocation movement for hardness enhancement independent of charge redistribution and VEC variations. This is in agreement with a recent study in HE metal diborides where it was demonstrated that incorporating softer WB_2 and MoB_2 made the resulting single phase HE diboride harder [43]. Such a conclusion confirms once again that unusual, unexpected, and often counter-intuitive phenomena can occur. In fact, if the enhanced complexity provided by the simultaneous presence of several elements was beneficial for achieving higher hardness, any attempt to dissolve an increasingly larger number of differing cations in the same stabilized structure could lead to harder and harder materials. However, when dealing with a property such as hardness, not only the solid solution strengthening and charge redistribution, but also local strains must be considered to fully explain the increase in hardness that have been reported to occur in the wider class of HE borides (which do not exclusively have AlB_2 -type structures) [48–51]. The study of the local structure becomes relevant in this regard, since it may be key to understanding of properties for which local strains have major influence. In the case at hand, the introduction of elements like W and/or Mo gave rise to deviations from the ideal rule-of-mixture model in real solid solutions. A further insight may be offered by Fig. 7(b), showing the EXAFS-calculated average deviation from $r_{1,i}$ (i.e. $\langle \delta r_{1,i} \rangle_{\text{EXAFS}}$) with respect to the difference in electronegativity between the relative TM and boron. Metals found on the top side of the graph ($\langle \delta r_{1,i} \rangle_{\text{EXAFS}} > 0$) would exert a negative “chemical pressure” (or “internal pressure”) on the B-sublattice (i.e., expanding the planes). In contrast, metals with negative values of $\langle \delta r_{1,i} \rangle_{\text{EXAFS}}$ can be described as having a positive “chemical pressure” effect. While Zr and Ti clearly show an opposite trend of “internal pressure”, with other atoms (i.e., Hf, Ta, Nb) displaying a milder attitude, they all have lower electronegativity than boron. Clearly, W and Mo, appearing at the bottom-right side of the graph, might be expected to lead to major deviations from properties predicted with rule-of-mixture calculations.

4. Conclusions

Synchrotron based techniques were applied to HEMs to investigate the existence and magnitude of strains arising from the gradual convergence of an increasing number of differing species forced to share and accommodate a new local environment. Contrary to expectations based on rule-of-mixture calculations, the local structure probed by EXAFS analysis in HE-DSSs clearly differs from the average structure measured by long-range techniques (i.e. XRPD), with larger deviations occurring for Zr, Ti, and W. When focusing on the 1st d-metal-to-boron shell, a different combination of transition metals produces variations at the long range (i.e. cell-parameter), for a selected metal, and also changes the local struc-

ture from one combination to another, following a linear trend. Nevertheless, the ranking of calculated distances are in line with that expected on the basis of the metallic radii of the different metals. As a result of the above, we can surmise that not only the local structure affects the long-range order but also the opposite seems to happen, regardless the number and type of metals, which ultimately denote an intimate interconnection between both levels of order.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. XAFS

The EXAFS oscillation can be modelled using the equation:

$$\chi(k) \sim S_0^2 \sum_j N_j \frac{f_j(k)}{k r_j^2} \sin(2k r_j + \phi_j(k)) \exp(-2\sigma_j^2 k^2) \quad (\text{A.1})$$

where S_0^2 is the amplitude reduction factor, N_j is the path degeneracy of the j -th path, σ_j^2 the mean square displacement, $f_j(k)$ the scattering amplitude, r_j the scattering path distance, and $\phi_j(k)$ the phase-shift. Let us consider the first three single-scattering paths in a random n -elements AlB_2 -type lattice (cf. Fig. 1). While the first shell is always coordinated by 12 boron atoms; the second shell ($N=6$ in a mono-atomic diboride) should be split in $\binom{n}{2} + n$ non-degenerate contributions, each one with $N = \frac{6}{n}$. The 3rd shell ($N=2$ in a mono-atomic diboride) will give us the same number of contributions with degeneracy of $N = \frac{2}{n}$. While N_j and $f_j(k)$ are fixed for a determined path, for a sample made of n transition metals (thus n EXAFS spectra to analyse) we can count a minimum of $2n$ parameters (i.e. one S_0^2 -amplitude factor and one E_0 -shift for each edge), plus n distances for the 1st shell (central metal coordinated to 12 borons), 3 mean square displacements (one for each shell, assuming negligible differences between different transition metals), and $\binom{n}{2} + n$ mixed r_j -distances for the 2nd and 3rd shells.

Due to the exponential increase in parameters with the number of d -metals, few approximations were taken into account and the whole fitting procedure is described in the following, with the purpose of fitting the best parameters for the 1st shell (hereafter r_1). The first approximation involves the mean square displacements relative to the first shell (M-B), assumed to be the same for all metals in the same chemical mixture. We also considered a single thermal displacement parameter for the paths relative to the 2nd and 3rd shells (i.e. $\sigma_2 = \sigma_3$, yet different from that of the 1st shell, σ_1). Due to the marginal amplitude resulting from the third-shell scattering paths (compared to that of the first two), their contributions were parametrized in order to fit all paths with a single parameter, α , such that $r_3^{ij} = \alpha r_2^{ij}$, where i and j are the indexes relative to the path generated by M_i - M_j . The double scattering paths resulting from the interaction of the central TM-atom with the first-to-first and first-to-second neighbour borons (forming respectively an acute and obtuse triangle) produce a feeble and

broad amplitude in the region 2–3.8 Å and were thus neglected from the fitting procedure. Metallic and covalent distances were calculated for all possible combinations of atoms in the AlB_2 -type structure and used as reference for the assessment of the 2nd and 3rd shells distance parameters (r_2 and r_3) during the refinement steps. To reduce correlations in the first stages of refinement, r_2 was constrained in groups based on the calculated values (for example, the distances calculated for the pairs Zr-Ta, Zr-Nb, and Ti-Hf share the same value of r_2). After reaching a reasonable fitting for the base parameters, i.e. S_0^2 , E_0 , σ_1 , and r_1 ; the r_2 constraints were lifted in order to improve their values and the overall fitting of r_1 . In few cases (i.e., when M^i - M^j distances were highly correlated due to similar values) it was considered reasonable to keep the constraints on r_2^{ij} .

Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.actamat.2022.118294.

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