Short communication

Processing-dependent stabilization of a dissimilar rare-earth boride in high-entropy (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Ta$_{0.2}$Er$_{0.2}$)B$_2$ with enhanced hardness and grain boundary segregation

Mingde Qin$^{a,b}$, Sashank Shivakumar$^{a,b}$, Tianjiao Lei$^{c,d}$, Joshua Gild$^{a,b}$, Esther C. Hessong$^{c,d}$, Haoren Wang$^{a,b}$, Kenneth S. Vecchio$^{a,b}$, Timothy J. Rupert$^{c,d}$, Jian Luo$^{a,b,*}$

$^a$ Program of Materials Science and Engineering, University of California San Diego, La Jolla, CA 92093, USA
$^b$ Department of NanoEngineering, University of California San Diego, La Jolla, CA 92093, USA
$^c$ Department of Mechanical and Aerospace Engineering, University of California Irvine, Irvine, CA 92697, USA
$^d$ Department of Materials Science and Engineering, University of California Irvine, Irvine, CA 92697, USA

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ABSTRACT

This study demonstrates that 20% of a rare-earth (RE) diboride (ErB$_2$) can be stabilized in a high-entropy transition metal (TM) diboride, despite the dissimilar chemical properties of RE and TM elements and large differences in lattice parameters of ErB$_2$ and typical TM$_2$B$_2$. However, the phase formation depends on the fabrication route, which is a noteworthy observation. Specifically, single-phase (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Ta$_{0.2}$Er$_{0.2}$)B$_2$ is synthesized via reactive spark plasma sintering (SPS) using elemental boron and metal elements. In contrast, a specimen made by borocarbothermal reduction of binary oxides and SPS possess significant amounts of two Er-rich secondary phases. Notably, the RE addition in high-entropy TM diboride leads to improved hardness. Aberration-corrected scanning transmission electron microscopy (AC STEM) and energy-dispersive X-ray spectroscopy (EDS) elemental analyses further reveal significant Er segregation at grain boundaries. This work suggests that high-entropy ceramics can have significant solubilities of dissimilar components that may enable new, tunable, and improved properties.

1. Introduction

The research on high-entropy materials took off since the independent studies by Yeh et al. [1] and Canter et al. [2] on transition metal (TM) high-entropy alloys (HEAs) in 2004. As the ceramic counterparts to metallic HEAs, various high-entropy ceramics (HECs) have been fabricated in bulk form, including various high-entropy oxides [3–7], borides [8–12], carbides [13–15], and silicides [16–18]. These HECs have been demonstrated to possess superior and sometimes unexpected properties when compared with their components [5,19,20]. In 2020, it was further proposed to broaden HECs to compositionally complex ceramics (CCCs), where non-equimolar ceramics can outperform their high-entropy counterparts (e.g., in their thermomechanical properties) [5,21,22] and various long- and short-range orders can be further introduced [6,7,17,23].

Among the HECs, high-entropy borides [12], carbides [15,24], and nitrides [25,26] have been extensively studied as a new type of ultrahigh temperature ceramics (UHTCs) due to their potential ability to withstand extreme environments in nuclear and aerospace engineering applications [27]. Particularly, Gild et al. [12] synthesized (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Ta$_{0.2}$)B$_2$ and five other single-phase high-entropy diborides (HEDBs) from binary diborides in hexagonal AlB$_2$-type structure in 2016, which were the first non-oxide HECs synthesized in bulk form. These HEDBs have been demonstrated to possess improved hardness and oxidation resistance going beyond the simple mixture effect of each component. Since then, more fabrication routes, involving borocarbothermal reduction of metal oxides [18,28] and reactive sintering of elemental powders [29], have been developed to synthesize dense HEDBs. Dual-phase high-entropy UHTCs have also been fabricated [30]. Notably, Qin et al. [29] successfully incorporated Mo and W into HEDBs via reactive spark plasma sintering (SPS) of elemental powders after high-energy ball milling (HEBM). A similar method has

* Corresponding author at: Department of NanoEngineering; Program of Materials Science and Engineering, University of California San Diego, La Jolla, CA 92093, USA.
E-mail address: jluo@alum.mit.edu (J. Luo).

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been adopted to fabricate high-entropy monoborides [9,31], M$_2$B$_4$ borides [11], as well as a broader content of rare earth (RE) high-entropy tetraborides [10] and hexaborides [8]. In other studies, RE high-entropy hexaborides have also been synthesized via the route of borocarbothermal reduction [32,33], together with the composites containing borates [33] or tetraborides [34]. It is well-known that RE elements have the ability to form stable boride compounds at a much wider range of metal-to-boron stoichiometric ratio, from AlB$_5$-type diborides to YB$_{12}$-type hexaborides [35]; hence, it inspires us to further explore novel high-entropy borides containing RE elements. Specifically, the ability to adding RE in high-entropy TM diborides may enable new opportunities to engineer their oxide scales.

Diborides of AlB$_5$-prototype have been widely discovered in RE elements, including Sc, Y, Sm, Gd, Tb, Tb, Dy, Ho, Er, Tm, Yb and Lu, as summarized in earlier handbooks [35,36]. These RE diborides have the same structure as TM diborides, but with noticeably larger lattice parameters than typical TM diborides [35,36]. Moreover, they feature a unique paramagnetic-to-ferromagnetic transition at low temperature (<150 K) [35,36]. Nevertheless, the RE diborides still remain less studied because they are extremely difficult to prepare in single-phase form. Conventional synthesis routes from elemental precursors usually requires extremely high static pressure (6 GPa) or high temperature (>1000 °C) [35], and common impurities involve tetraborides, oxides, as well as unreacted metals [37,38].

Here, we hypothesize that HECs can have more solubilities of dissimilar components (with normally less mutual solubilities). To test this hypothesis, this study demonstrates that 20% of a RE diboride (ErB$_2$) can be stabilized in a high-entropy TM diboride, despite the dissimilar chemical properties of RE and TM elements and large differences in lattice parameters of ErB$_2$ and typical TM$_2$B$_4$ (or the radii of RE and TM). Unfortunately, the solid solubility of ErB$_2$ and typical TM$_2$B$_4$ (TM = Zr, Hf, Ti, Ta, and Nb) has not been reported, while we suspect the low solid solubility given the large difference in atomic and ionic radii and dissimilar chemical properties based on the famous Hume-Rothery rules. In this study, we investigate two independent routes (viz. boron-metals reactive SPS of elemental powders and borocarbothermal reduction of oxides followed by SPS) to synthesize a novel RE-containing HEDB with nominal composition of (Ti$_0.2$Zr$_0.2$Hf$_0.2$Er$_0.2$)$_2$B$_2$. The specimen synthesized via boron-metals reactive SPS demonstrates a perfect single-phase AlB$_5$-type structure without measurable impurity. Furthermore, this novel HEDB with 20% Er features enhanced hardness compared to typical (Ti$_0.2$Zr$_0.2$Hf$_0.2$Er$_0.2$)$_2$B$_2$ HEDB, even though ErB$_2$ is predicted to be much softer by itself [53-55]. Moreover, Er (with the lattice parameters of ErB$_2$ larger than those of typical TM diborides) has been revealed to exhibit significant segregation along grain boundaries in (Ti$_0.2$Zr$_0.2$Hf$_0.2$Er$_0.2$)$_2$B$_2$ specimen.

In general, this study suggests a new paradigm by showing that HECs can enable enhanced solubility of dissimilar cations. Subsequently, it provides new opportunities to tailor their mechanical properties (e.g., improvement of hardness or impediment of high-temperature dislocation motion due to lattice distortion) and grain boundary properties (e. g., via the expected strong segregation that can significantly change grain growth and grain boundary mechanical properties).

2. Experimental

Specimens with the same nominal composition (Ti$_0.2$Zr$_0.2$Hf$_0.2$. Ta$_0.2$Er$_0.2$)$_2$B$_2$ were synthesized via two different routes: (1) reactive SPS from elemental (boron + metals) precursors, and (2) borocarbothermal reduction of binary metal oxides followed by SPS. For the first route of boron-metals reactive SPS, elemental powders of Ti, Zr, Hf, Ta (>99%, purity, ~325 mesh, purchased from Alfa Aesar, MA), Er (99.9% purity, ~40 mesh, purchased from Alfa Aesar, MA), and B (99% purity, 1–2 µm, purchased from US Research Nanomaterials, TX) were utilized as precursors. Stoichiometric amounts of elemental powders were weighed out in batches of 5 g, together with 3 at% of additional boron (i.e., a nominal metal-to-boron atomic ratio of 1:2.06) to compensate for boron loss in the reaction with the native oxide [29,39] and to minimize the formation of secondary borides [10,30]; moreover, 1 wt% (0.05 g) of stearic acid was added as lubricant for each batch of powder mixture. The powders were first mixed by a vortex mixer, and subsequently transferred into a tungsten carbide (WC) lined stainless steel milling jar with 11.2 mm diameter WC milling media (at ball-to-powder ratio of ~4.5:1) then high-energy ball milled (HEBM) in a SPEX 8000D mill (SPEX CertiPrep, NJ) for 50 min. The as-milled powders were subsequently loaded into 10 mm graphite dies lined with graphite foils in batches of 2.5 g, and sintered into dense pellets in vacuum (10$^{-2}$ Torr) using a Thermal Technology 3000 series SPS (Thermal Technology LLC, CA) at a final densification temperature of 1590 °C for 10 min. The optimized SPS heating profile can be found in a prior publication [29], where the specimens were first isothermally held at 1400 and 1600 °C before the final densification. It should also be noted that the HEBM and the successive handling of the as-milled powders were conducted in an argon atmosphere (O$_2$ < 10 ppm) to prevent oxidation.

For the second route of borocarbothermal reduction followed by SPS, binary metal powders of TiO$_2$, ZrO$_2$, HfO$_2$, Ta$_2$O$_5$ (>99% purity, >45 µm, purchased from Alfa Aesar, MA), and Er$_2$O$_3$ (99.9% purity, 5 µm, purchased from US Research Nanomaterials, TX), as well as B$_4$C (99.9% purity, 1–3 µm, purchased from US Research Nanomaterials, TX) were utilized as precursors. Appropriate amounts of precursors were weighted out in batches of 10 g to formulate the target composition of (Ti$_0.2$Zr$_0.2$Hf$_0.2$Ta$_0.2$Er$_2$)$_2$B$_2$ via nominal chemical reaction 14TiO$_2$ + 14ZrO$_2$ + 14HfO$_2$ + 2Ta$_2$O$_5$ + 7Er$_2$O$_3$ + 50B$_2$C → 70(Ti$_0.2$Zr$_0.2$Hf$_0.2$. Ta$_0.2$Er$_2$)$_2$B$_2$ + 30B$_2$O$_3$ + 50CO. Similarly, 20 mol.% of excess B$_2$C (i.e., an actual stoichiometric number of 60B$_2$C in the reaction above) was added into the mixture to fully consume the metal oxides and to minimize remaining B$_4$C as well as metal carbide formation [18,40]. The borocarbothermal reduction and the subsequent SPS followed the procedure originally developed in a prior study [18]: the mixture powders were first planetary ball milled in a PQN04 mill (Across International LLC, NJ), then loaded into a Red Devil graphite furnace (R.D. Webb, MA) and annealed at 1550 °C for 90 min in vacuum (~10$^{-4}$ bar) for borocarbothermal reduction, and finally densified in the SPS at 2000 °C for 30 min. Ref. [18] provides additional experimental details.

After SPS, specimens with the same nominal composition (Ti$_0.2$Zr$_0.2$Hf$_0.2$Ta$_0.2$Er$_2$)$_2$B$_2$ synthesized via two different routes were ground and successively polished for further characterization. X-ray diffraction (XRD) spectra were obtained from a Miniflex II diffractometer (Rigaku, Japan) at 30 kV and 15 mA. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD) data were acquired in an Apreo microscope (Thermo Fisher Scientific, MA) equipped with Oxford N-Max$^3$ EDS detector and an Oxford Symmetry EBSD detector. For the specimen synthesized via reactive SPS, bulk density was measured by Archimedes’ method, the lattice parameters were determined by XRD unit cell refinement, and its theoretical density was calculated based on lattice parameters and the composition measured by SEM-EDS.

Vickers microhardness measurement was carried out by a Duramin-40 automatic hardness tester (Struers, DK) with indentation loads between 0.49 N (50 g) and 9.8 N (1 kgf) and dwell time of 10 s by adjusting with ASTM C1327–15. Over 50 valid measurements were conducted at each indentation load to ensure the statistical accuracy and minimize the surface morphology effects.

Scanning transmission electron microscopy (STEM) samples were fabricated by using the focused ion beam (FIB) lift-out method with a Ga$^+$ ion beam in an FEI Quanta 3D FEG dual-beam SEM/FIB microscope equipped with an OmniProbe. High-angle annular dark-field (HAADF) STEM-EDS were performed to study the grain boundary chemistry, by using a JEOL JEM-ARM300F Grand Arm STEM with double Cs correctors operated at 300 kV. A probe current of 115 pA was used. For HAADF-STEM imaging, the camera length was 6 cm, with the corresponding inner and outer collection angles being 106 and 180 mrad,
3. Results and discussion

XRD spectra of (Ti<sub>0.2</sub>Zr<sub>0.2</sub>Ho<sub>0.2</sub>Ta<sub>0.2</sub>Er<sub>0.2</sub>)B<sub>2</sub> specimens synthesized via boron-metals reactive SPS and borocarbothermal reduction followed by SPS are illustrated in Fig. 1(a) and (b), respectively. For the fabrication route of boron-metals reactive SPS, the measured XRD spectrum of the as-milled powder mixture (after HEBM) and the corresponding calculated XRD spectrum for an AlB<sub>2</sub>-typed (Ti<sub>0.2</sub>Zr<sub>0.2</sub>Ho<sub>0.2</sub>Ta<sub>0.2</sub>Er<sub>0.2</sub>)B<sub>2</sub> solid solution, assuming random cation occupation and grain orientation, are also shown in Fig. 1(a). After HEBM, the as-milled powder mixture of six elemental precursors demonstrates multiple distinct BCC (Ti, Zr, Hf, and Ta) and HCP (Er) phases in Fig. 1(a). This implies that the reaction between boron and metals, as well as the formation of high-entropy solid solution, takes place during the following SPS (not the preceding HEBM). The peak broadening observed in this spectrum can be associated with grain size reduction, lattice distortion, and microstrains that are commonly induced by HEBM. For the sintered pellet after reactive SPS, however, the XRD spectrum exhibits a perfect single phase or impurity. Interestingly, in this XRD spectrum of sintered pellet, asymmetric peak broadening has been observed for all planes that intercept c-axis ([001] direction), i.e., (001), (101), (002), etc.; in contrast, no obvious asymmetry has been recognized for diffraction peaks corresponding to the planes that are parallel to c-axis. This could relate to the layered structure of AlB<sub>2</sub>-type solid solution, where the interplanar distance along c-axis depends more on large components [12,29]. In Ti<sub>0.2</sub>Zr<sub>0.2</sub>Ho<sub>0.2</sub>Ta<sub>0.2</sub>Er<sub>0.2</sub>B<sub>2</sub> solid solution, ErB<sub>2</sub> has significantly larger lattice parameters (a = 3.261 Å, c = 3.779 Å) [41] than the other TMB<sub>3</sub>-type components, viz. TiB<sub>2</sub> (a = 3.031 Å, c = 3.237 Å) [42], ZrB<sub>2</sub> (a = 3.168 Å, c = 3.531 Å) [43], HfB<sub>2</sub> (a = 3.142 Å, c = 3.477 Å) [43], and TaB<sub>2</sub> (a = 3.097 Å, c = 3.226 Å) [43], and the expanded lattice (by larger ErB<sub>2</sub>) has induced considerable tensile lattice strain, especially along c-axis, with the existence of other smaller components, which further engenders the asymmetric peak broadening towards the high-angle side for planes that intercept c-axis ([001] direction).

In contrast to the single-phase specimen by boron-metals reactive SPS, the specimen with the same nominal composition synthesized via borocarbothermal reduction of binary oxides followed by SPS demonstrates a major diboride phase with substantial amounts of secondary phases in Fig. 1(b), and these secondary phases have been revealed to be Er-rich (by EDS analysis in Fig. 2(d)), and they can be further identified as ErBO<sub>3</sub> and ErB<sub>4</sub>-based solid solutions by the XRD spectrum. RE borate is an intermediate phase during the borocarbothermal reduction which can be found in RE boride systems, following the nominal reaction 4REO<sub>3</sub> + 3B<sub>2</sub>O<sub>3</sub> → 4REBO<sub>3</sub> + 4REB<sub>2</sub> + 3C, when binary oxides are not fully reduced [33]; on the other hand, RE tetraborides can also be reduced from binary oxides, complying with the equation 7REO<sub>3</sub> + 15B<sub>2</sub>O<sub>3</sub> → 14REBo<sub>4</sub> + 2B<sub>2</sub>O<sub>3</sub> + 15CO, and have been reported from raw materials with lower oxide contents [34]. In fact, borocarbothermal reduction of RE binary oxides is a rather complicated process with intermediate phases and boride products of different RE valence states; hence, the existence of the secondary phases is anticipated. The content of these secondary phases may be reduced (or even eliminated) at optimized reduction conditions (e.g., oxide-to-reductant ratio, reduction temperature and time, etc.).

SEM micrographs of the polished surface in Fig. 2(a) illustrates that the specimen made by reactive SPS is highly dense (~1% porosity); in fact, this specimen exhibits an exceptional relative density of 99.1% by comparing its experimentally measured bulk density (8.74 g/cm<sup>3</sup>) with the theoretically calculated density (8.82 g/cm<sup>3</sup>). Moreover, this specimen also manifests a largely homogenous solid solution without noticeable secondary phase or particles. The SEM-EDS elemental maps in Fig. 2(c) further confirms the uniform distributions of its constituent elements. At the same time, quantitative EDS analysis measured a composition of (Ti<sub>0.18</sub>Zr<sub>0.2</sub>Ho<sub>0.2</sub>Ta<sub>0.2</sub>Er<sub>0.2</sub>)B<sub>2</sub>, which is within typical EDS measurement errors from the nominal equimolar composition. Hence, the nominal composition is still adopted in the following discussion. We note that tungsten carbide milling media can often cause contamination of tungsten; e.g., a prior study showed 1–5 at% tungsten can be introduced from aggressive HEBM [30]. Nevertheless, tungsten contamination in the specimen made in this study was below the EDS detection limit. We believe that this is due to the following reasons. First, this study used a relatively short the HEBM duration of 50 min (vs. 100 min in the prior study [30]). Second, our precursor powders...
and typical TMB diborides and carbides mixtures utilized in the previous case \[30\], which (elemental metals and boron) used here are much softer than the binary phases was measured to be 18.6 ± 1.4 GPa at 0.49 N. At the same indentation size effect \[48\], this specimen demonstrates increasing measured hardness with decreasing indentation load, going from 18.9 ± 1.4 GPa at 9.8 N to 35.8 ± 5.5 GPa at 0.49 N. At the same indentation load of 1.96 N, this specimen is noticeably harder than a (Ti\(_{0.2}Zr_{0.2}Hf_{0.2}Ta_{0.2}Er_{0.2}\))B\(_2\) specimen synthesized by the same direct boron-metals reactive SPS method with a similar 98.1% relative density \[18,29\]. Similar to other brittle and incompressible materials that are subjected to indentation size effect \[46\], this specimen demonstrates increasing measured hardness with decreasing indentation load, going from 18.9 ± 1.4 GPa at 9.8 N to 35.8 ± 5.5 GPa at 0.49 N. At the same indentation load of 1.96 N, this specimen is noticeably harder than a (Ti\(_{0.2}Zr_{0.2}Hf_{0.2}Ta_{0.2}Er_{0.2}\))B\(_2\) specimen synthesized by the same direct boron-metals reactive SPS method with a similar 98.1% relative density (24.4 ± 2.5 GPa for (Ti\(_{0.2}Zr_{0.2}Hf_{0.2}Ta_{0.2}Er_{0.2}\))B\(_2\) here vs. 20.9 ± 1.1 GPa for the reference (Ti\(_{0.2}Zr_{0.2}Hf_{0.2}Ta_{0.2}Nb_{0.2}\))B\(_2\) \[29\]), as compared in Fig. 4(b). It is comparable to those so-called “superhard” HEDBs recently made with addition of CrB\(_2\), MoB\(_2\), and/or WB\(_2\) \[18,29\].

The hardness of the parent TMB\(_2\) phases was measured to be 18.6
The hardness value of bulk ErB$_2$ is 4.49 ± 1.65 GPa, which is significantly softer than refractory metal diborides (TM diborides) such as HfB$_2$, TaB$_2$, and NbB$_2$, which have hardness values of 25.0 ± 1.8 GPa for TaB$_2$, 15.4 ± 1.1 GPa for ZrB$_2$, and 17.5 ± 10.8 GPa for TaB$_2$, respectively. The hardness value of 1.96 N indentation load. Moreover, Rice et al. [50] reported a 5% increase in hardness (G) when grain size decreases from 13 µm to 4.5 µm, but the Hall-Petch dependence of G-0.5 on grain size G only becomes phenomenal when the grain size is smaller than ~1 µm. Thus, we conclude that relative density and grain size do not play a significant role on the observed enhanced hardness.

To discuss the effects of relative density and grain size, we adopt a $e^{-b\rho}$ dependence of hardness on porosity (P) [49], with value $b = 1.9$ [50] or 5.5 [51]. This suggests a mere 2-5% increase in hardness when relative density increase from ~98% to ~99%. Moreover, Rice et al. [52] suggests small increase in hardness (≤2%) when grain size decreases from 13 µm to 4.5 µm, but the Hall-Petch dependence of G-0.5 on grain size G only becomes phenomenal when the grain size is smaller than ~1 µm. Thus, we conclude that relative density and grain size do not play a significant role on the observed enhanced hardness here.

In this instance, it can be concluded that the hardness of HEDB has been noticeably enhanced by addition of 20% RE element, where the large lattice strain induced by the great difference in lattice parameters between ErB$_2$ and the rest TM diborides (discussed above) may have a contribution. Although the hardness of binary ErB$_2$ has never been experimentally measured to the best of our knowledge, simulation studies have predicted that ErB$_2$, as well as other RE diborides, have significantly lower hardness than TM diborides [53-55]. Hence, this HEDB, which can attain higher hardness by incorporation of softer REB$_2$ component, provides another example where HECs can attain unexpected properties beyond what the simple rule of mixtures can predict.

To further explore the elemental distribution near grain boundaries in the single-phase (Ti$_{0.2}$Zr$_{0.2}$Hf$_{0.2}$Ta$_{0.2}$Er$_{0.2}$)$_2$B$_2$ specimen, STEM samples of two independent grain boundaries were prepared and characterized. The locations of these two grain boundary samples were selected randomly from the polished specimen surface to ensure the validity and representational character. Their STEM micrographs, as well as the STEM-EDS results, are shown in Fig. 5. It is obvious that all five elements exhibit very homogenous distributions within the crystal grains. Nevertheless, RE element Er demonstrates significant grain boundary segregation in both samples, as clearly indicated by STEM-EDS mappings (Fig. (a2) and (b2)) and STEM-EDS line-scan profiles (Fig. (a3) and (b3)) over the grain boundaries. Contrarily, depletion of Zr and Hf on the grain boundaries have also been observed, while the contents of Ti and Ta stay relatively constant across the grain boundaries. As ErB$_2$ has significantly larger lattice parameters than the rest TM diborides (see discussion above), this Er segregation on grain boundary can be expected due to lattice mismatch and lattice strain. In fact, grain boundary segregation has also observed in W-containing HEDBs [56], where WB$_2$ bears smaller lattice than the other TM diboride constituents. Similarly, the Er grain boundary segregation, together with the associated lattice strain and dislocation, could suppress the grain growth.
and contribute to the improvement of material hardness for this 
\((\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Er}_{0.2})\text{B}_2\) HEDB solid solution. It should be pointed out that the enhancement in hardness should be a synergic effect of many factors, and Er grain boundary segregation may not have the dominating influence.

Nonetheless, the ability to dissolve substantial dissimilar metal cations (with large chemical and size mismatches) in HECs suggest new opportunities to tailor grain boundary properties, e.g., via the expected strong segregation that can significantly change grain growth and grain boundary mechanical (e.g., high-temperature sliding) properties. Thus, this may open a new window to engineer grain boundary properties and distributions across the grain boundaries. Strong Er segregation at grain boundaries is evident.

To the best of our knowledge, we were not aware of any prior report of RE-containing HEBs during our experiments. In our final manuscript preparation stage, we noticed that parallel work published by Zhang et al. (just a few days before the submission of this manuscript) also successfully synthesized several RE-containing HEDBs (with different compositions as we reported here) [57] and a Sc-containing HEDB [58]. In Zhang et al.’s most recent simultaneous and independent work [57, 58], no property has been measured and reported, and grain boundaries have not been characterized. In addition to the enhanced hardness and strong grain boundary segregation of the RE, another unique observation made in the current study is the fabrication-dependent phase formation.

4. Conclusions

In this study, a novel HEDB containing 20% RE element with nominal composition of \((\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Er}_{0.2})\text{B}_2\) has been synthesized via two distinctive routes: boron-metals reactive SPS from elemental precursors and borocarbothermal reduction of binary oxides followed by SPS. The specimen fabricated via borocarbothermal reduction contain Er-rich ErBO\(_3\)- and ErB\(_2\)-based solid solutions. On the other hand, specimen synthesized via boron-metals reactive SPS demonstrates a perfect single-phase high-entropy solid solution of AlB\(_2\)-prototype without any detectable impurity or secondary phase. This specimen has an exceptional relative density of 99.1%, and its elemental homogeneity has been verified by SEM-EDS analysis. The successful fabrication of single-phase \((\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Er}_{0.2})\text{B}_2\) specimen with 20% RE element (Er) stabilized in a high-entropy TM diborides, despite the dissimilar chemical properties of RE and TM elements and large differences in lattice parameters of ErB\(_2\) and typical TM\(_2\)B\(_2\) suggests a new paradigm by showing that HECs can enable significant solubility of dissimilar cations. Moreover, the existence of borate and secondary boride impurities from borocarbothermal reduction indicates the formation of single-phase \((\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Er}_{0.2})\text{B}_2\) depends on the fabrication route. Here, the large thermodynamic driving force in the reactive sintering of elemental precursors may play a key role for incorporating certain components that are otherwise difficult to dissolve in significant amounts.

Notably, with 20% ErB\(_2\) addition, \((\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Er}_{0.2})\text{B}_2\) has featured an increase in hardness, in comparison with typical \((\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2})\text{B}_2\) high-entropy TM diboride, despite the fact that ErB\(_2\) is predicted to be substantially softer. Specific STEM-EDS elemental analyses further revealed significant Er segregation at grain boundaries.

In broader context, the validation of our hypothesis that a substantial amount of dissimilar metal cations (with large chemical and size mismatches) can be stabilized in HECs and CECs suggest new opportunities to tailor their mechanical properties, e.g., promoting more lattice distortion to improve hardness or impede high-temperature dislocation motion, or grain boundary properties via the expected strong segregation that can alter microstructural evolution (e.g., inhibit grain growth) and high-temperature properties (e.g., grain boundary sliding or preferred grain boundary oxidation). Specifically, for RE-containing HEDBs, in addition to the enhanced hardness (that already has been demonstrated here), the ability to add a substantial amount of RE...
in high-entropy TM diborides opens a new window to tailor their oxidation resistance, including the formation/stability of oxide scales and potentially the grain boundary oxidation resistance with the expected strong RE segregation (since preferred grain boundary oxidation was observed in high-entropy UHTCs [59]).

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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