High Entropy Carbides Synthesized via Microwave-Induced Plasma

THE UNIVERSITY OF ALABAMA AT BIRMINGHAM

M. Shiraz Ahmad[1], Bria Storr[1], Cheng-Chien Chen[1], Luke Moore[1] and Shane A. Catledge[1]

1. Department of Physics, University of Alabama at Birmingham, Birmingham, AL 35294-1170, U.S.A.

Aims:

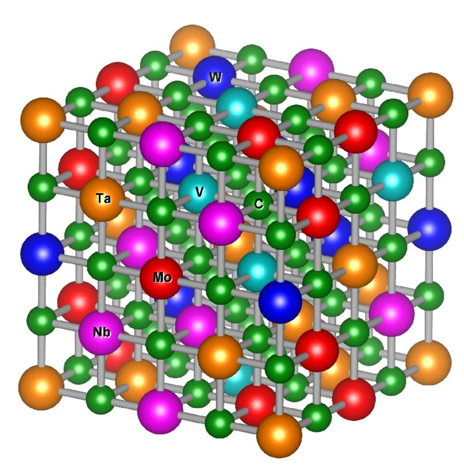
- Explore the novel approach of using microwave induced plasma to synthesize high entropy carbides
- Evaluate the propensity to form a solid solution rock-salt structure based on the high entropy carbide: $(Hf_{0.2}Zr_{0.2}Ti_{0.2}Ta_{0.2}Nb_{0.2})C$

Microwave Plasma Annealing:

- Rapid MW heating of ceramic core
- Plasma discharge promotes chemical reactions as highly active species
- Potential benefits: Reduced sintering temperature, increased densification rate, and minimized grain coarsening

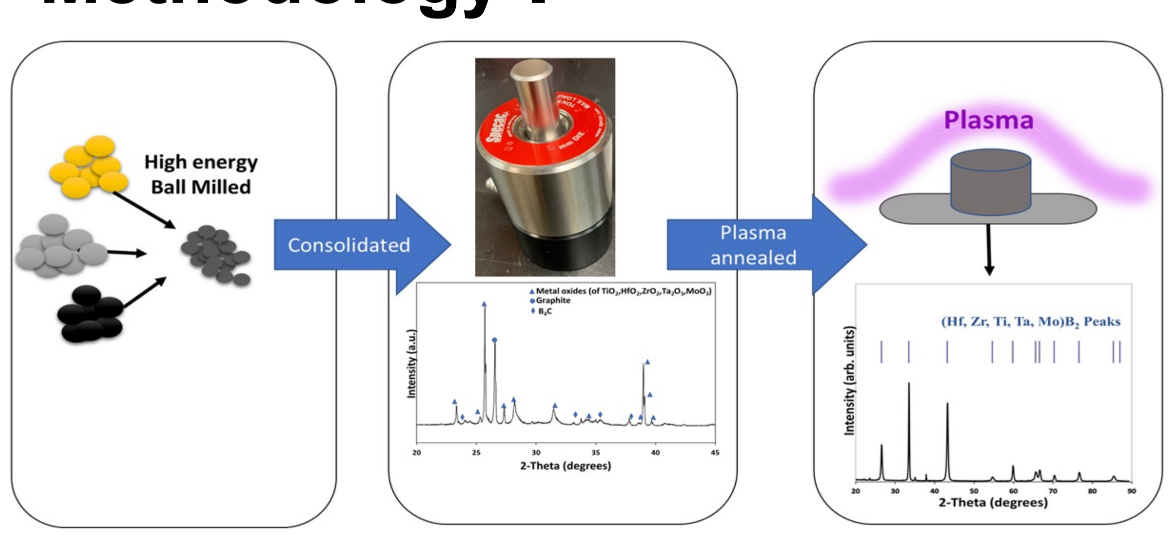
High Entropy Carbides:

- Rock-salt crystal structure
- Known for thermal stability, high strength and modulus, good oxidation resistance and can withstand extreme conditions



Kaufmann, Kevin, et al. "Discovery of high-entropy ceramics via machine learning." *Npj Computational Materials* 6.1 (2020): 42.

Methodology :

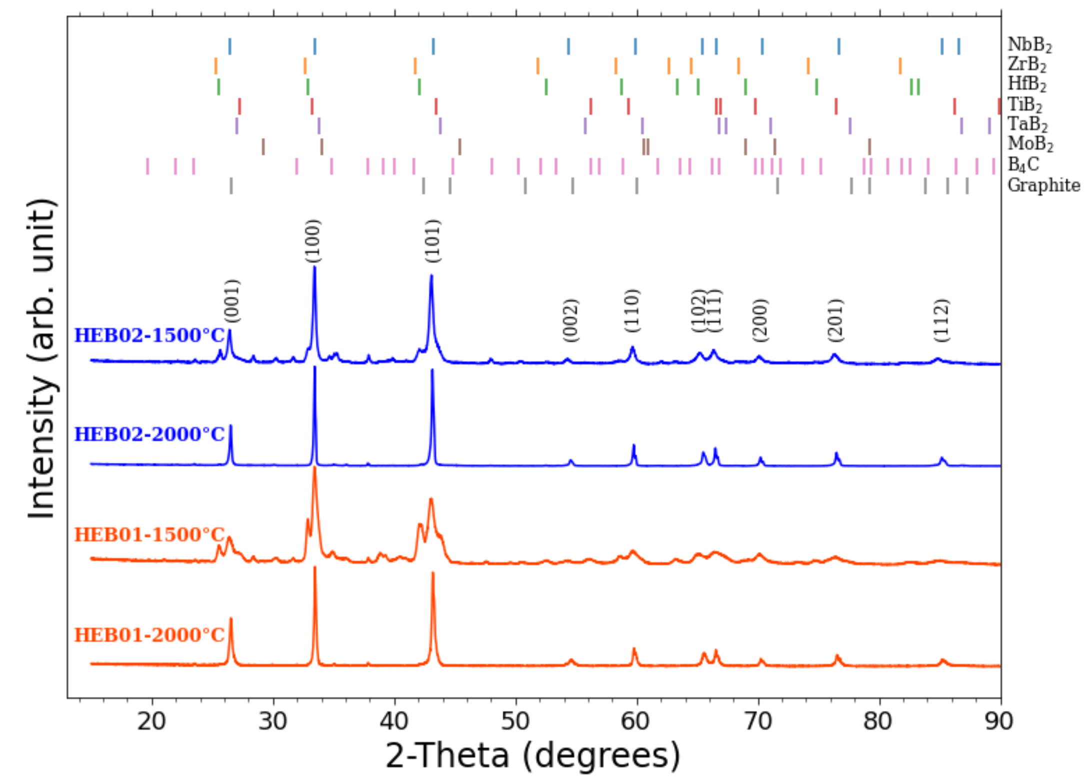


Start with metal oxides + graphite as reducing agent

High energy ball mill then press into pellet.

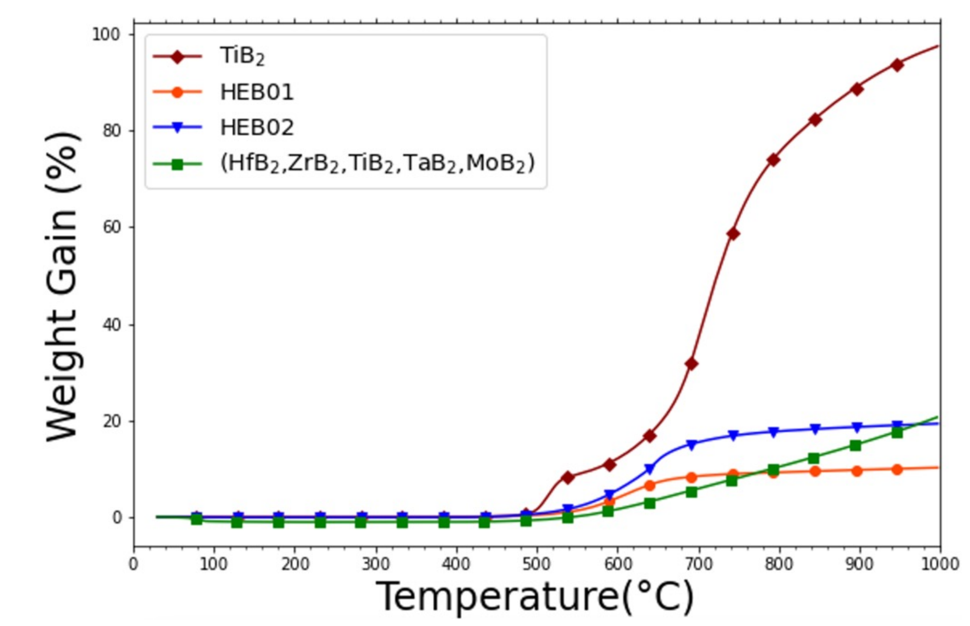
The pellet is MW plasma annealed to 1800°C or 2000°C for 1hr in an argon-rich feedgas.

Prior Success in High-Entropy Borides:



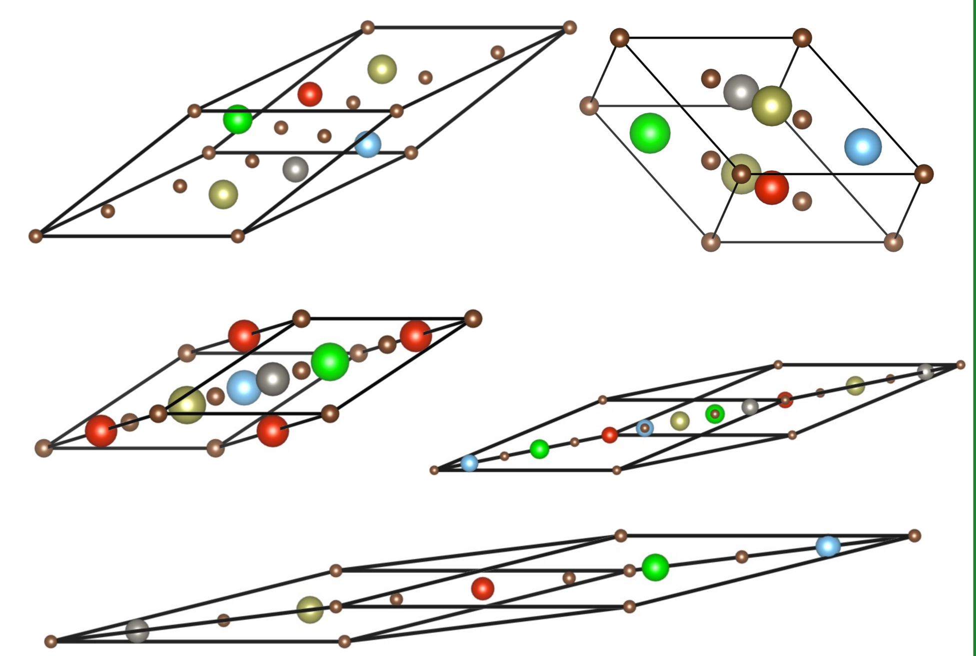
XRD for two HEB configurations plasma annealed at 1500 °C and 2000 °C. The Entropy Forming Ability (EFA) is higher for HEB02, resulting in more complete conversion to the high entropy phase at lower annealing temperature.

- **HEB01: $HfZr\mathit{Ti}TaMoB_{10}$ EFA : 207(eV/atom)-1**
- **HEB02: $HfZr\mathit{Nb}TaMoB_{10}$ EFA : 294(eV/atom)-1**



Weight gain (in air) vs. sample temperature measured from thermogravimetric analysis. Samples measured include the plasma annealed HEBs made at 2000 °C: HEB01 (orange), HEB02 (blue), a mixture consisting of five commercial diborides (green), and TiB2 (brown).

Progress on High-Entropy Carbides:



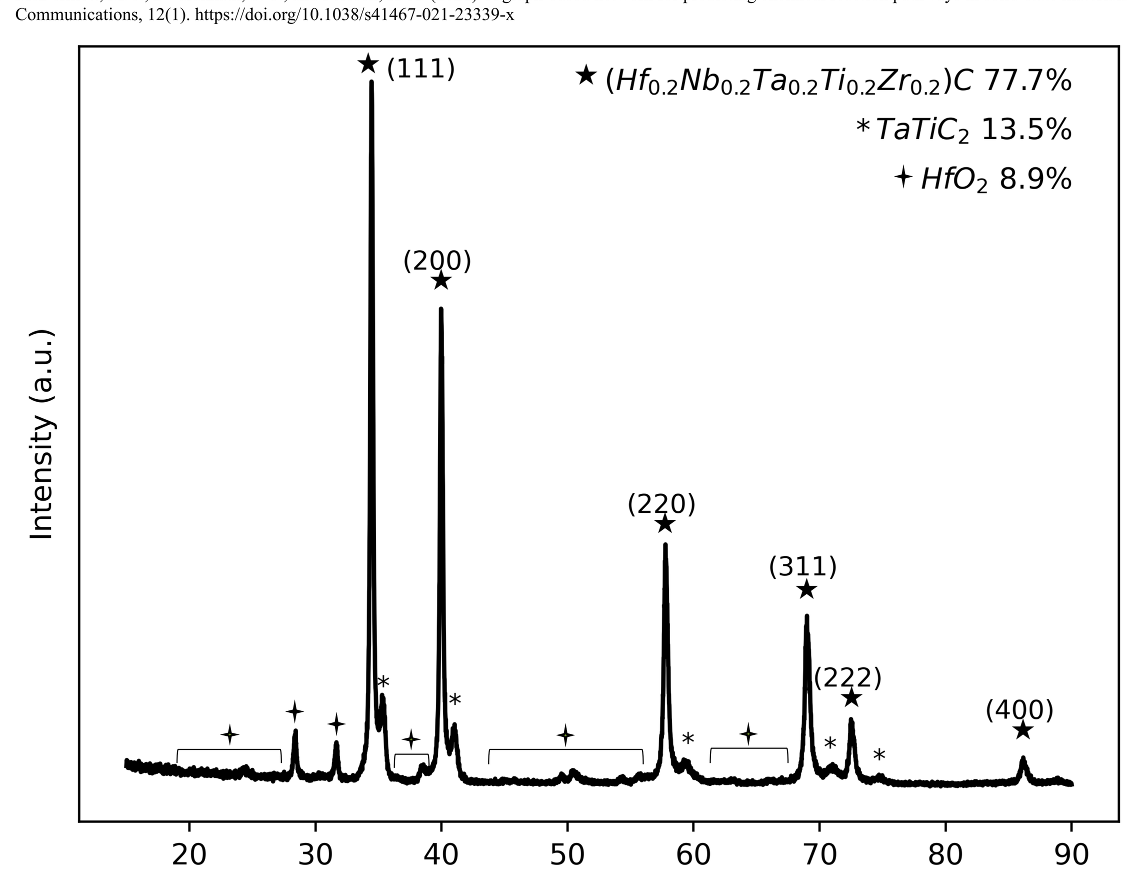
Carbothermal Reduction (CTR) Reactions At 1600^{O}C

$$HfO_{2(s)} + 3C_{(s)} \rightarrow HfC_{(s)} + 2CO_{(g)} \text{ (dG = 0.131 eV/atom)}$$
$$ZrO_{2(s)} + 3C_{(s)} \rightarrow ZrC_{(s)} + 2CO_{(g)} \text{ (dG = −0.041 eV/atom)}$$
$$TiO_{2(s)} + 3C_{(s)} \rightarrow TiC_{(s)} + 2CO_{(g)} \text{ (dG = −0.177 eV/atom)}$$
$$1/2Ta_2O_{5(s)} + 7/2C_{(s)} \rightarrow TaC_{(s)} + 5/2CO_{(g)} \text{ (dG = −0.3 eV/atom)}$$
$$1/2Nb_2O_{5(s)} + 7/2C_{(s)} \rightarrow NbC_{(s)} + 5/2CO_{(g)} \text{ (dG = −0.323 eV/atom)}$$

Solid Solution (SS) Formation At 2000^{O}C

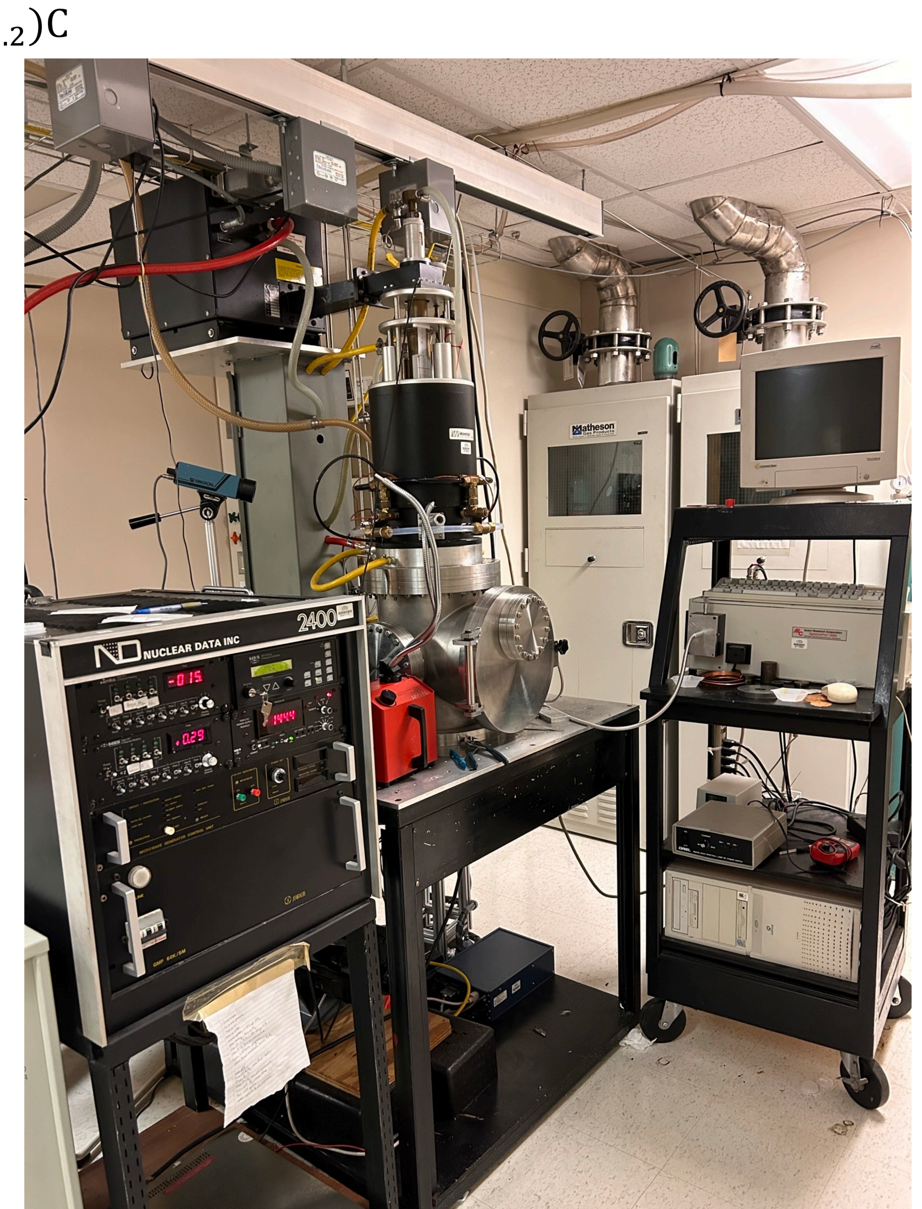
$$1/5(HfC_{(s)} + ZrC_{(s)} + TiC_{(s)} + TaC_{(s)} + NbC_{(s)}) \rightarrow (Hf_{0.2}Zr_{0.2}Ti_{0.2}Ta_{0.2}Nb_{0.2})C$$

1. Feng, Lun, et al. "Synthesis of single-phase high-entropy carbide powders." Scripta Materialia 162 (2019): 90-93.
2. McDermott, M. J., Dwaraknath, S. S., and Persson, K. A. (2021). A graph-based network for predicting chemical reaction pathways in solid-state materials synthesis. Nature Communications, 12(1). https://doi.org/10.1038/s41467-021-23339-x

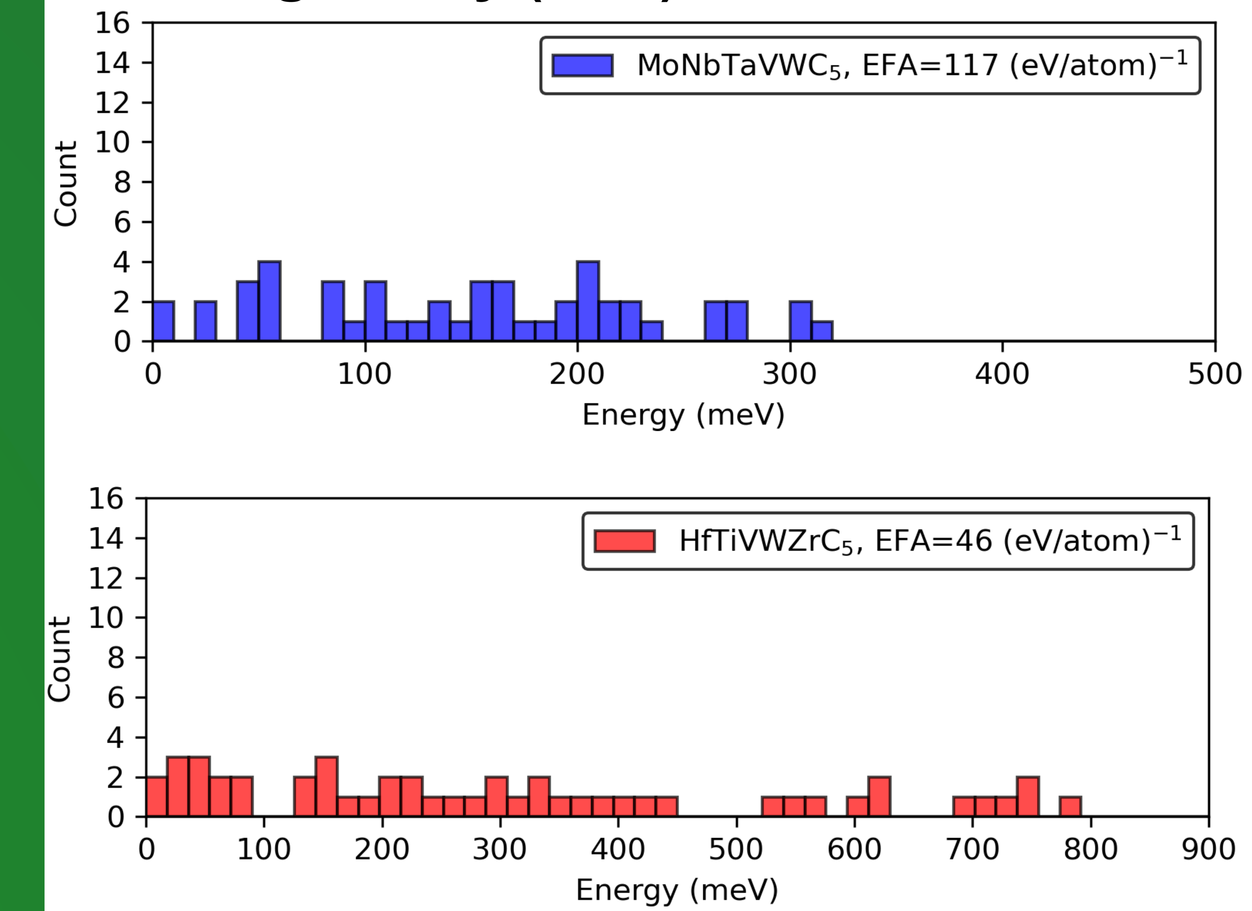


X-ray diffraction after MWPP of precursor metal-oxide powders (with graphite) to form HEC based on $(Hf_{0.2}Nb_{0.2}Ta_{0.2}Ti_{0.2}Zr_{0.2})C$

- **Lattice parameter from literature[1]:** 0.4524 nm
- **Lattice parameter from the experiment:** 0.4517 nm



Computational Modeling of Entropy Forming Ability (EFA):



$$\text{EFA}(N) \equiv \left\{\sigma[\text{spectrum}(H_i(N))]_{T=0}\right\}^{-1}$$

Challenges:

- Resistance to increase in temperature in the range of 1700-2000^{O} C
- Large fluctuations in the temperature
- Gibbs free energy for CTR of $HfO_{2(s)}$ is positive
- Hf is limiting element for SS reaction

Conclusion:

- Predominately single-phase HEC can be made by MW plasma-annealing

Future Work:

- Investigate the role of excess graphite reducing agent as well as temperature and time to increase the propensity toward full conversion to the HEC single phase.

Acknowledgement

This work is supported by the NSF EPSCoR RII-Track-1 Cooperative Agreement OIA-2148653