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Synthesis and Static Oxidation Testing of Doped HfB2 Powders

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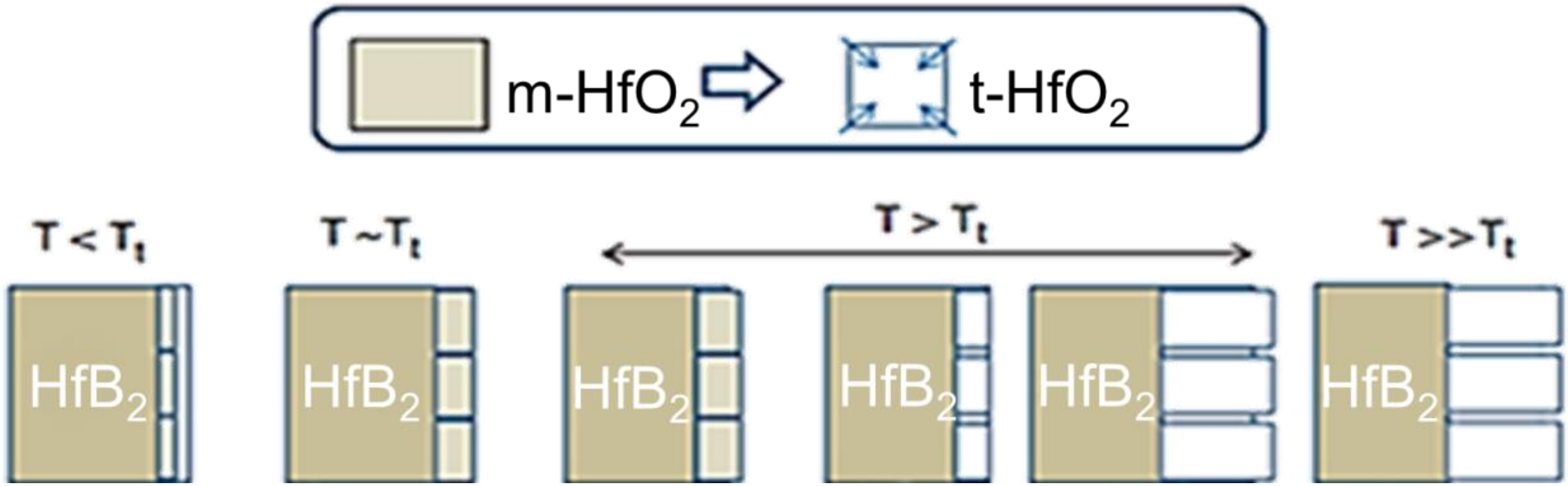
Problems with HfB_2 Ceramic Oxidation

HfB_2 oxidises to HfO_2 readily; whilst not a problem in itself, like ZrO_2, HfO_2 undergoes a phase transformation with an associated volume change that opens up porosity.



Phase transformation of the oxide product of HfB_2

One solution is to dope the HfB_2 so that on oxidation it forms stabilised, tetragonal HfO_2

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Dopant Selection

Compound	Melting point /°C	Crystal structure	Covalent radius of the metal atom / pm
HfB_2	3250	Hexagonal	175±10
YB_4	2150	Tetragonal	190±7
TaB_2	2850	Hexagonal	170±8
LaB_6	2250	Cubic	207±8
MgB_2	830	Hexagonal	141±7

TaB_2 was chosen because of its similar crystal structure and atomic radius to that of HfB_2

Addition of Ta-Dopant

$TaCl_5$ | $HfCl_4$

$TaCl_5$ dispersed in ethanol, $HfCl_4$ in de-ionised water. Ammonia used to form hydroxides & remove Cl^- ions.

Co-precipitates

H_3BO_3 | Phenolic resin

Dissolved in ethanol

↓

Refluxing & stirring (100°C for 24 h)

↓

Drying & calcining (200°C for 2 h)

↓

Grinding

↓

Carbo/borothermal reduction (1600°C for 2 h)

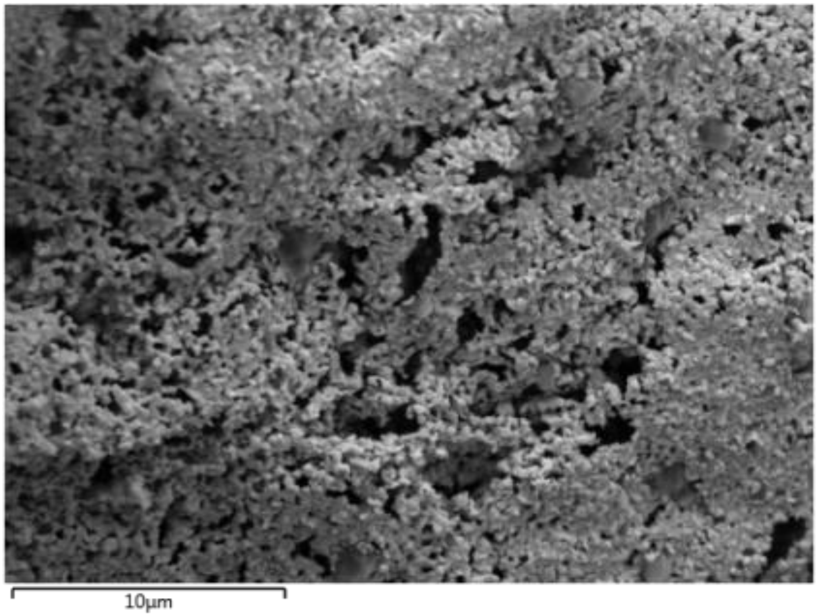
$$HfO_2 + B_2O_3 + 5C \rightarrow HfB_2 + 5CO\uparrow$$

$$\Delta G<0 \text{ at } >1350\,^{o}C$$

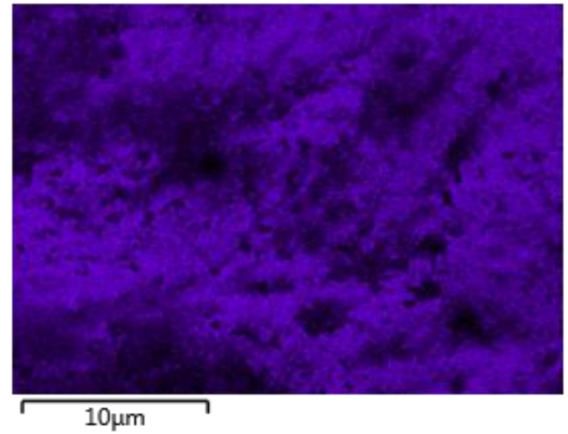
$$Ta_2O_5 + 2B_2O_3 + 11C \rightarrow 2TaB_2 + 11CO\uparrow$$

$$\Delta G<0 \text{ at } >1327\,^{o}C$$

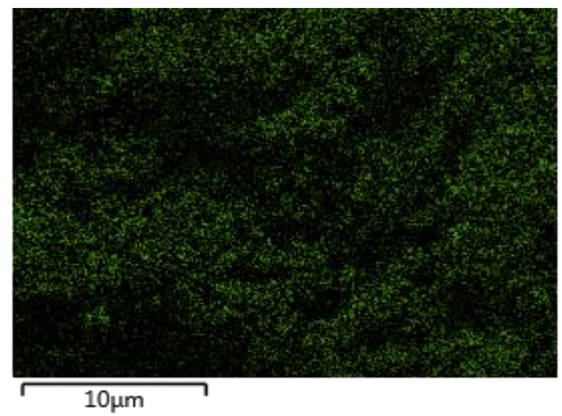
Ta-Doped HfB_2 Powder



10 wt% Ta-doped HfB_2 powder



Hf



Ta

EDX mapping shows the Ta distributed homogeneously. The particle size was ~0.5 µm, but the final product contained hard agglomerates.

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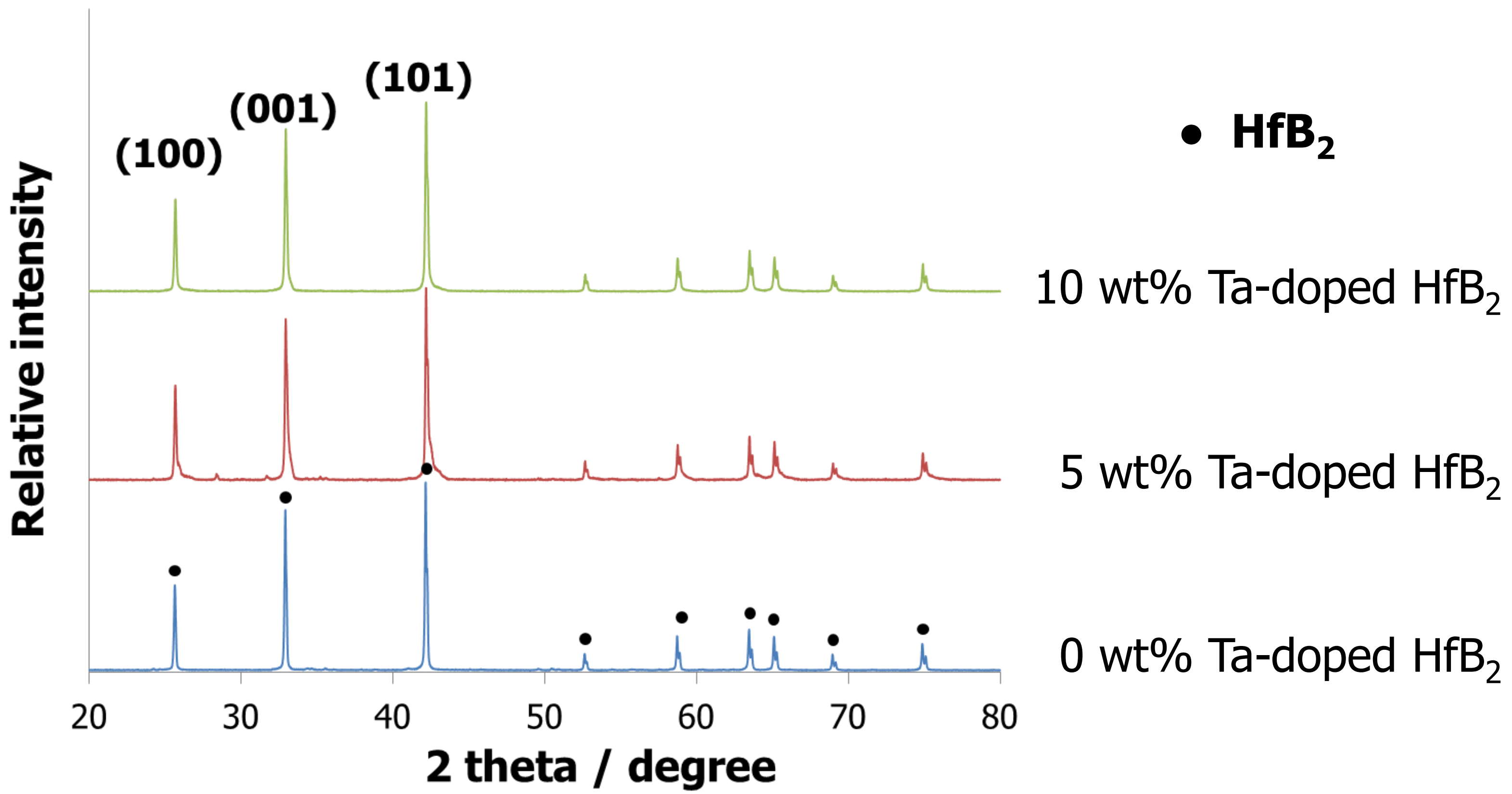
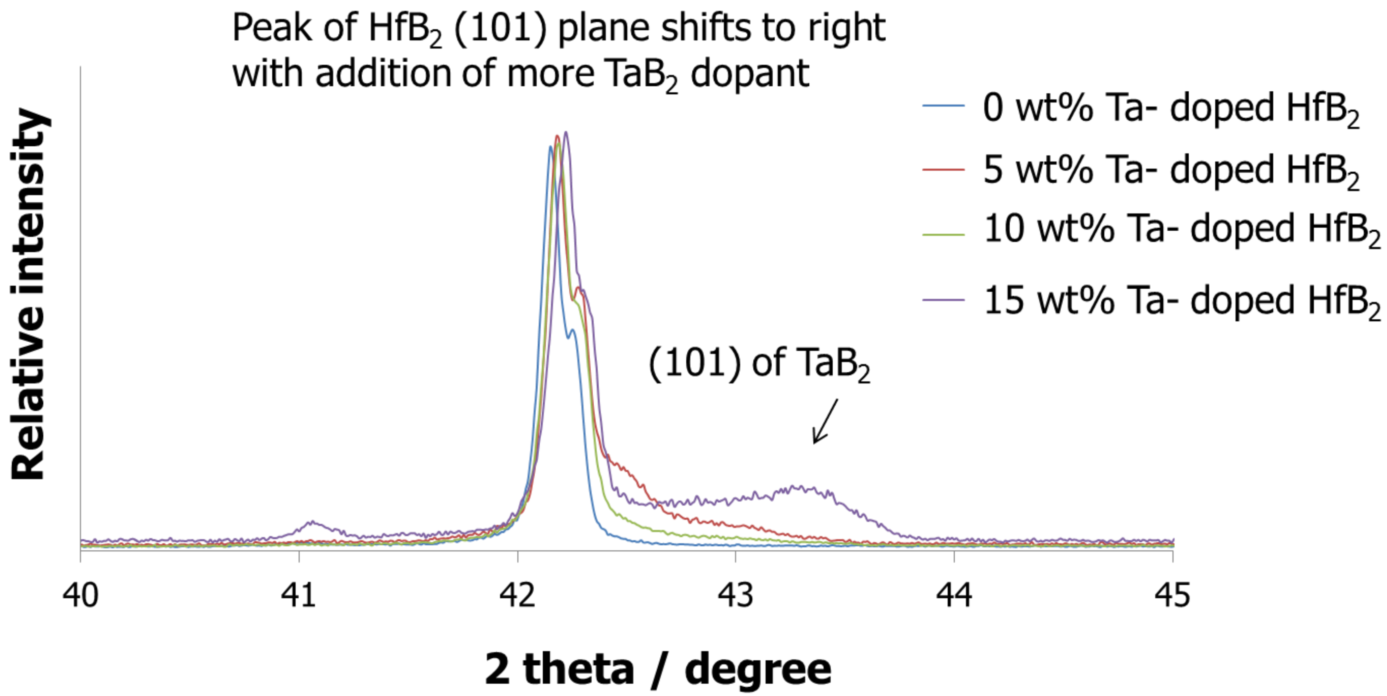
XRD of Ta-Doped HfB_2 Powder



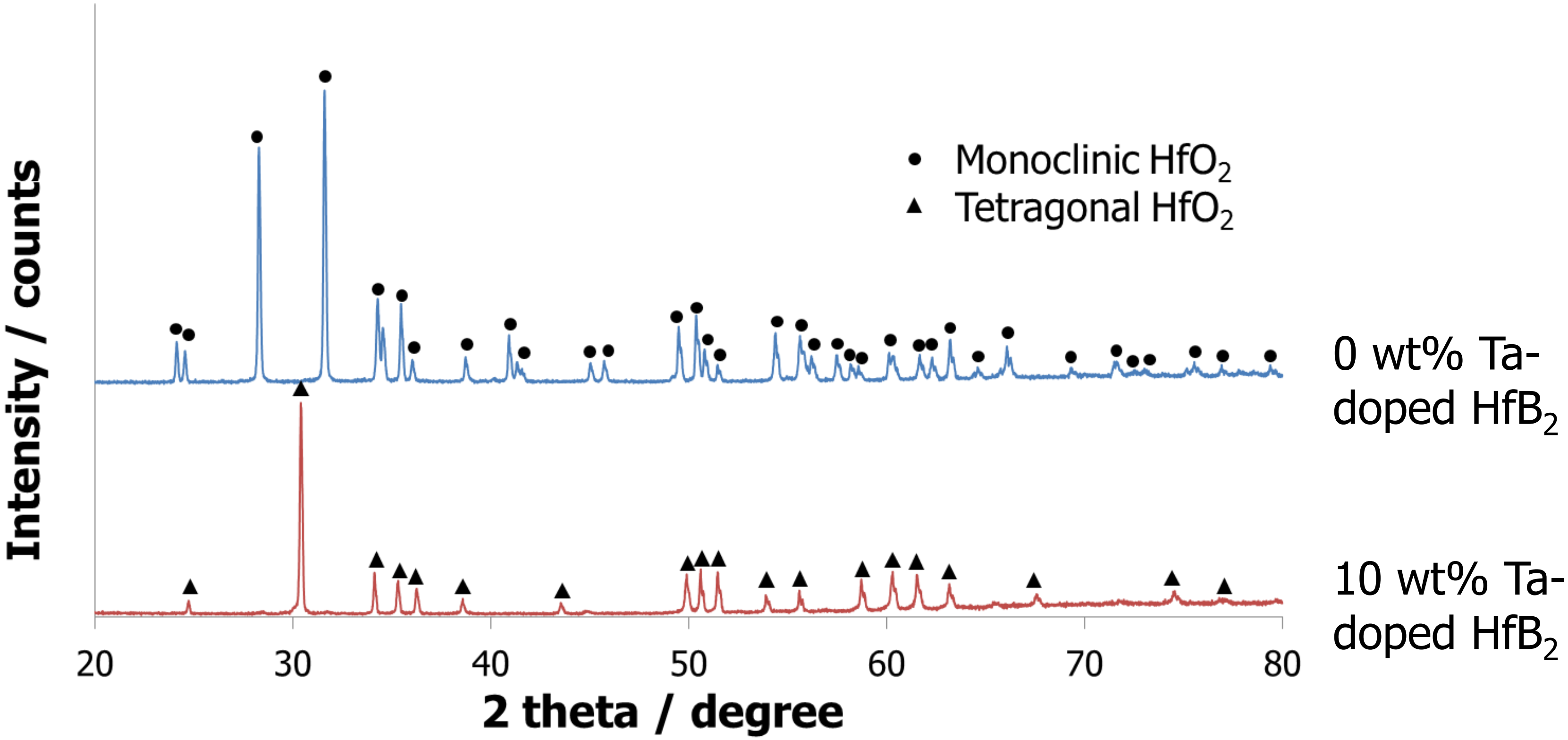
All the peaks correspond to HfB_2 confirming the formation of $(Ta,Hf)B_2$ solid solution

Lattice Parameter of Pure and Doped HfB_2



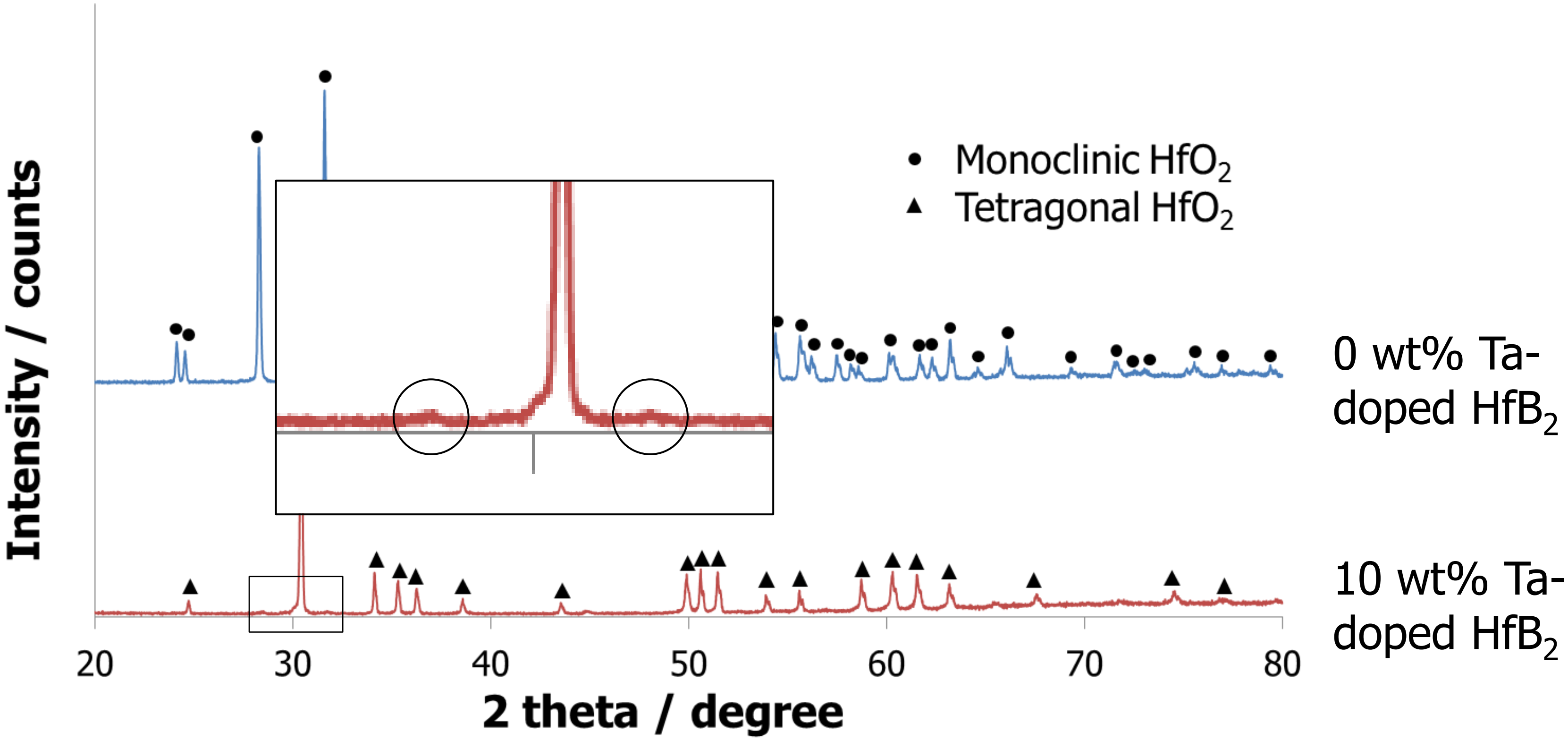
Lattice parameter	HfB_2 (literature)	HfB_2 (this study)	5% TaB_2-doped HfB_2	10% TaB_2-doped HfB_2	15% TaB_2-doped HfB_2	TaB_2
a / nm	0.3141	0.3142	0.3140	0.3139	0.3138	0.3088
c / nm	0.3470	0.3470	0.3468	0.3466	0.3464	0.3241

XRD Results after 1600ºC Oxidation of Powder



After 1600ºC oxidation, pure HfB_2 yielded entirely monoclinic HfO_2 whilst the 10%TaB_2-doped HfB_2 gave almost phase pure tetragonal HfO_2.

XRD Results after 1600^{o}C Oxidation of Powder



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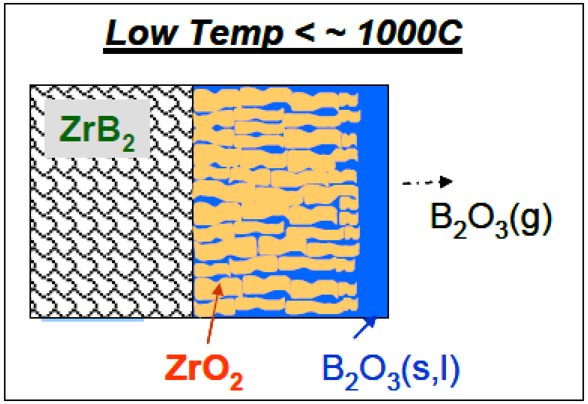
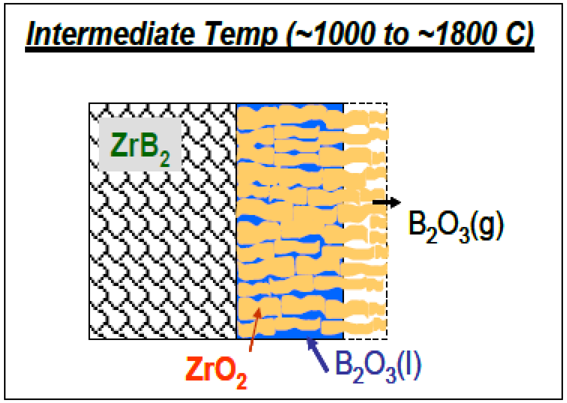
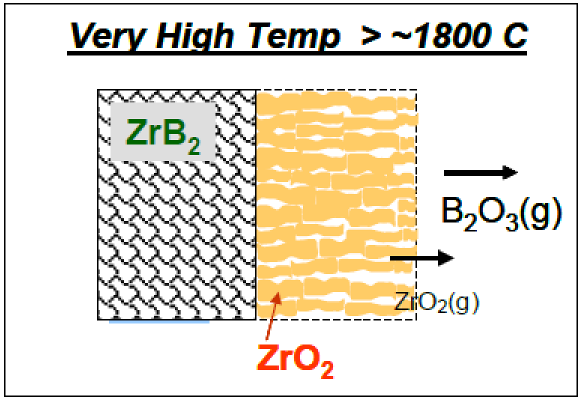
Modelling



Porous ZrO_2 – Wetted by B_2O_3



Porous ZrO_2 – partially filled



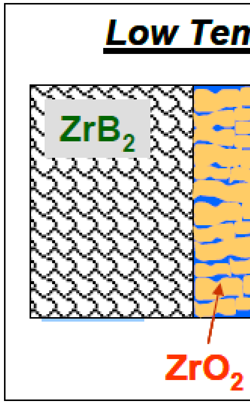
Porous ZrO_2 – Enhanced Oxidation

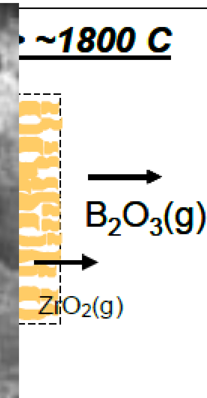
Predicted: recession rates, scale thicknesses, weight gain (all validated against expts)

Phase transformation of ZrO_2 and HfO_2 plays a significant role (increases pore volume)

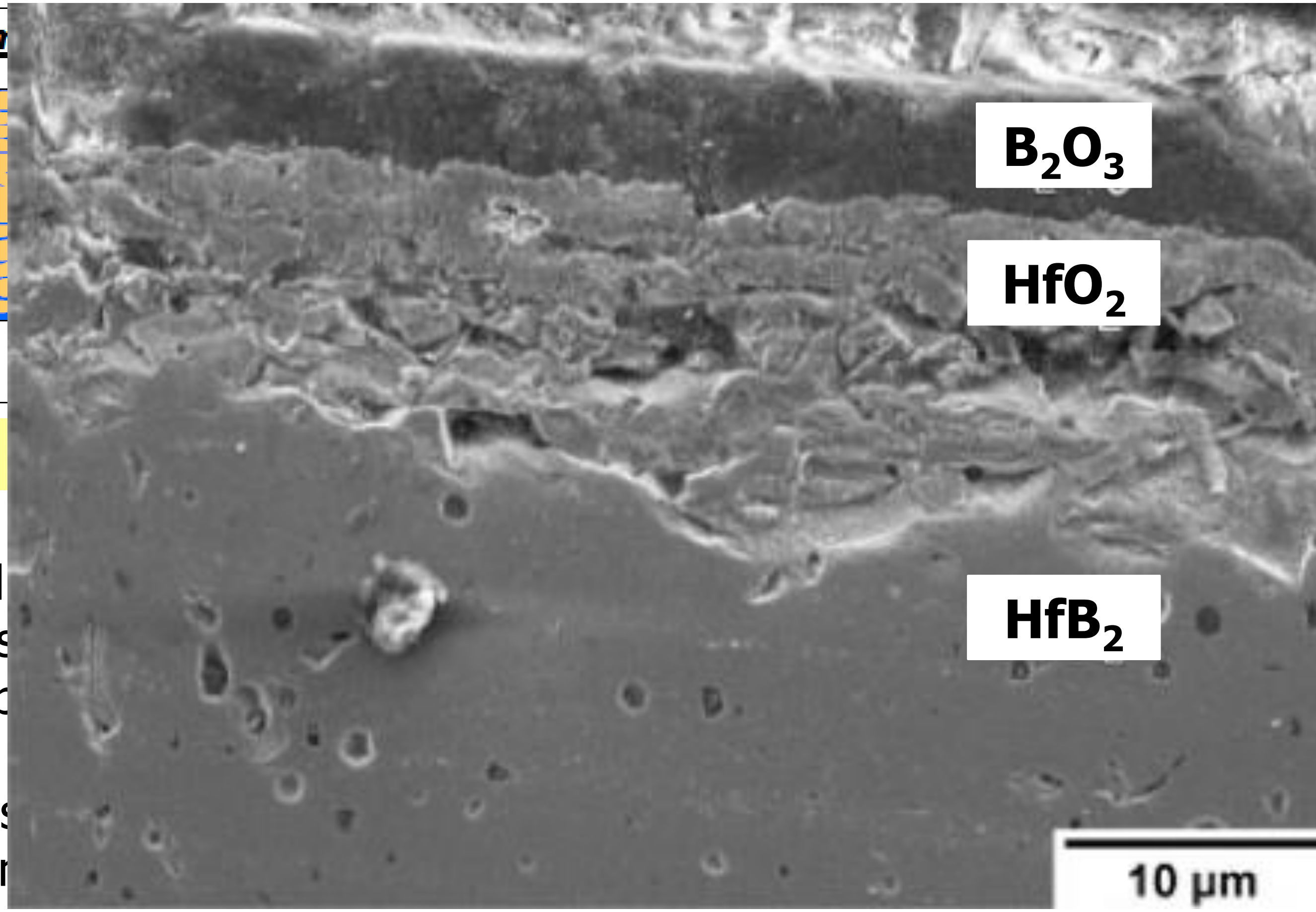
TA Parthasarathy

Modelling





Porous ZrO2 … ed Oxidation

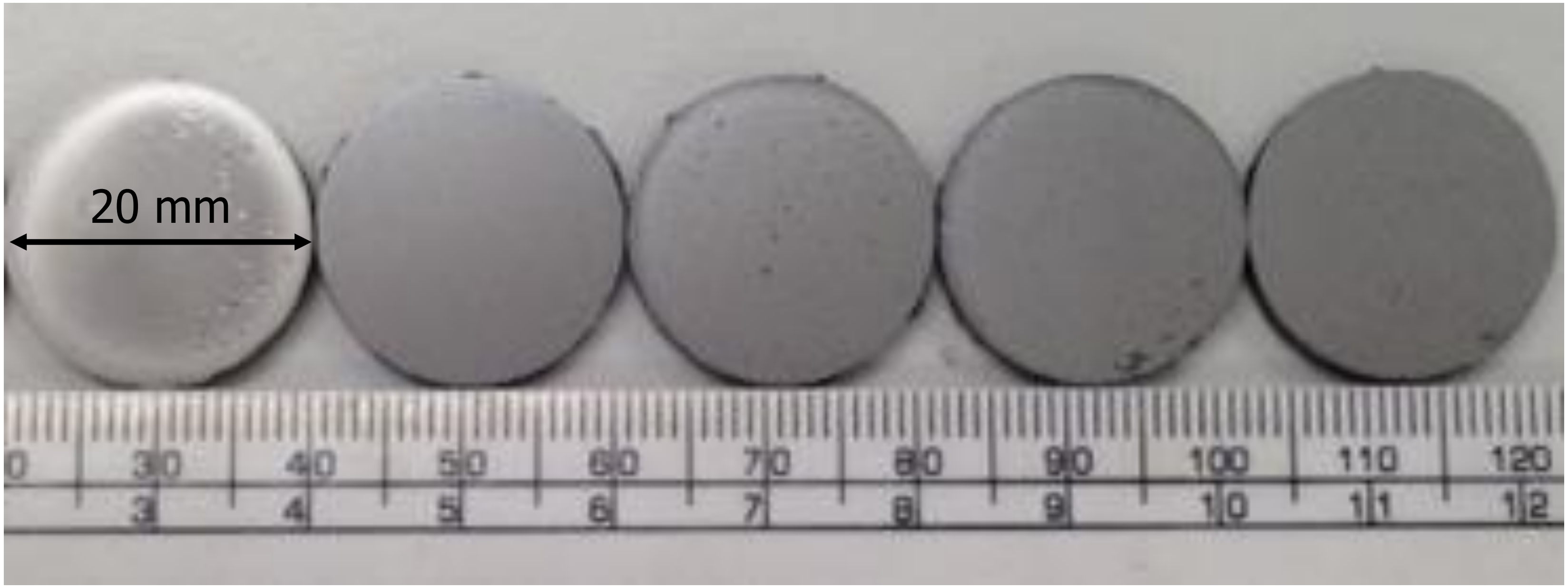


Predicted thicknesses … against exp … sarathy

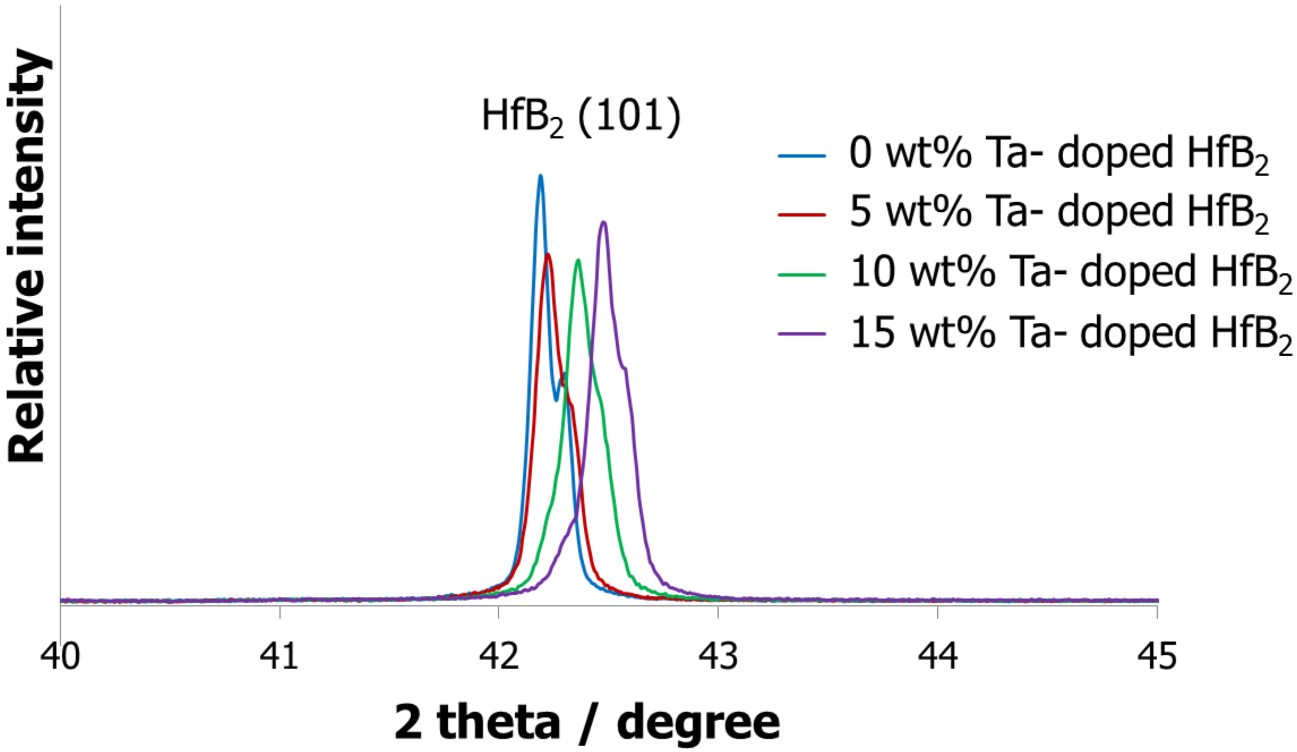
Phase trans… plays a sign… volume)

Ta-Doped Samples after SPS at 2100ºC, 50 MPa

Treibacher HfB_2	0 wt% Ta-doped HfB_2	5 wt% Ta-doped HfB_2	10 wt% Ta-doped HfB_2	15 wt% Ta-doped HfB_2



Ta-Doped Samples after SPS at 2100ºC, 50 MPa



- Peak shifts shows that Ta atoms remain in solid solution
- No residual TaB_2 in the 15 wt% Ta-doped HfB_2 sample

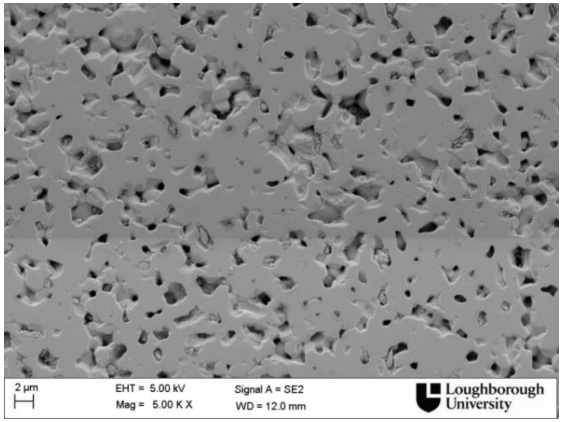
Ta-Doped Samples after SPS at 2100ºC, 50 MPa

Samples	Density / g cm^{-3}	Relative density
Treibacher HfB_2	9.83	93.62%
0 wt% Ta-doped HfB_2	8.93	85.04%
5 wt% Ta-doped HfB_2	9.24	87.73%
10 wt% Ta-doped HfB_2	9.36	88.59%
15 wt% Ta-doped HfB_2	9.55	90.12%

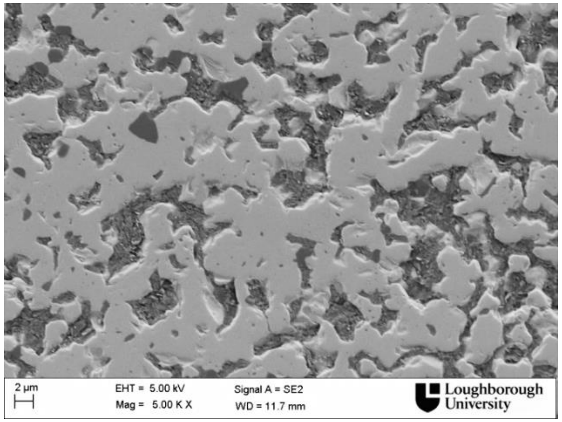
Theoretical value for HfB_2	*10.50*
Theoretical value for TaB_2	*11.15*

The addition of Ta improves the sinterability of HfB_2

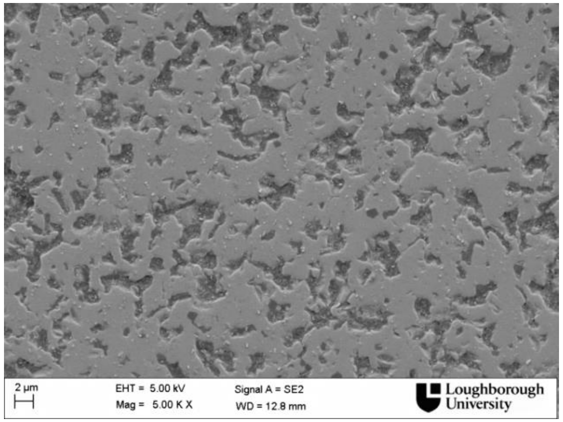
Ta-Doped Samples after SPS at 2100ºC, 50 MPa



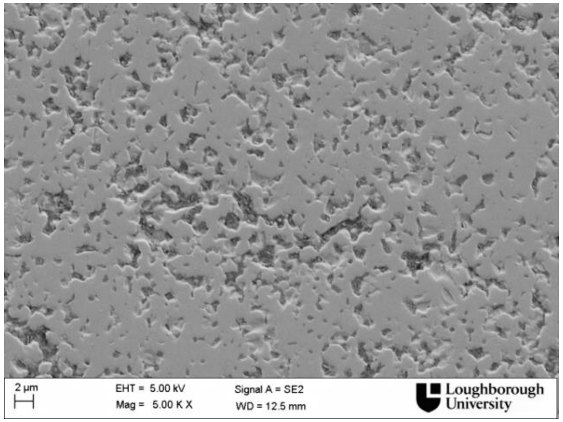
Treibacher HfB_2



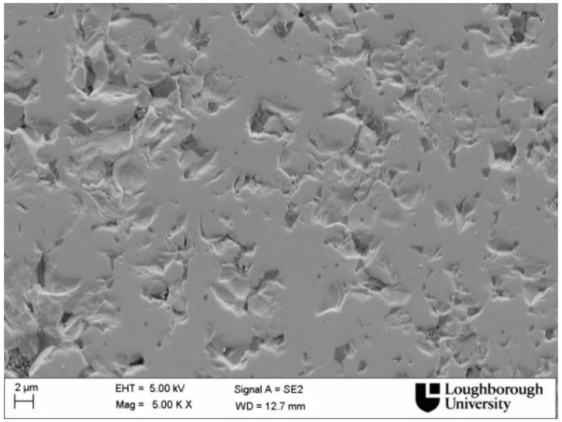
0 wt% Ta-doped HfB_2



5 wt% Ta-doped HfB_2



10 wt% Ta-doped HfB_2



15 wt% Ta-doped HfB_2

The addition of Ta improves the sinterability of HfB_2

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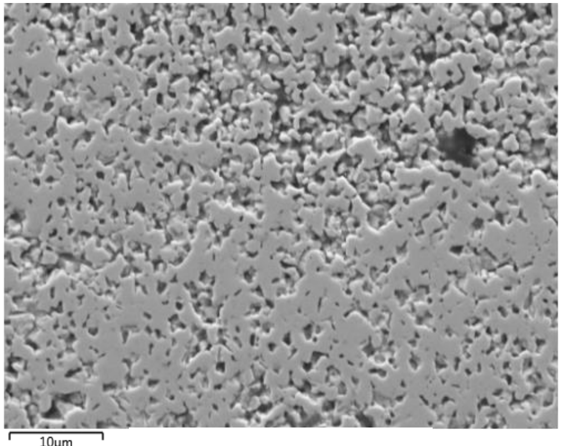
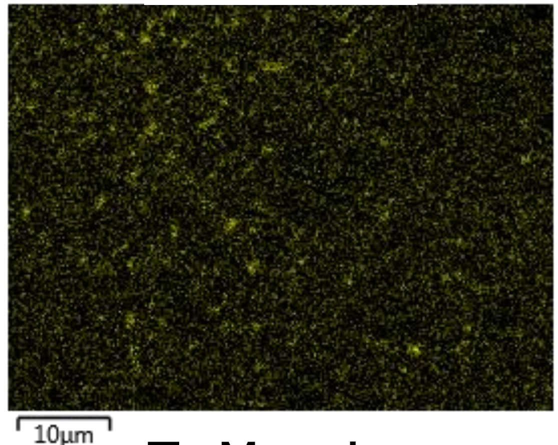
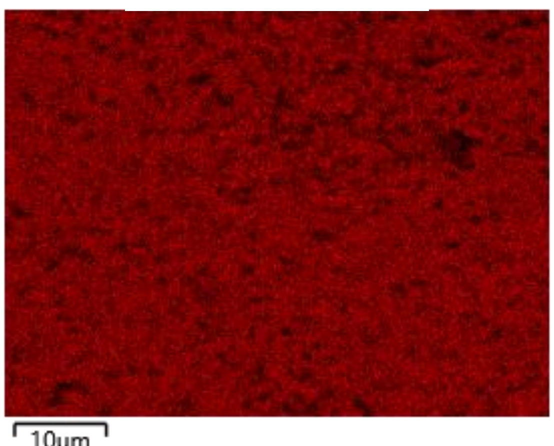
Compositional Analysis



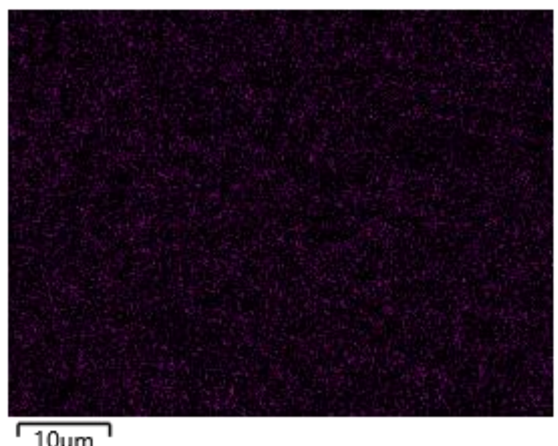
C K series



Hf M series



Ta M series



10 wt% Ta-doped HfB_2

Ta homogeneously distributed.

Carbon was found in all the samples (including the commercial HfB_2). It is probably from the protective graphite sheet used for SPS.

Ta-Doping of HfB_2 – Summary & Future Work

- High purity, sub-micron (~0.5 µm) Ta-doped HfB_2 has been synthesized.
- The 10 wt% Ta-doped HfB_2 was able to almost fully stabilize HfO_2 in the tetragonal phase after oxidation of the powder at 1600^oC.
- The addition of Ta-dopants improve the sinterability of HfB_2.

- In order to achieve higher density, the 10 wt% Ta-doped HfB_2 powders will be SPSed at 2400^oC and 500 MPa at QML.
- Samples with satisfactory density (>98%) will be oxidized to investigate TAPs' model.

Thank You