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Overview of Boron Carbide Synthesis and Processing at Rutgers University

Tyler Munhollon, M. Fatih Toksoy, Anthony Etzold, William Rafaniello and Richard A. Haber

Rutgers University, Department of Materials Science and Engineering

Outline

- Background
- Synthesis and Processing of Carbon Free Boron Carbide
- Processing of Boron Rich Boron Carbide
- Silicon Doping of Boron Carbide
- Scaling Up
- Conclusions

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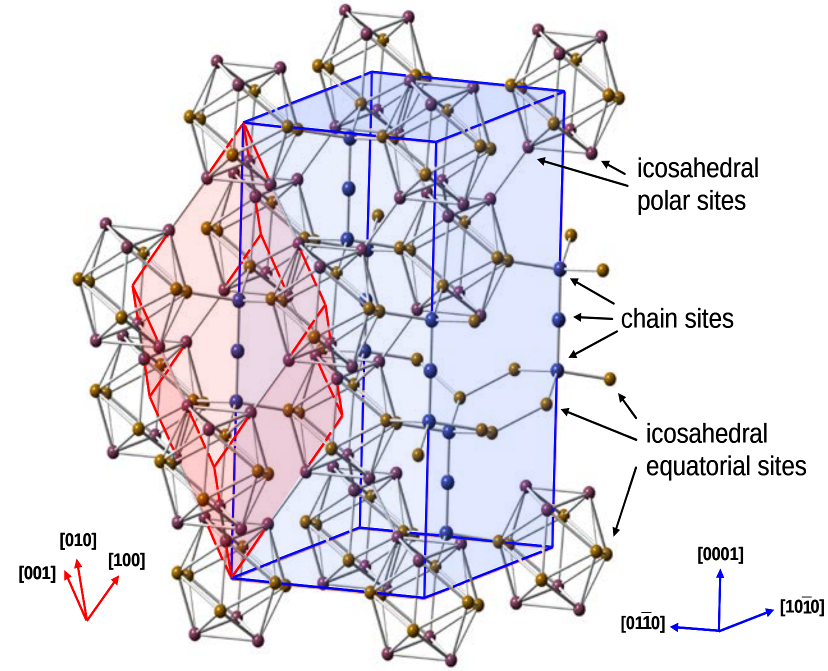
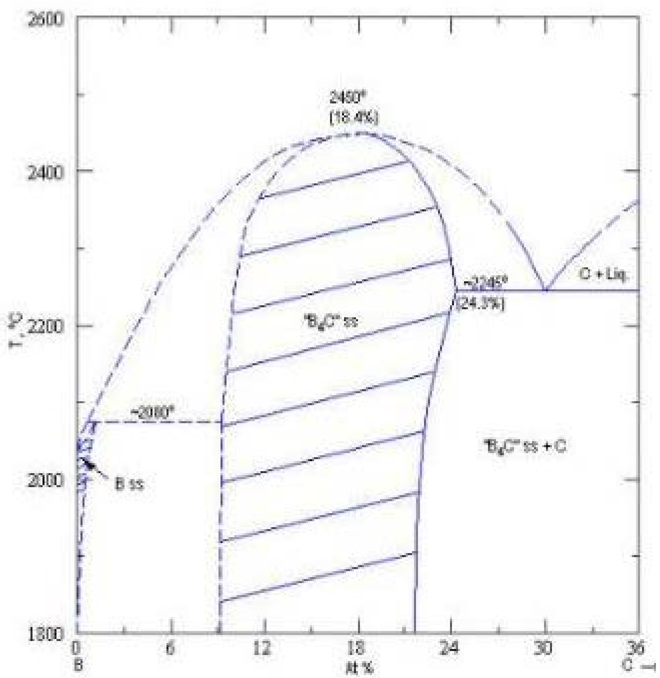
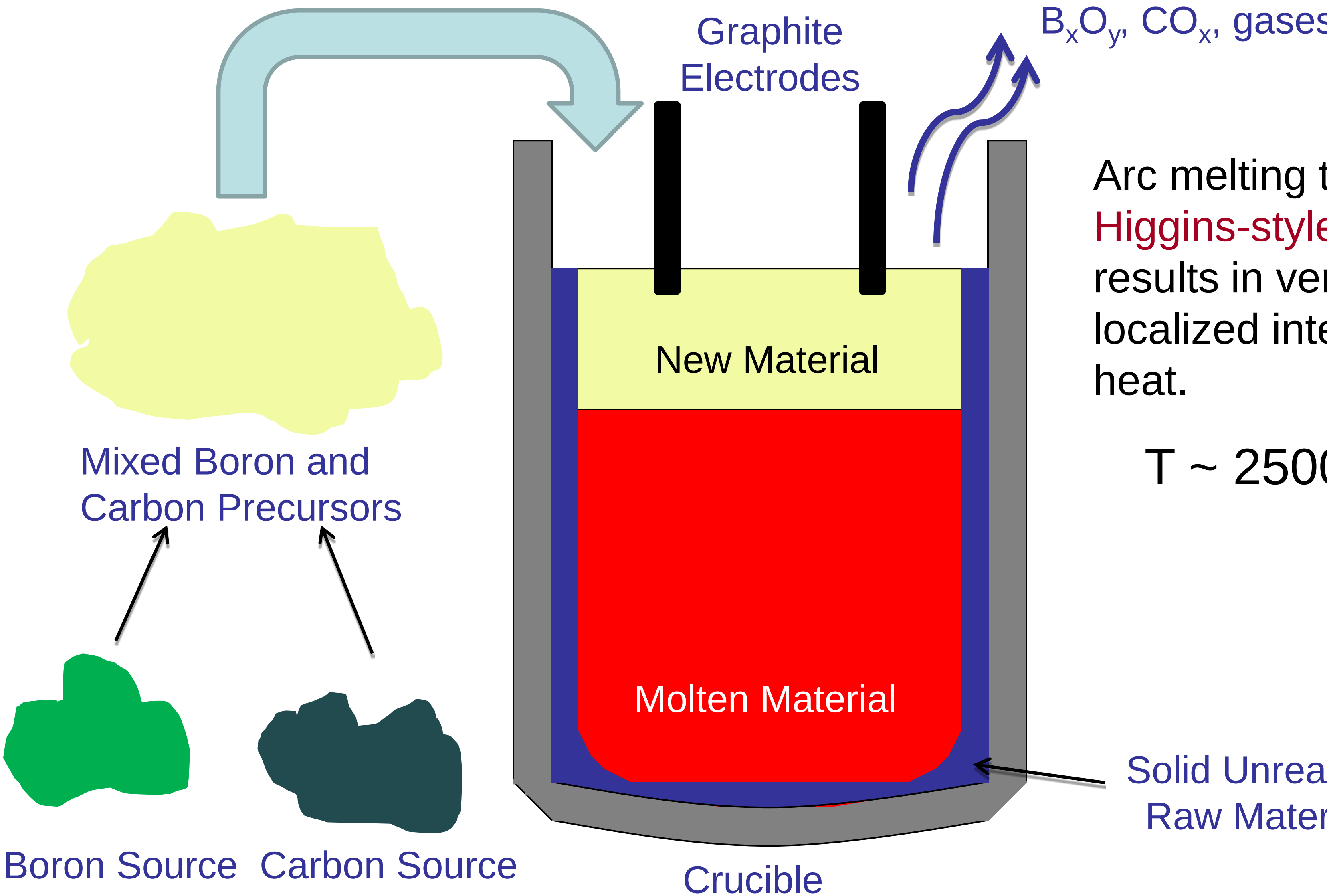
Density	2.52 g/cm^3
Young's Modulus	490 GPa
Shear Modulus	197 Gpa
Poisson's Ratio	0.18
HK_{100}	3000 kg/mm^2
Fracture Toughness	3.1 - 4.1 MPa m$^{1/2}$





- Thevenot, F., JECerS., 1990. **6**: p. 205-225.
- Lipp, A., Internal Publication,1966, Elektroschmelzwerk Kempten GmbH: Munich.
- Steinbruck, M., J. Nuc. Mat'ls, 2005. **336**(2-3): p. 185-193.
- McClellan, K.J., et al., J. Mat'ls Sci., 2001. **36**(14): p. 3403-3407.
- Tariolle, S., et al., JECerS, 2005. **25**(16): p. 3639-3647.
- Werheit, H., J. Phys: Cond. Matter, 2006. **18**: p. 10655-10662.

$$2B_2O_3(s) + 7C(s) \rightarrow B_4C(s) + 6CO(g)$$



Arc melting through Higgins-style furnace results in very localized intense heat.

T ~ 2500 ºC

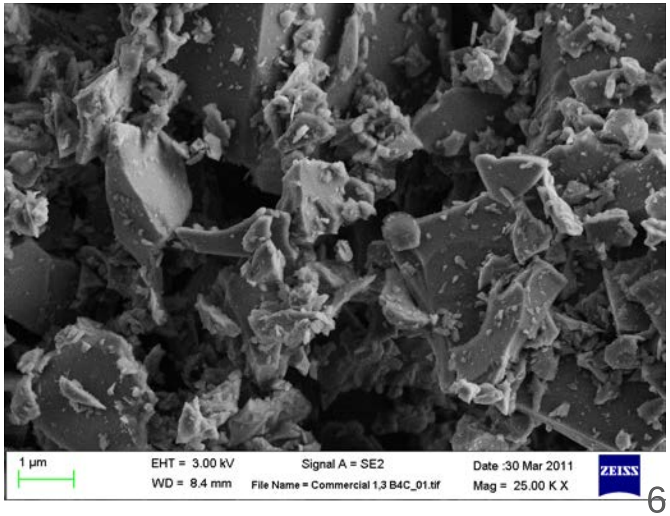
Images courtesy Washington Mills

•Slow non-uniform reactions → non-uniform chemical composition/stoichiometry

- Free carbon is impossible to eliminate
- Cannot produce controlled B:C ratios
- Cannot easily dope with other cations

•Size reduction through milling → morphology characterized by fractured surfaces and wide particle size distribution

- Impurities from milling



Characteristics

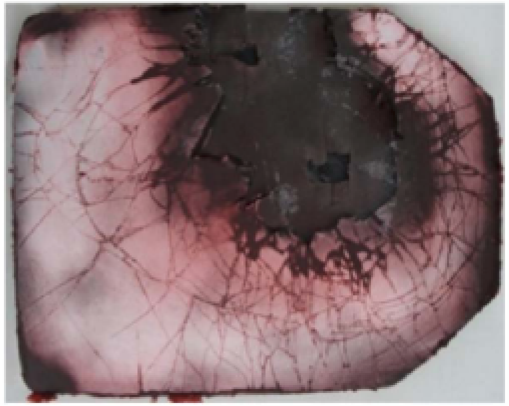
Low density, ρ = 2.52 g/cc, (~22% lower than SiC)

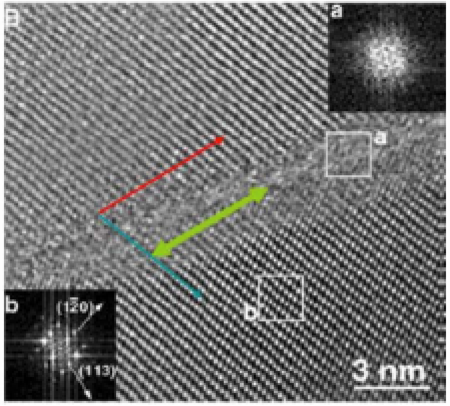
High hardness (Hv300) ~ 30 GPa; Low toughness ~ 3 MPa.√m

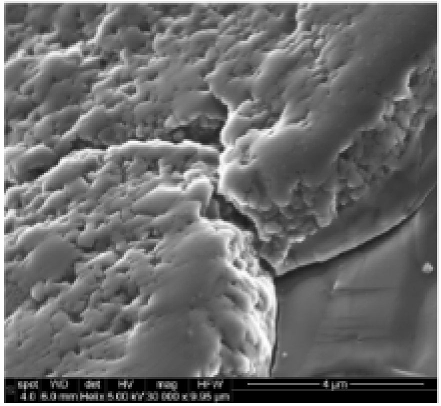
Material of choice for hard face of armor against **conventional small-arm threats**

Technology Gap and Opportunity

- Current commercial B_4C **cracks easily** leading to **poorer multi-hit performance**; also shows a **loss in single-hit performance for advanced small-arm and larger caliber threats possibly due to amorphization and shear localization**:



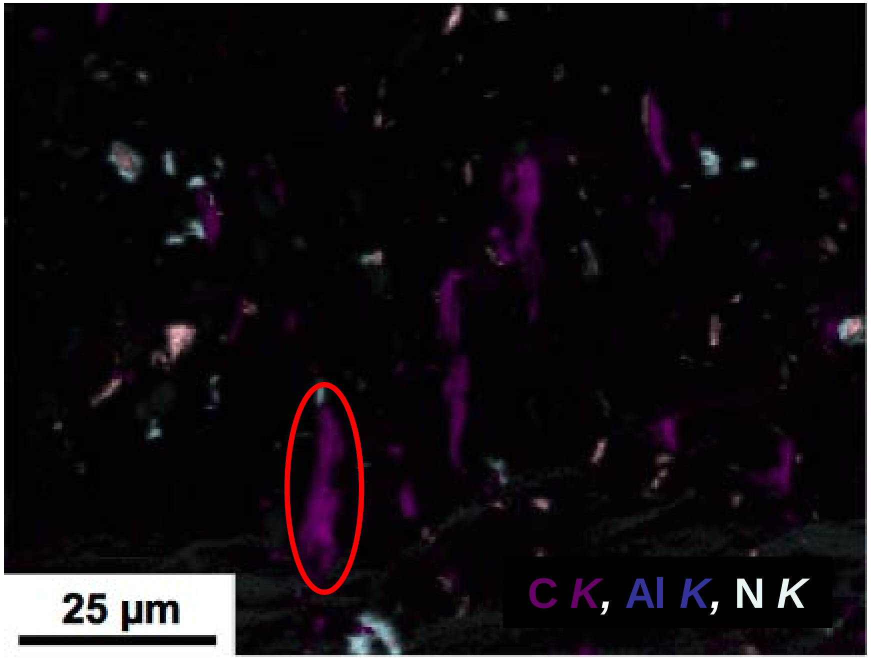


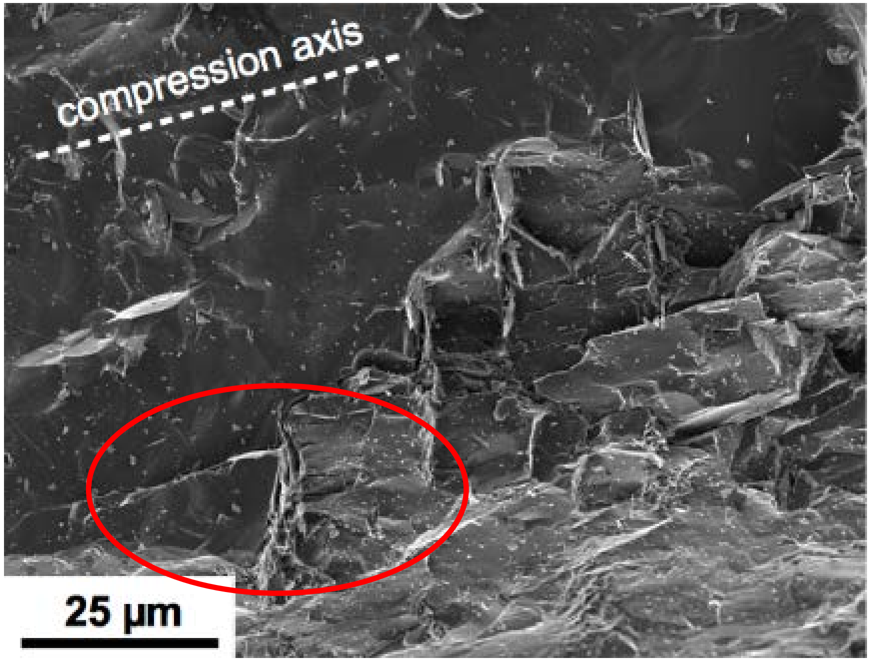


- **Performance gains** by **improving fracture toughness**, **quasi-plasticity (QP)**, and **suppressing shear localization** may be **significant** → **QP-B_4C**

How can we address these issues?

- Reduce or eliminate the impurities (free carbon, metallic, etc.)

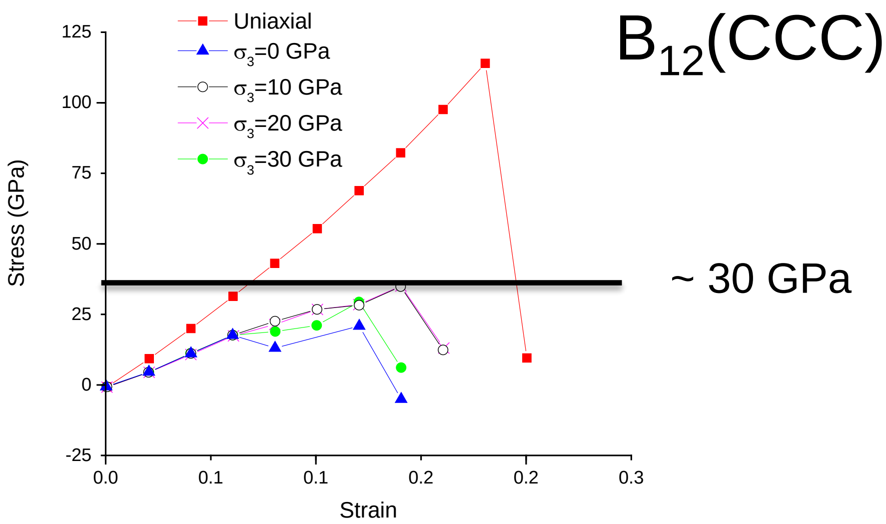


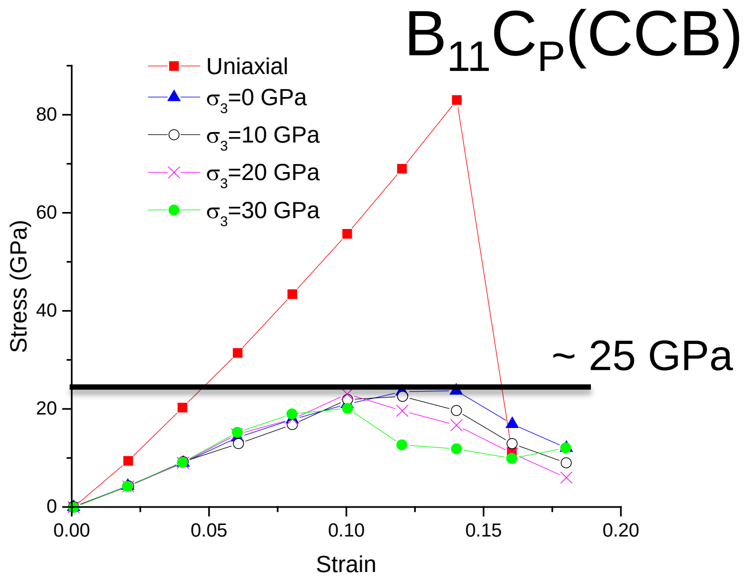


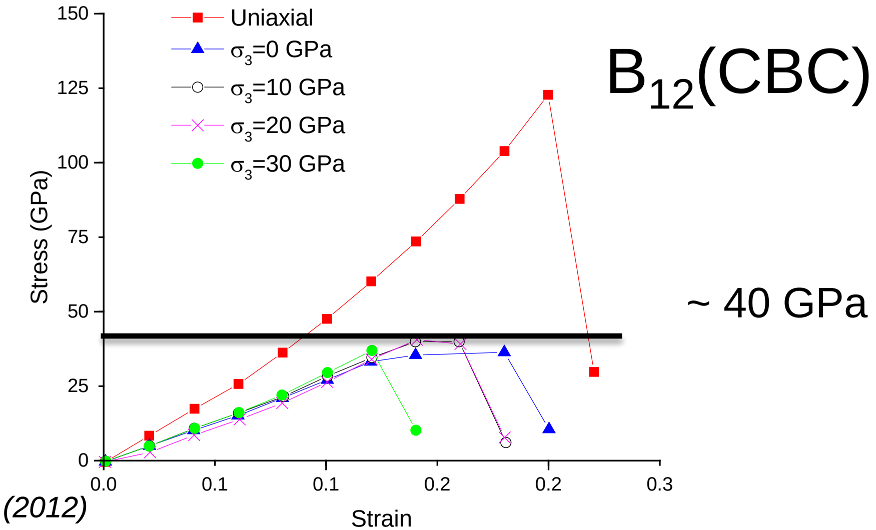
- Images from Lukasz Farbaniec (JHU)

How can we address these issues?

- Control the boron carbide stoichiometry



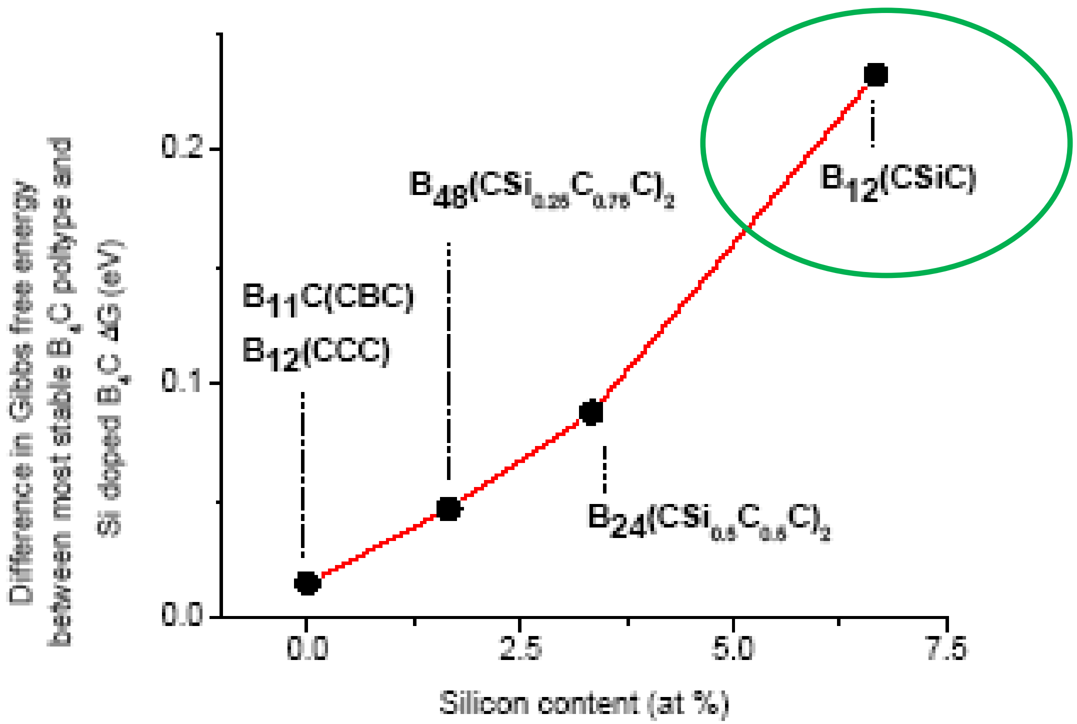




- D.E. Taylor, *J. Phys.: Condens. Matter, 24 (2012)*

How can we address these issues?

- Introduce different dopants into the boron carbide lattice



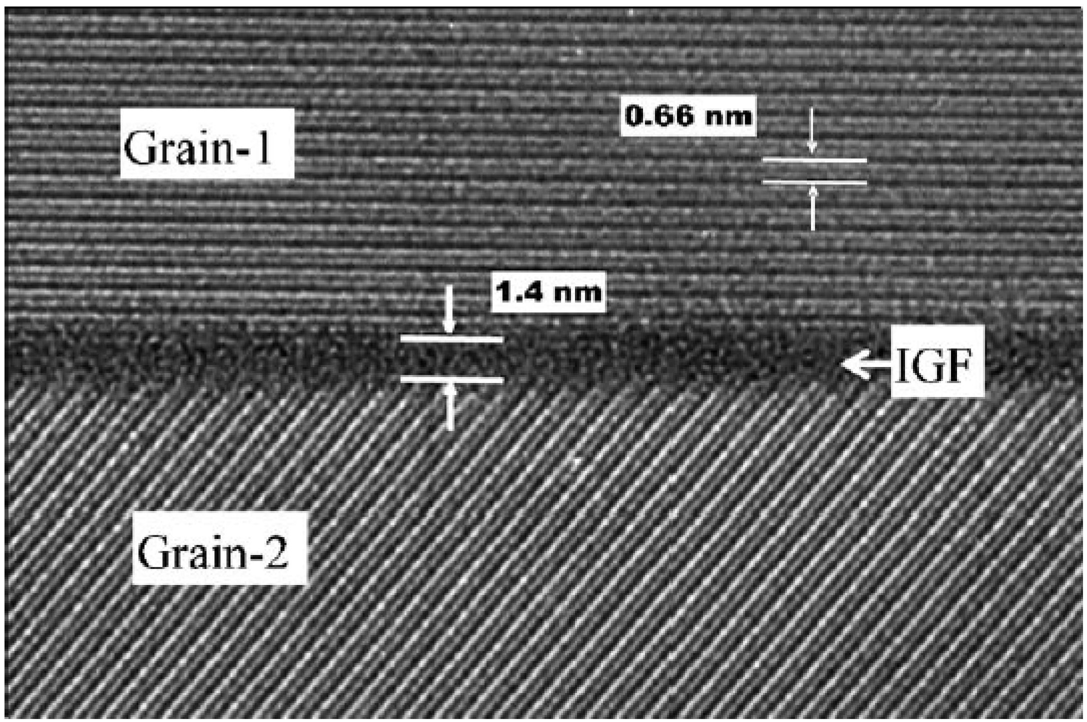
- Fanchini, MCOE Meeting Presentation, 2006

How can we address these issues?

- Process dense boron carbide with intergranular films

ntergranular
racture

Transgranu
fracture



- A. Subramanian, Mat. Sci. and Eng., 422(2006) 3-18

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Rapid Carbothermal Reduction

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO$$

$$\Delta G = +397 - 0.22\ T\ \text{kcal/mole}\ B_4C$$

- Reaction is endothermic up to 1542°C

- Boron oxide species are volatile,

$$B_2O_3 + C \rightarrow B_2O_2 + CO \qquad >1227^o\ C$$

- With sufficient heating rates, boron carbide can be synthesized via the following gas-solid reaction,

$$5C + 2B_2O_2(g) \rightarrow B_4C + 4CO$$

Experimental

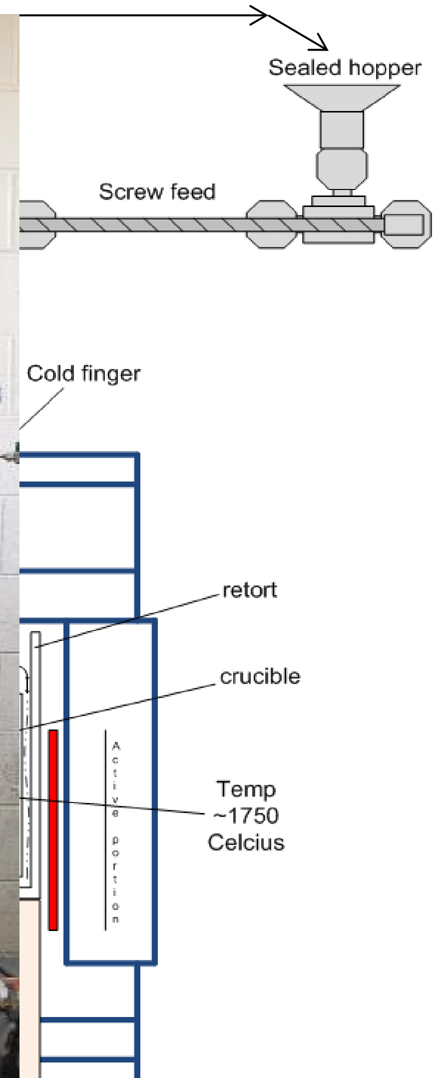
BORIC ACID
WATER
100°C

STI

MI

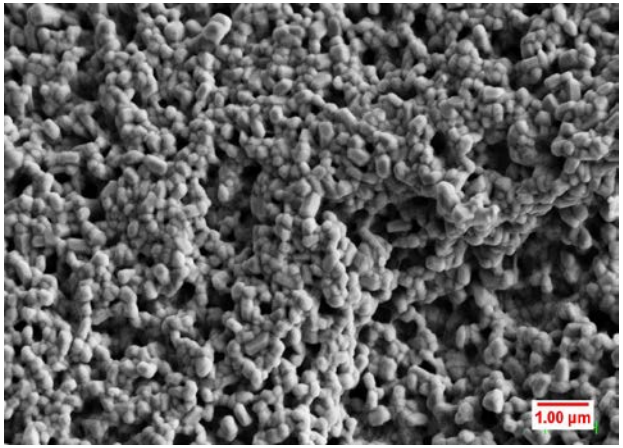
CA

MILLED TO
SIZ

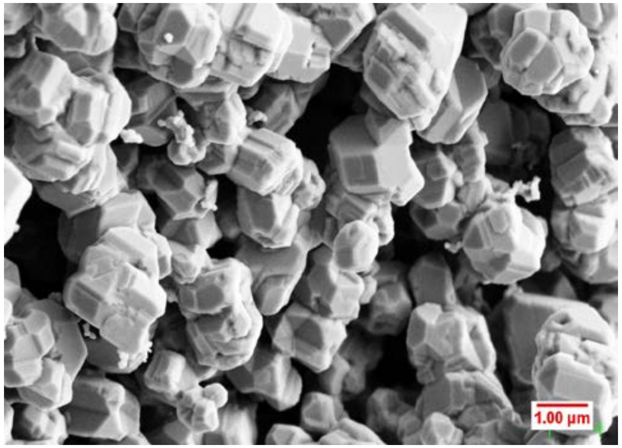


Rutgers Screw Fed Boron Carbide

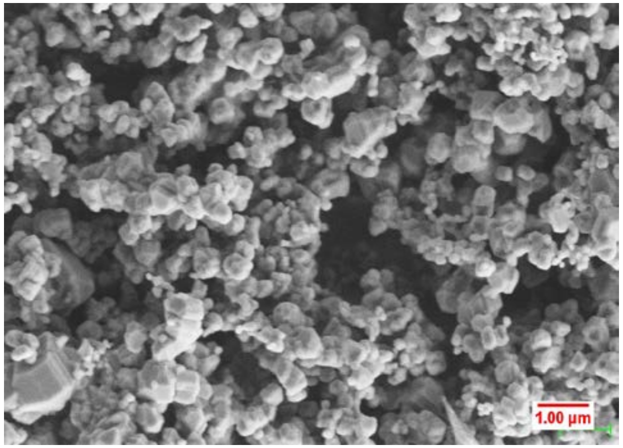
SF-4



SF-5



SF-6

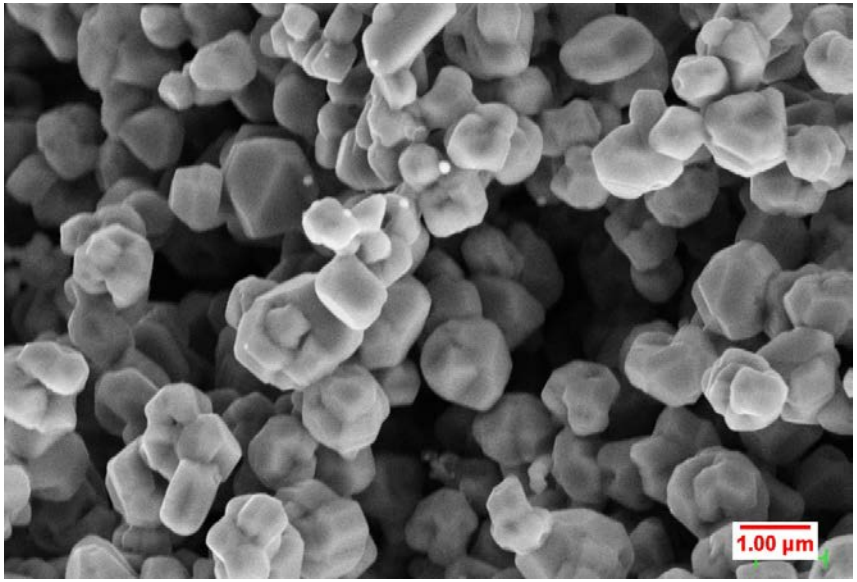


Name	Precursor	Temp. (˚C)	d_{90} (µm)	Free C(%)	Stoichiometry
R-SF1	30% ex LB	1800	1.00	6.00	4.10
R-SF2	10% ex CS	1800	0.30	8.50	3.86
R-SF3	0% ex CS	1800	0.40	4.00	3.90
R-SF4	0% ex CS	1850	0.30	0.00	4.09
R-SF5	50% ex LB	1850	0.90	0.00	4.23
R-SF6	50% ex VC	1850	0.50	0.00	4.22
R-SF7	50% ex VC	1825	0.50	0.00	4.19

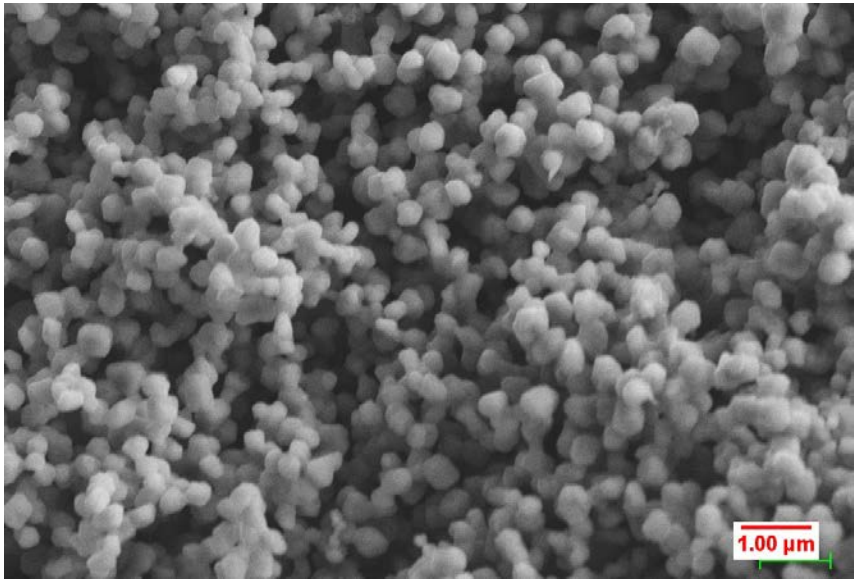
CS- Cornstarch   LB- Lamp Black   VC- Vulcan XC-72

Rutgers SF-9 and SF-10

SF-9



SF-10

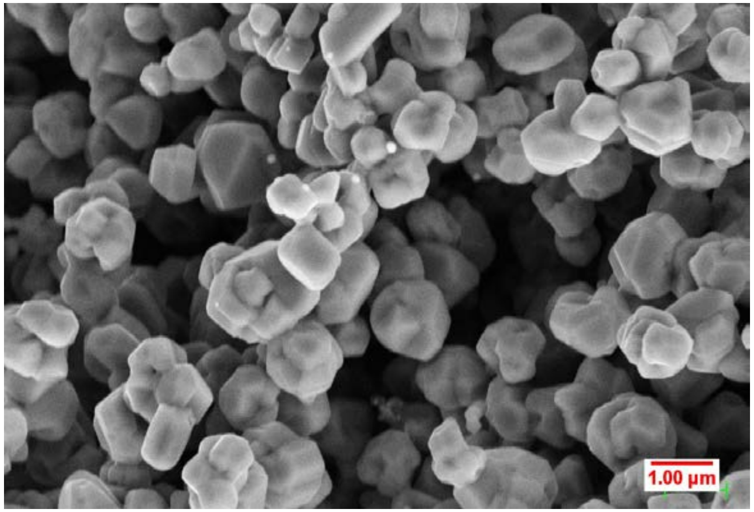


Name	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)	Free C (%)	C (%)	O (%)	N (%)	B(%)	B/C ratio
R-SR 9	0.20	0.50	0.90	0.40	21.15	0.44	0.16	77.87	4.17
R-SF10	0.10	0.20	0.45	0.10	20.50	0.47	0.01	78.93	4.28

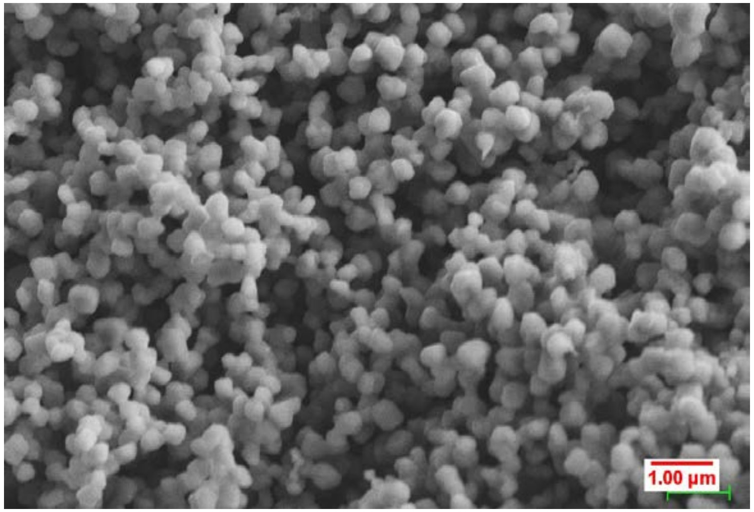
- Each powder was synthesized at 1825°C for approx. 60 min

Rutgers vs. Commercial

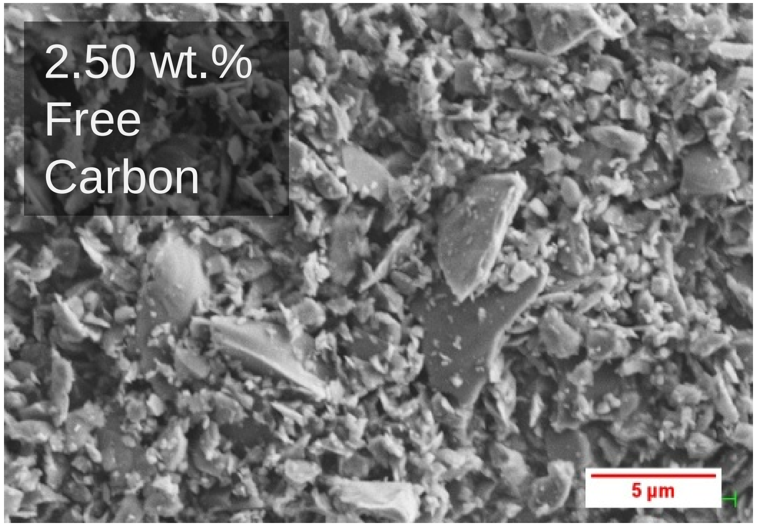
SF-9



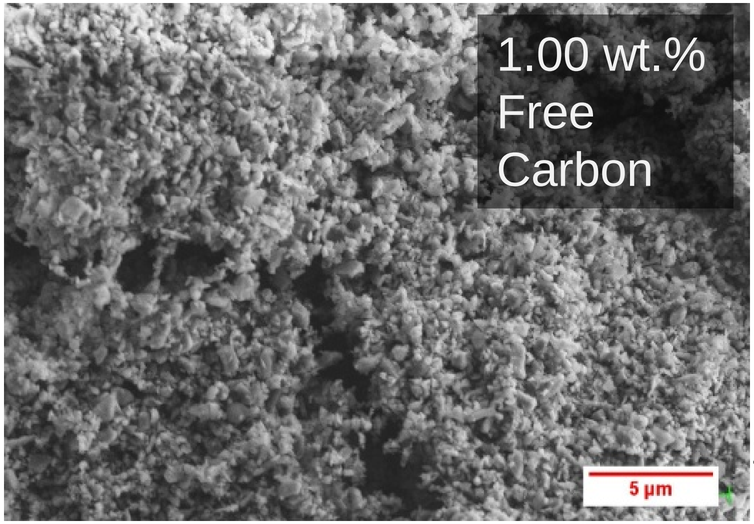
SF-10



UK

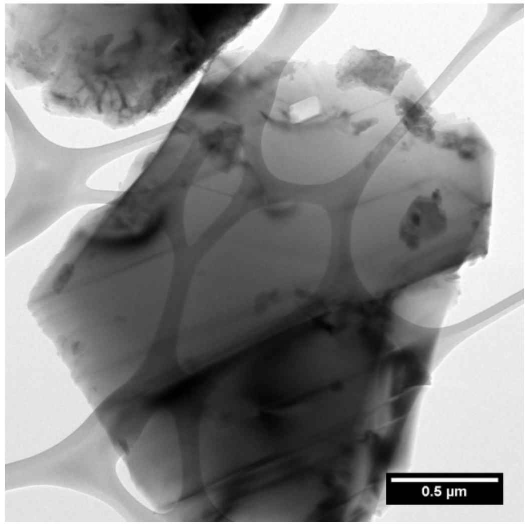


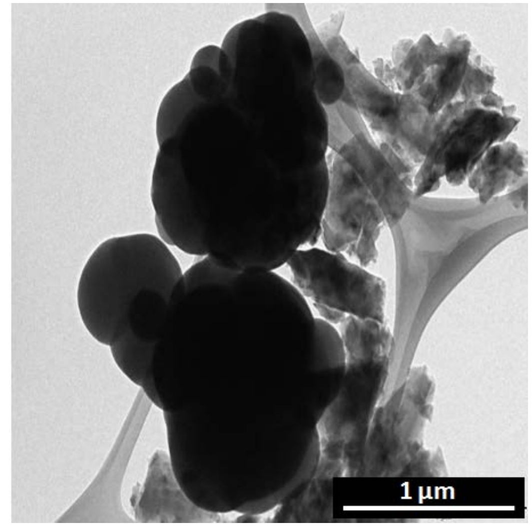
Starck



Rutgers vs. Commercial

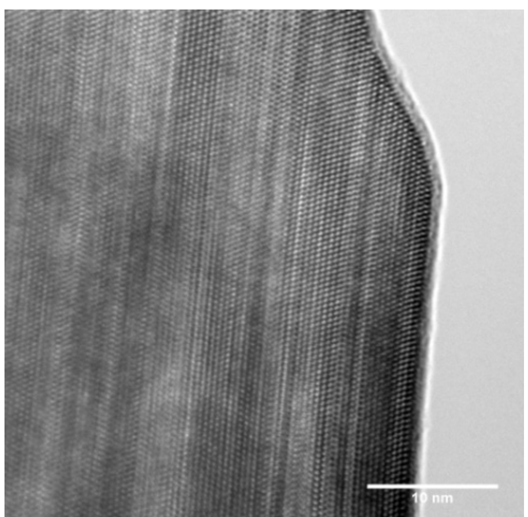
UK

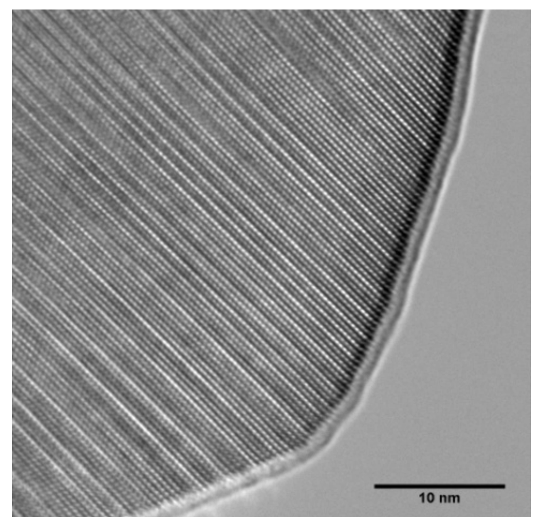




Starck

SF- 9
HRTEM



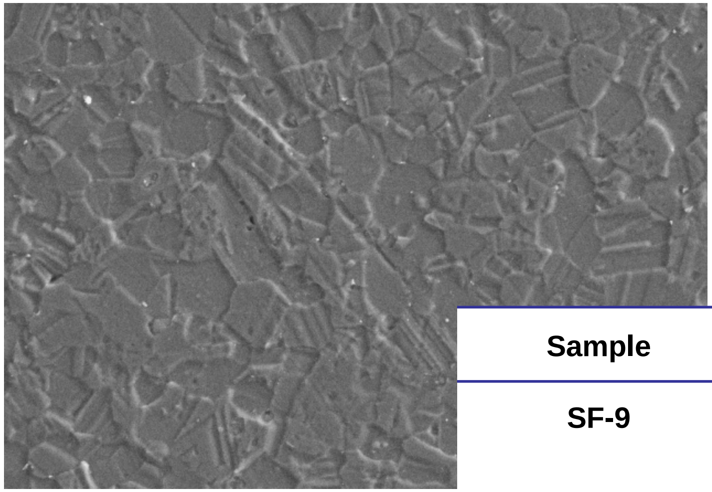


SF- 10
HRTEM

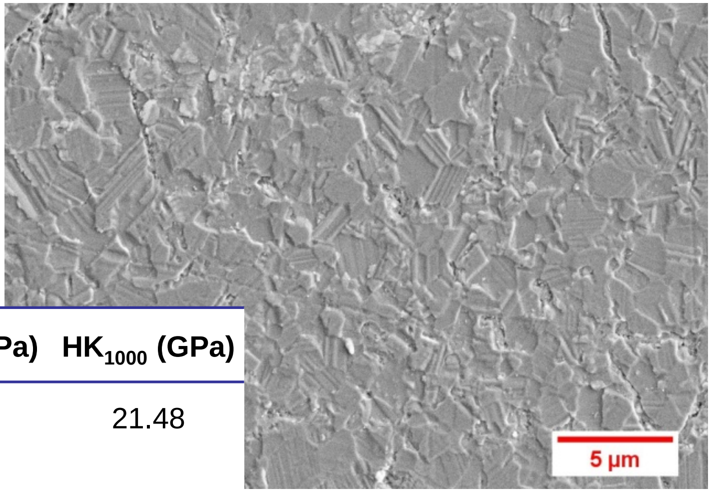
TEM images from
Kelvin Xie (JHU)

Dense Rutgers Boron Carbide

SF-9

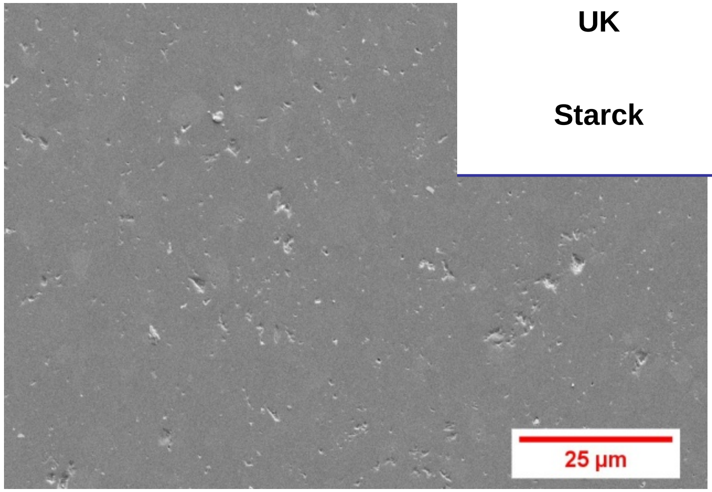


SF-10

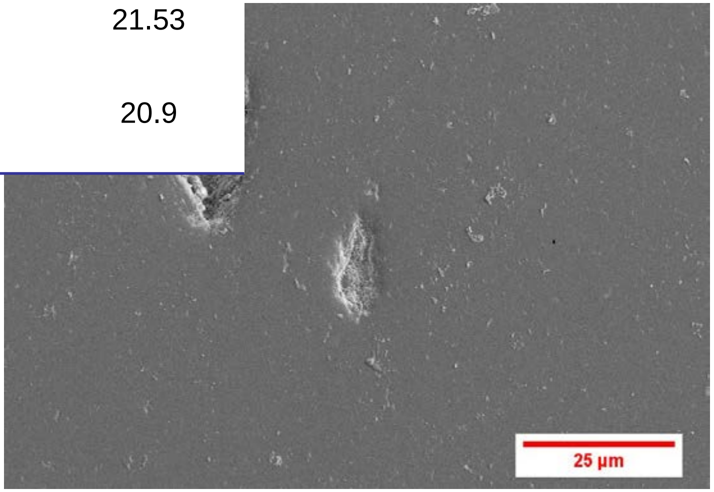


Sample	HK_{100} (GPa)	HK_{1000} (GPa)
SF-9	32.28	21.48
SF-10	32.95	21.8
UK	30.43	21.53
Starck	29.67	20.9

UK

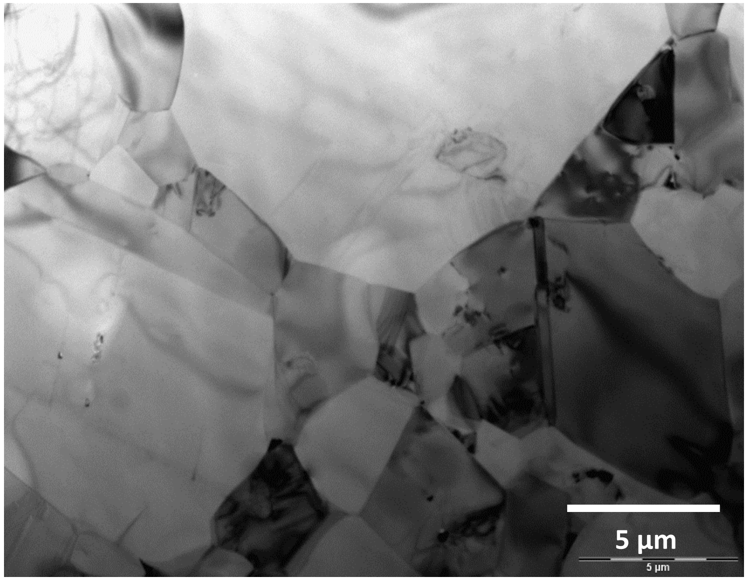


Starck

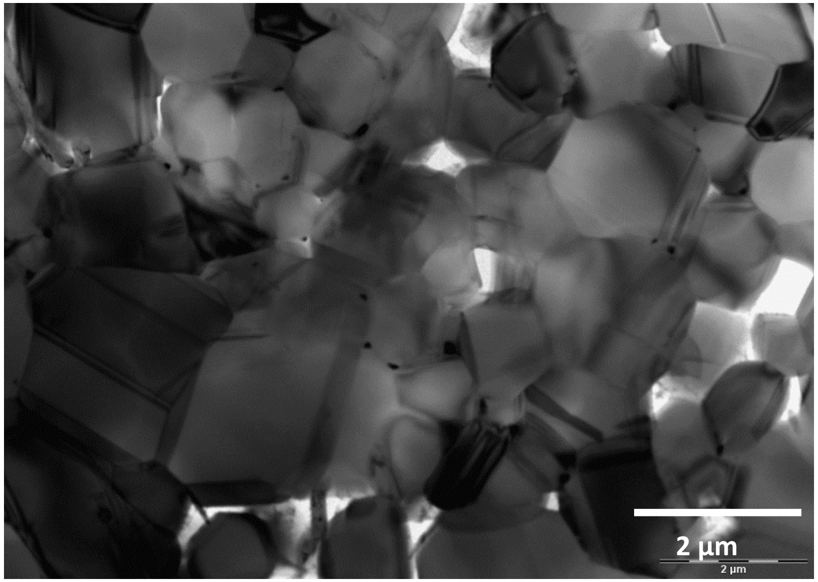


Samples were held at 1900°C for 5 min. under a 50 MPa load

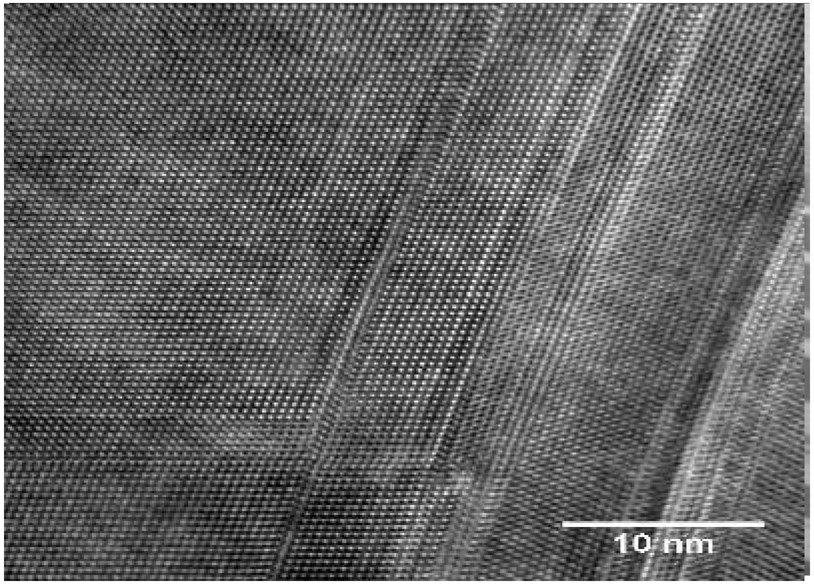
UK



Starck



SF-10



TEM images from Kelvin Xie (JHU)

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Experimental

- Commercial and rapid carbothermally reduced powders were mixed with various amounts of amorphous boron:

Sample	Starting Powder	Boron Carbide wt.%	Boron wt.%	Expected B/C Ratio
COM-35	Starck HD20	65	35	$B_{6.21}C$
COM-20	Starck HD20	80	20	$B_{4.81}C$
COM-0	Starck HD20	100	0	$B_{3.9}C$*
RCR-35	RCR	65	35	$B_{6.80}C$
RCR-25	RCR	75	25	$B_{5.74}C$
RCR-15	RCR	85	15	$B_{4.94}C$
RCR-0	RCR	100	0	$B_{4.03}C$*

- Mixed in high energy ball mill:
  - 10 min
  - SiC media
  - ZrO_2 Jar
- Spark Plasma Sintered:
  - 1900°C
  - 5 minutes
  - 50 MPa uniaxial load

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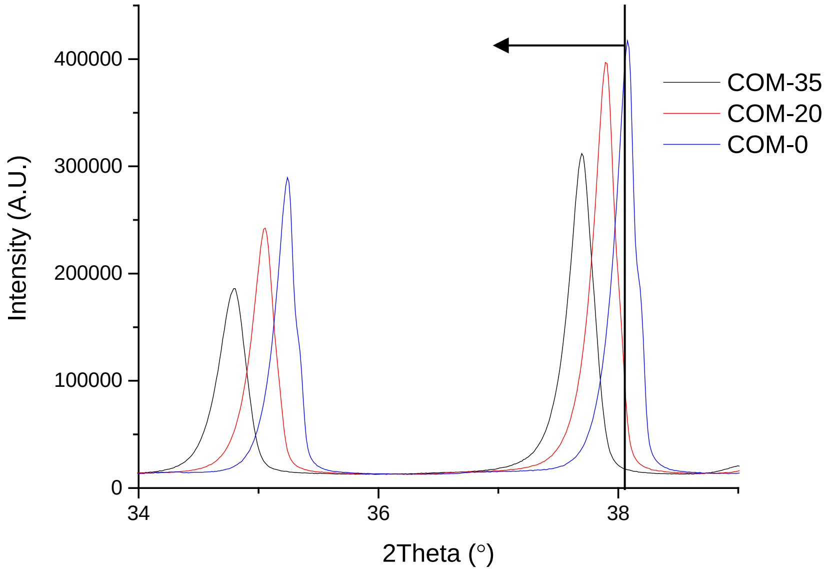
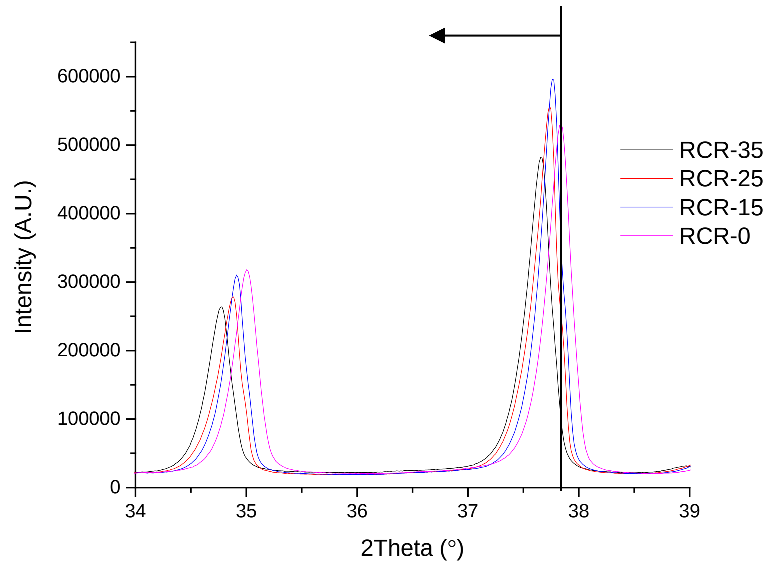
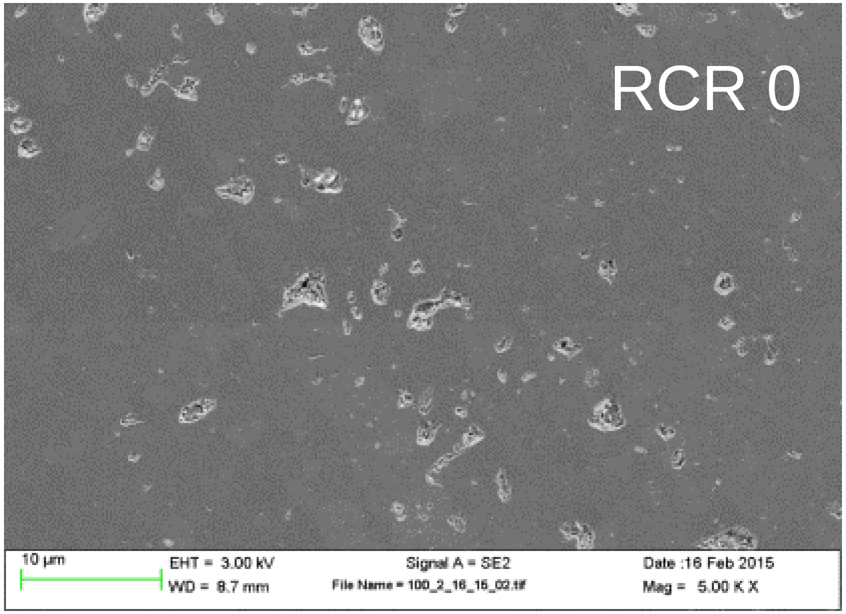
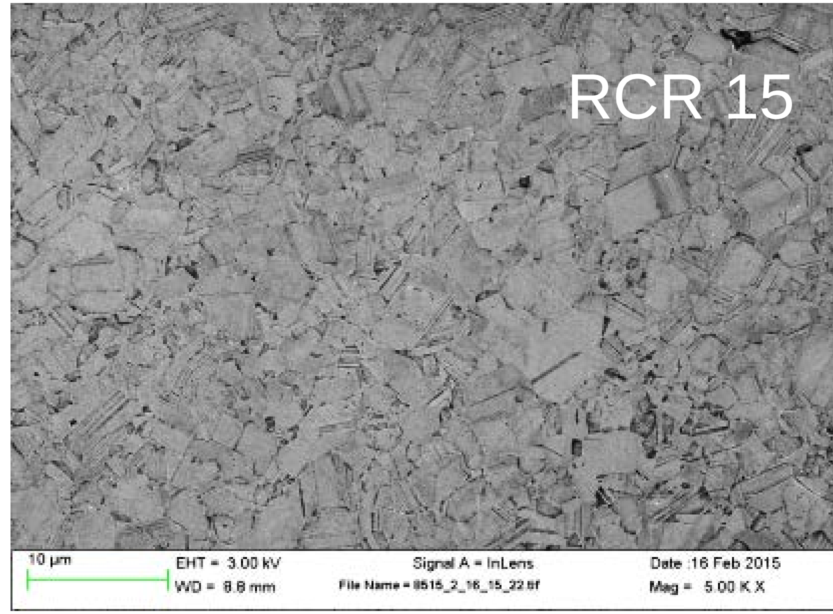
X-Ray Diffraction

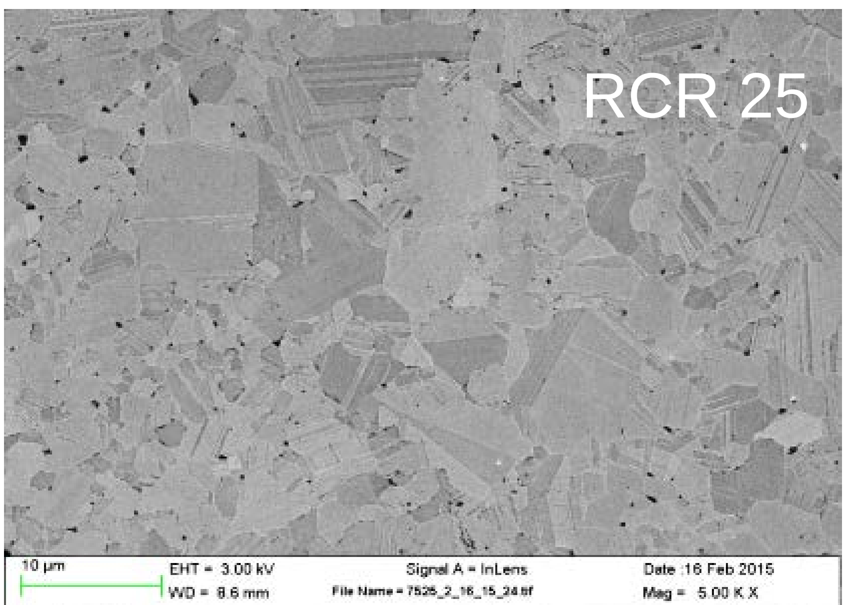


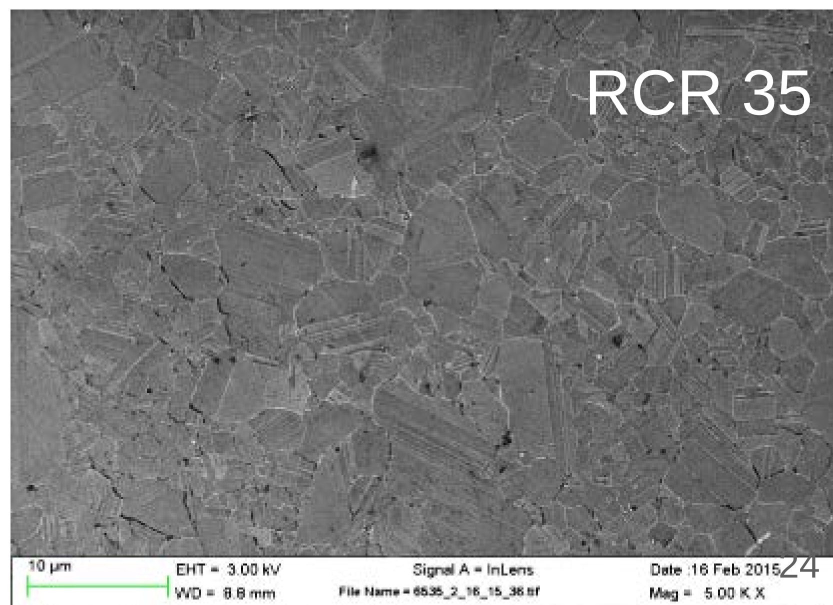


Sample	a (Å)	c (Å)	C Content (at. %) (Based on a)	C Content (at. %) (Based on c)	B/C Ratio (Based on a)	Expected B/C Ratio
COM-35 Face 1	5.6197	12.1625	14.50	13.50	$B_{5.89}C$	$B_{6.21}C$
COM-20 Face 1	5.6031	12.0937	18.70	18.30	$B_{4.35}C$	$B_{4.81}C$
COM-0 Face 1	5.5999	12.0780	19.59	19.38	$B_{4.10}C$	$B_{3.9}C$
RCR-35 Face 1	5.6265	12.1550	12.59	14.04	$B_{6.95}C$	$B_{6.80}C$
RCR-25 Face 1	5.6133	12.1276	16.06	15.94	$B_{5.23}C$	$B_{5.74}C$
RCR-15 Face 1	5.6036	12.0946	18.61	18.23	$B_{4.37}C$	$B_{4.94}C$
RCR-0 Face 1	5.6000	12.0759	19.56	19.53	$B_{4.11}C$	$B_{4.03}C$


RCR 0
10 µm
EHT = 3.00 kV
WD = 8.7 mm
Signal A = SE2
File Name = 100_2_16_15_02.tif
Date :16 Feb 2015
Mag = 5.00 K X

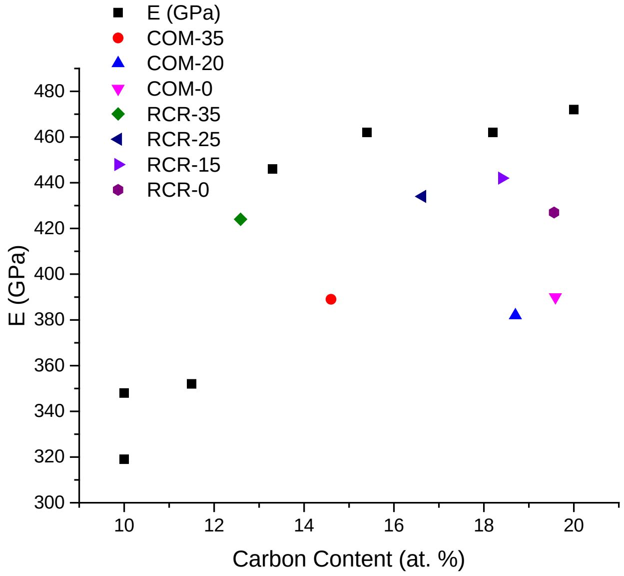

RCR 15
10 µm
EHT = 3.00 kV
WD = 8.8 mm
Signal A = InLens
Date :16 Feb 2015
Mag = 5.00 K X


RCR 25
10 µm
EHT = 3.00 kV
WD = 8.6 mm
Signal A = InLens
Date :16 Feb 2015
Mag = 5.00 K X

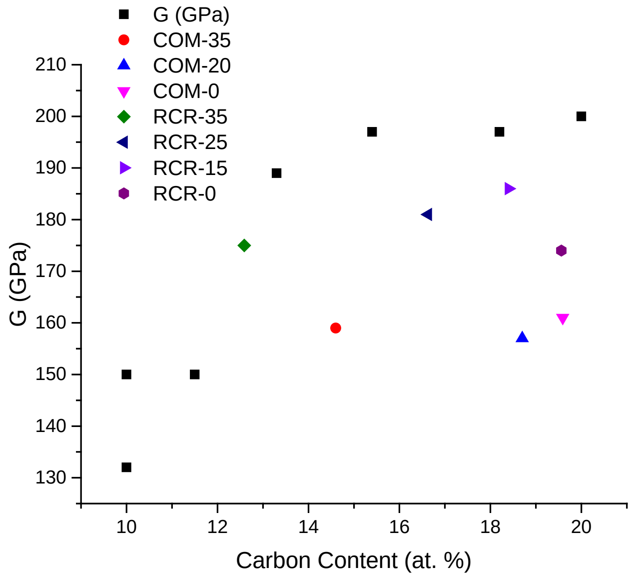

RCR 35
10 µm
EHT = 3.00 kV
WD = 8.8 mm
Signal A = InLens
Date :16 Feb 2015
Mag = 5.00 K X

Young's, Shear and Bulk Modulus

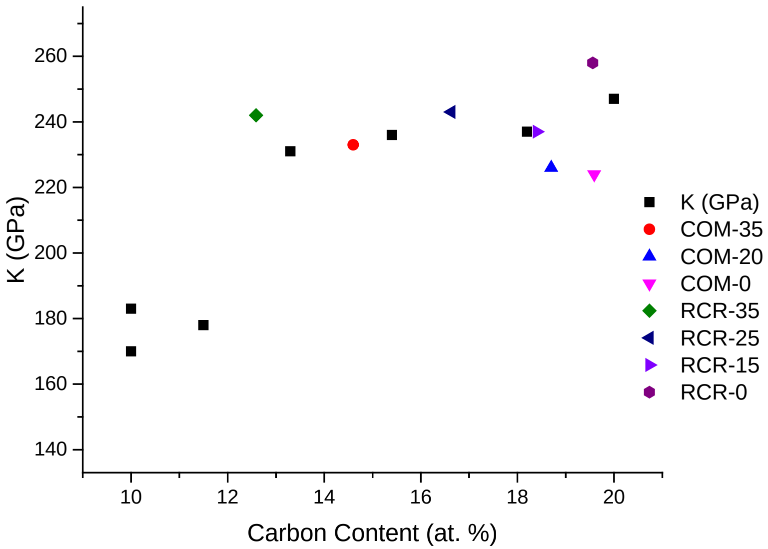
Young's Modulus



Shear Modulus

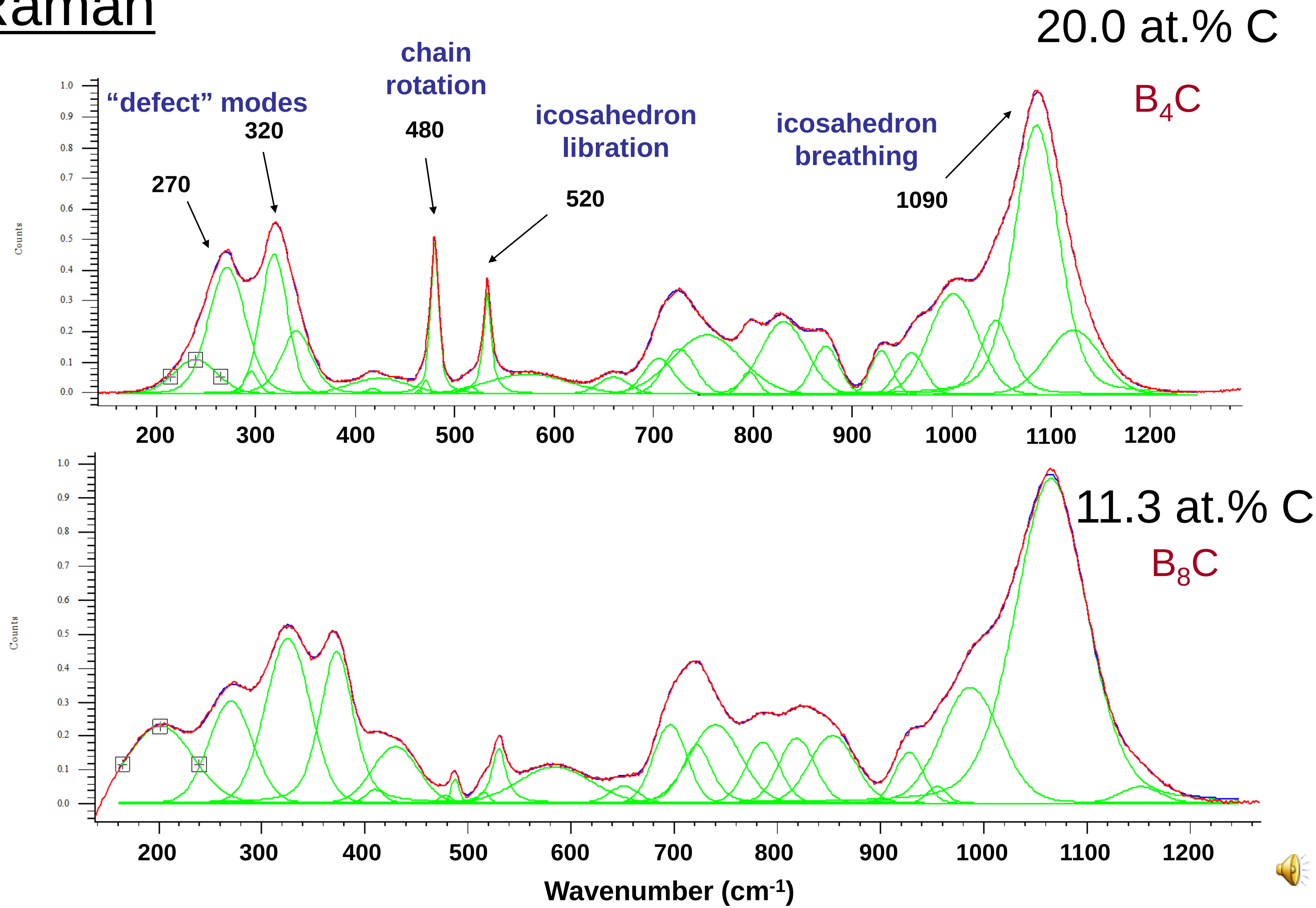


Bulk Modulus



- J.H. Gieske, T.L. Aselage, David Emin, "Elastic Properties of Boron Carbides"

Raman



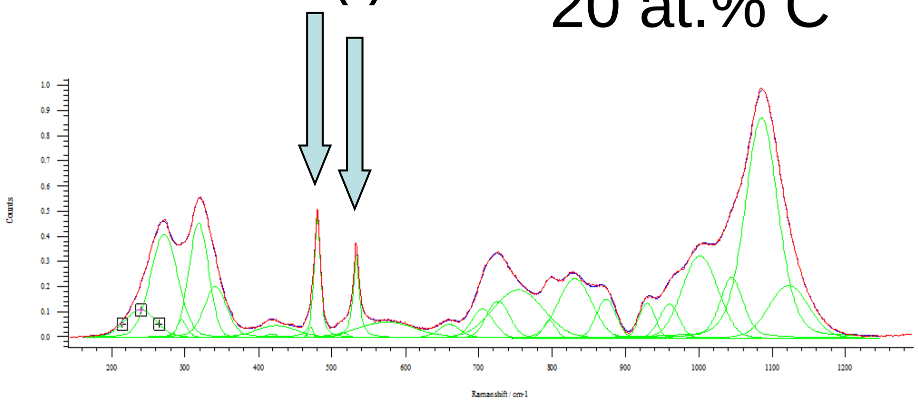
20.0 at.% C
B_4C
"defect" modes
chain rotation
icosahedron libration
icosahedron breathing
270
320
480
520
1090
Counts
200
300
400
500
600
700
800
900
1000
1100
1200
11.3 at.% C
B_8C
Wavenumber (cm^{-1})

Raman Reference Material

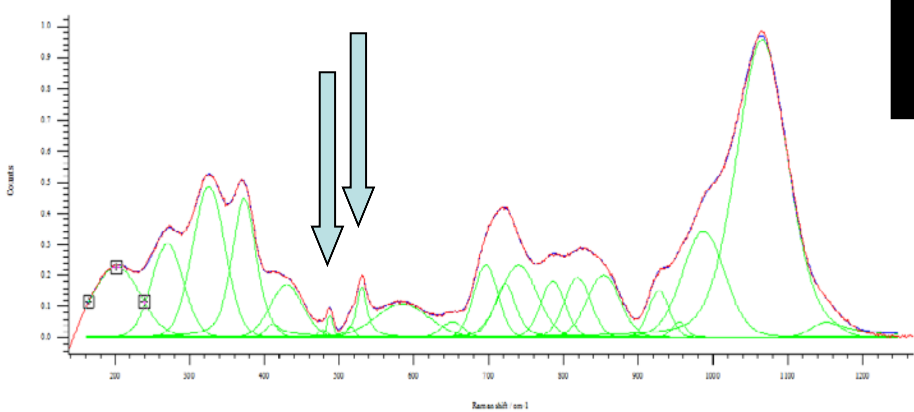
(1)

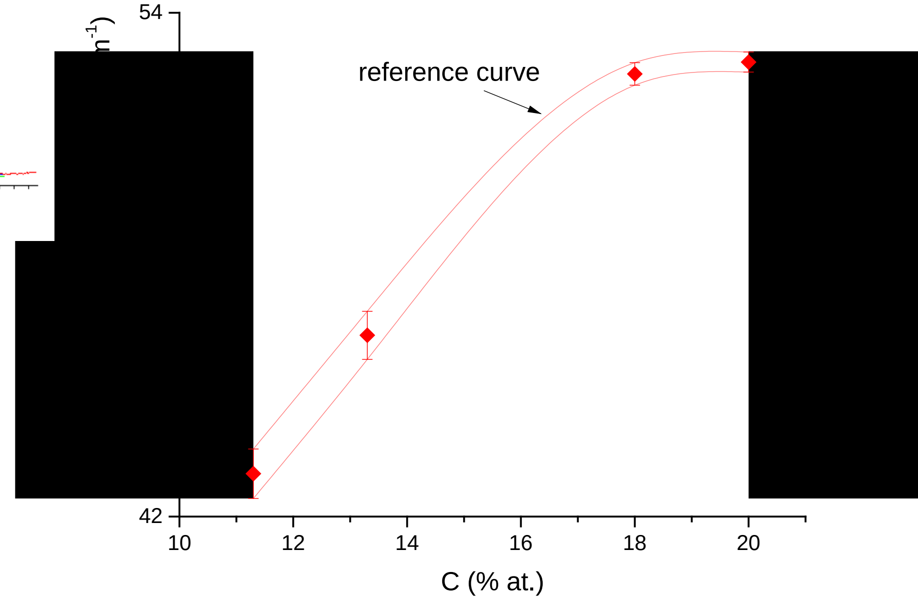
(2)

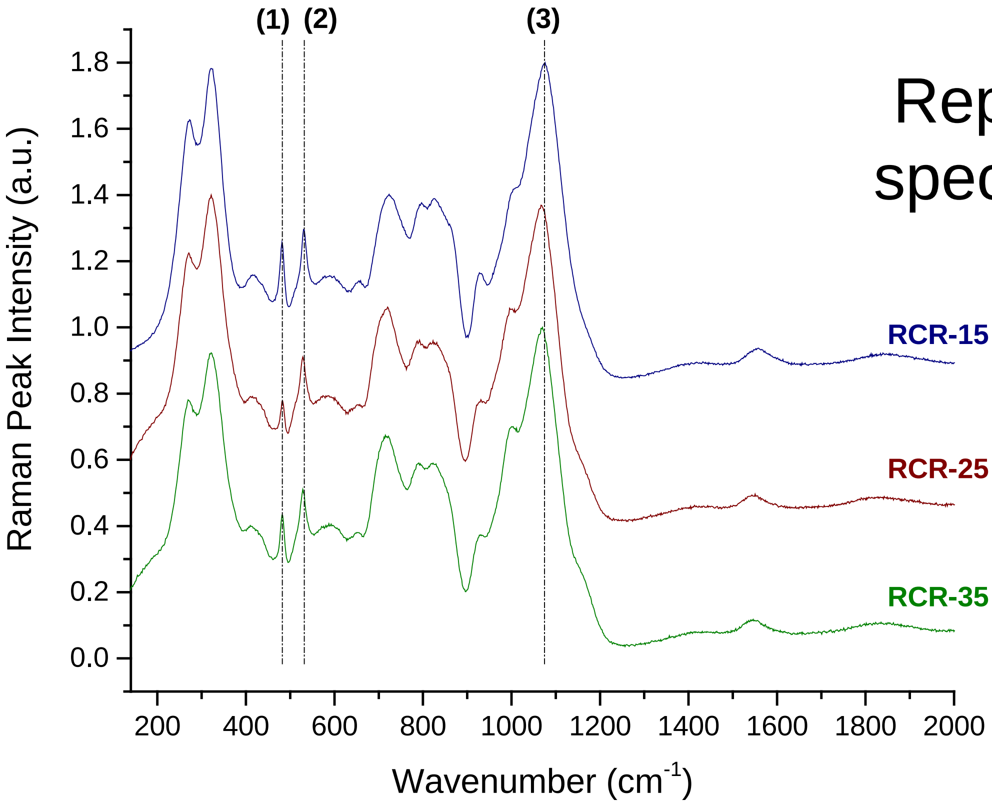
20 at.% C



11.3 at.% C

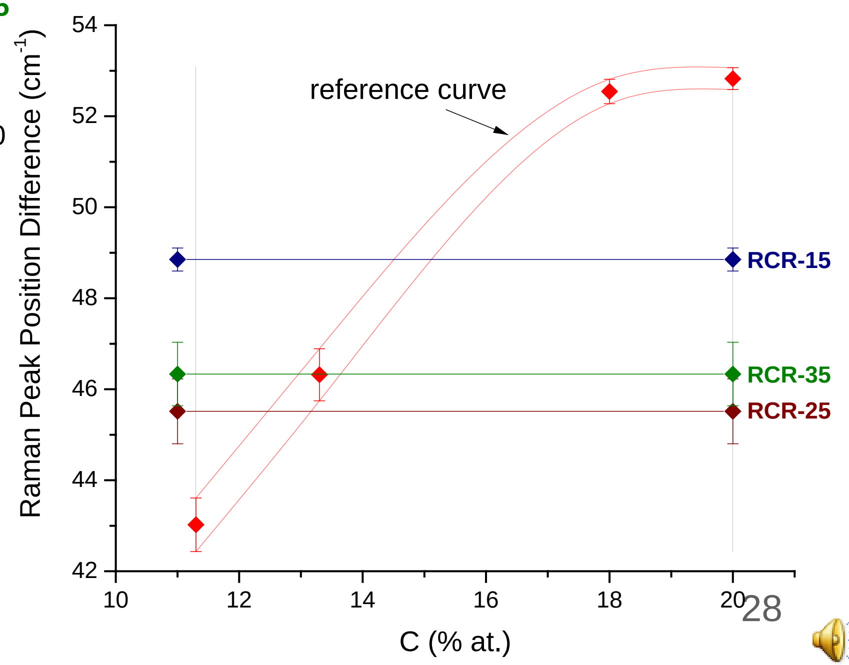


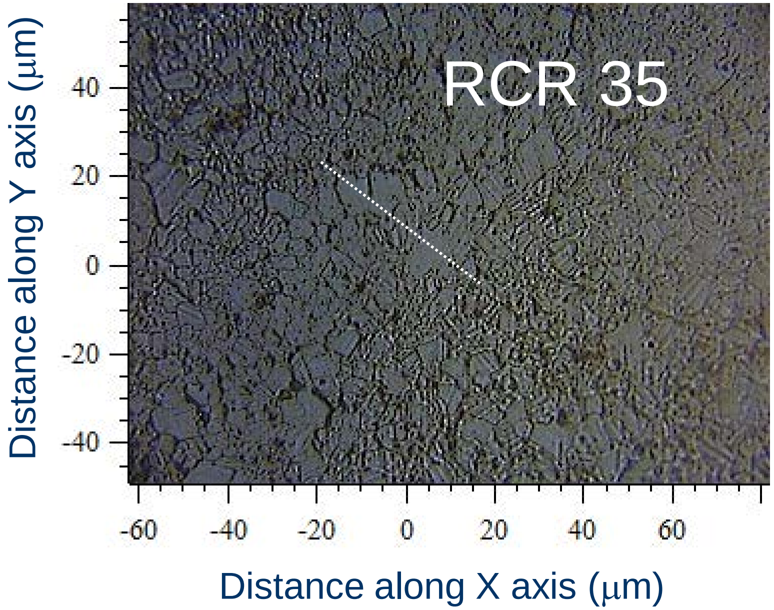




Representative Raman spectra of RCR samples

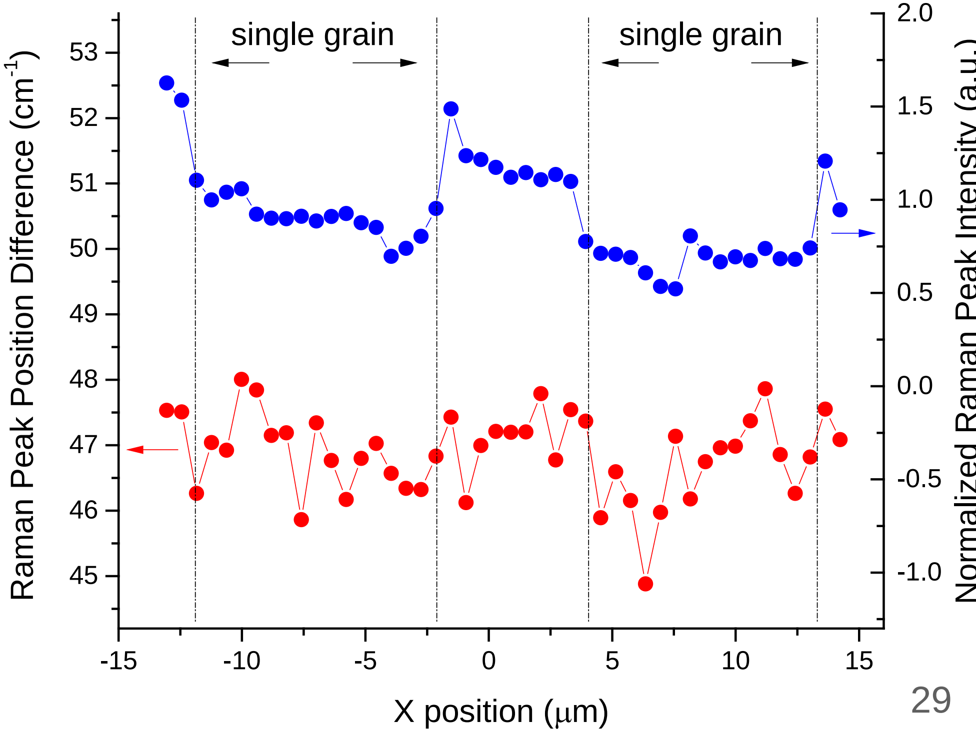
Peak separation fit to the reference curve





Optical microscope image of Raman line scan.

Raman peak intensity (Blue) and peak position difference (Red) measured for the above line scan.



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Outline

- Background
- Synthesis and Processing of Carbon Free Boron Carbide
- Processing of Boron Rich Boron Carbide
- Silicon Doping of Boron Carbide
- Scaling Up
- Conclusions

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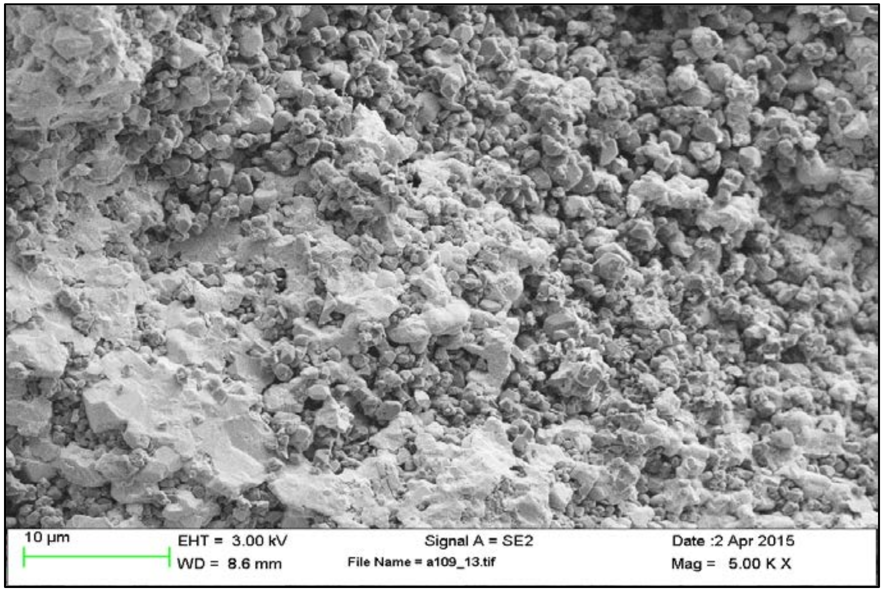
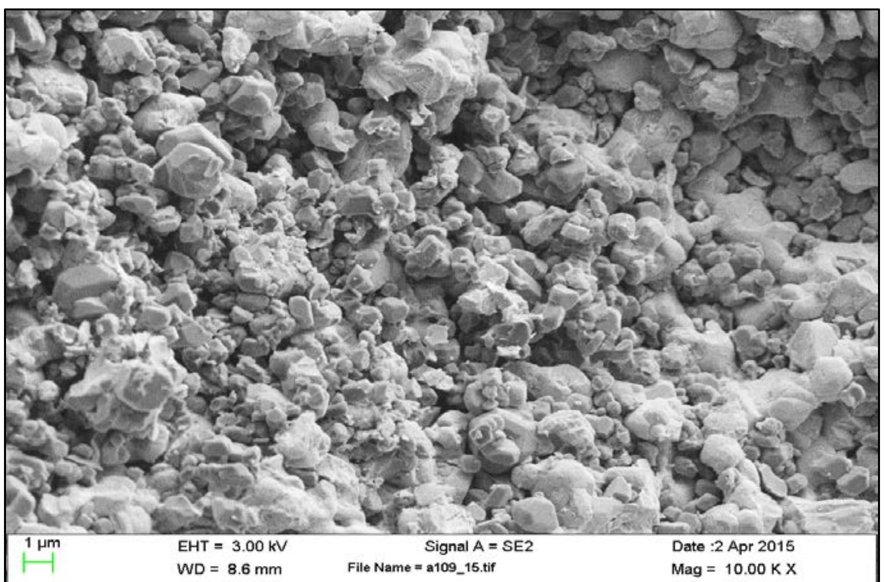
Experimental

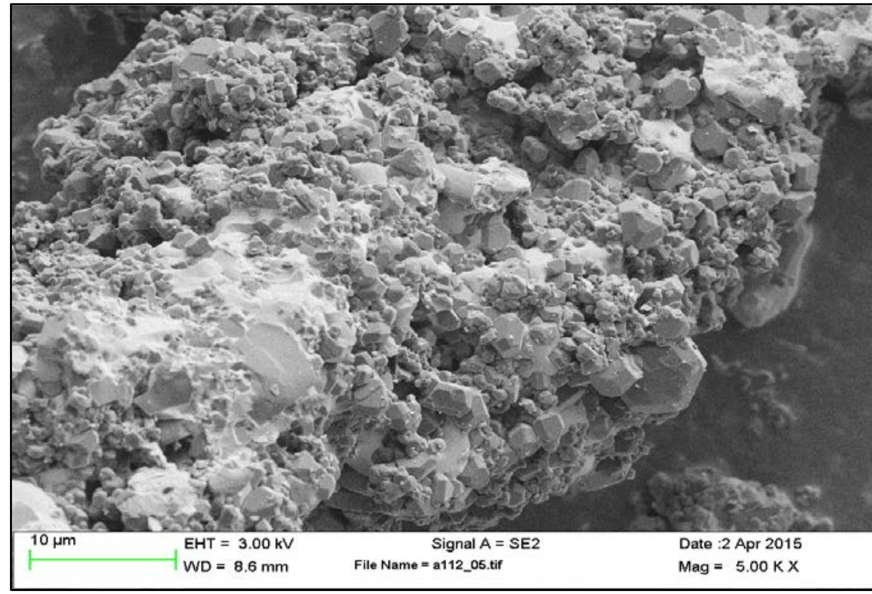
- Boron carbide (Starck HD20), amorphous boron (Starck Grade 1) and silicon were dry mixed via high energy ball milling.
- Samples were heated to 1700°C in an inert atmosphere for 1 hour.
- The resulting material was subsequently crushed and analyzed using XRD, SEM and Raman spectroscopy.
- Sample 1 was heated in a graphite crucible
- Sample 2 was heated in a BN coated graphite crucible

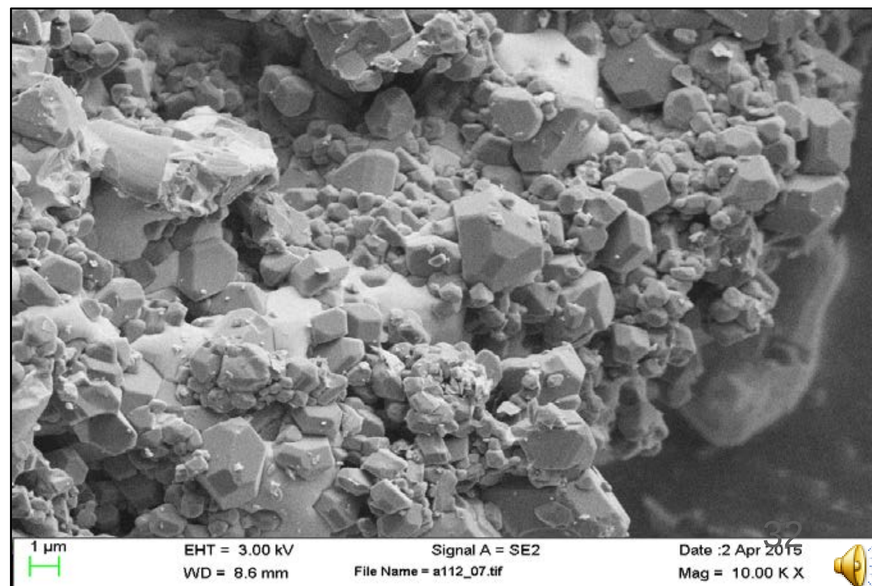
Sample 1



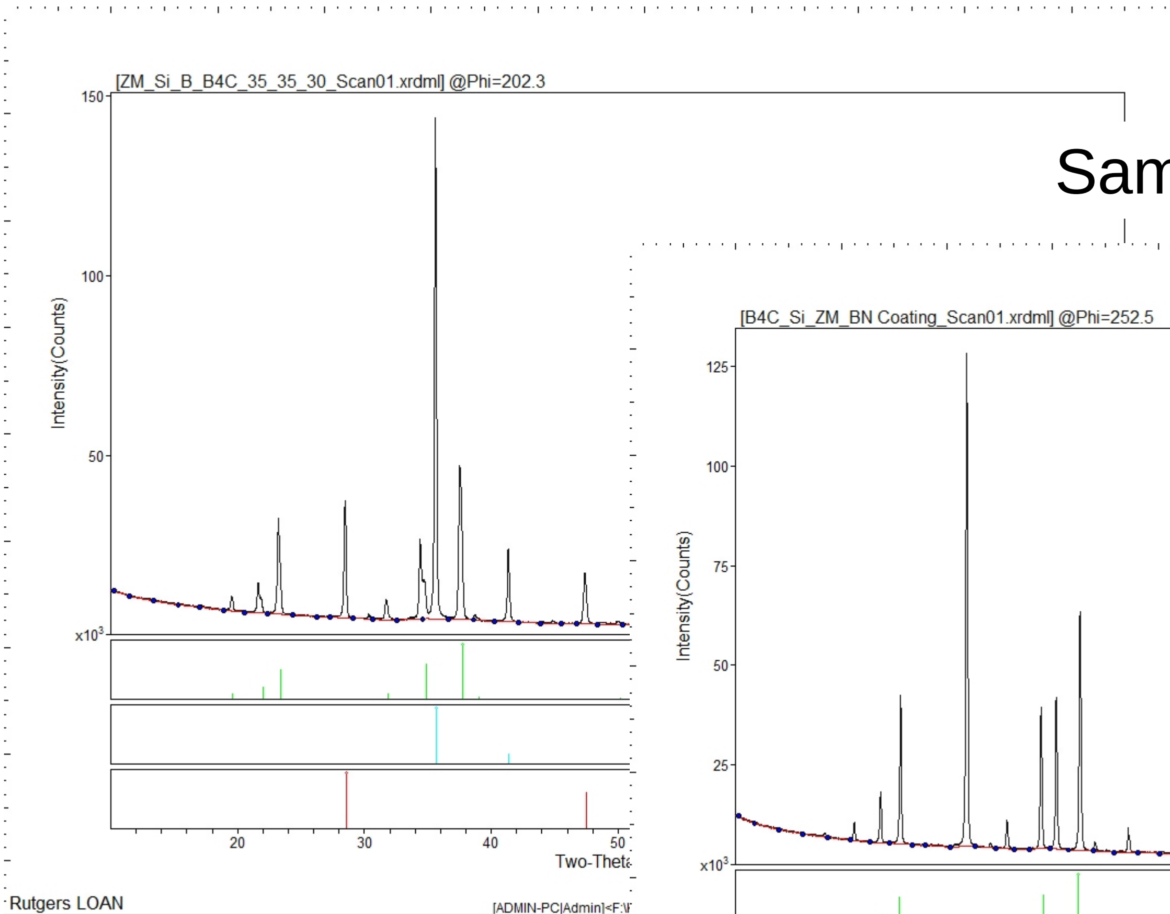


Sample 2

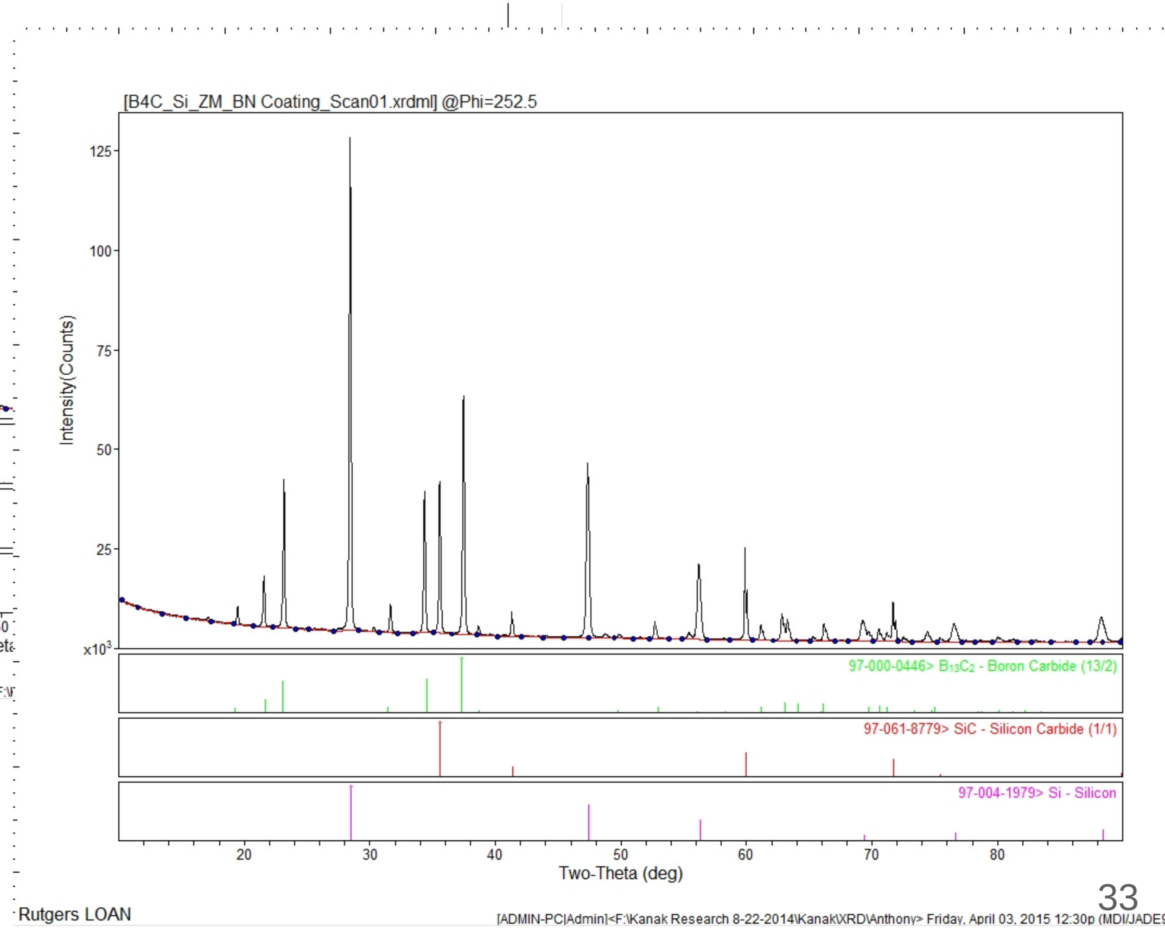




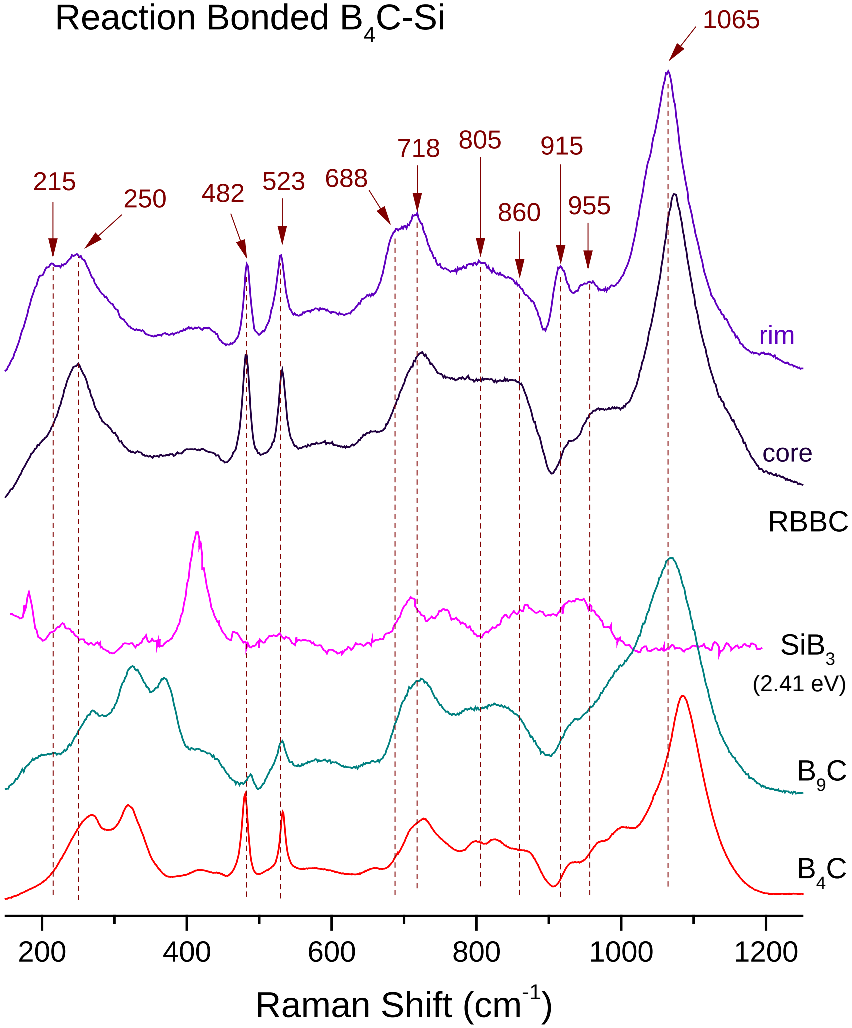
Sample 1



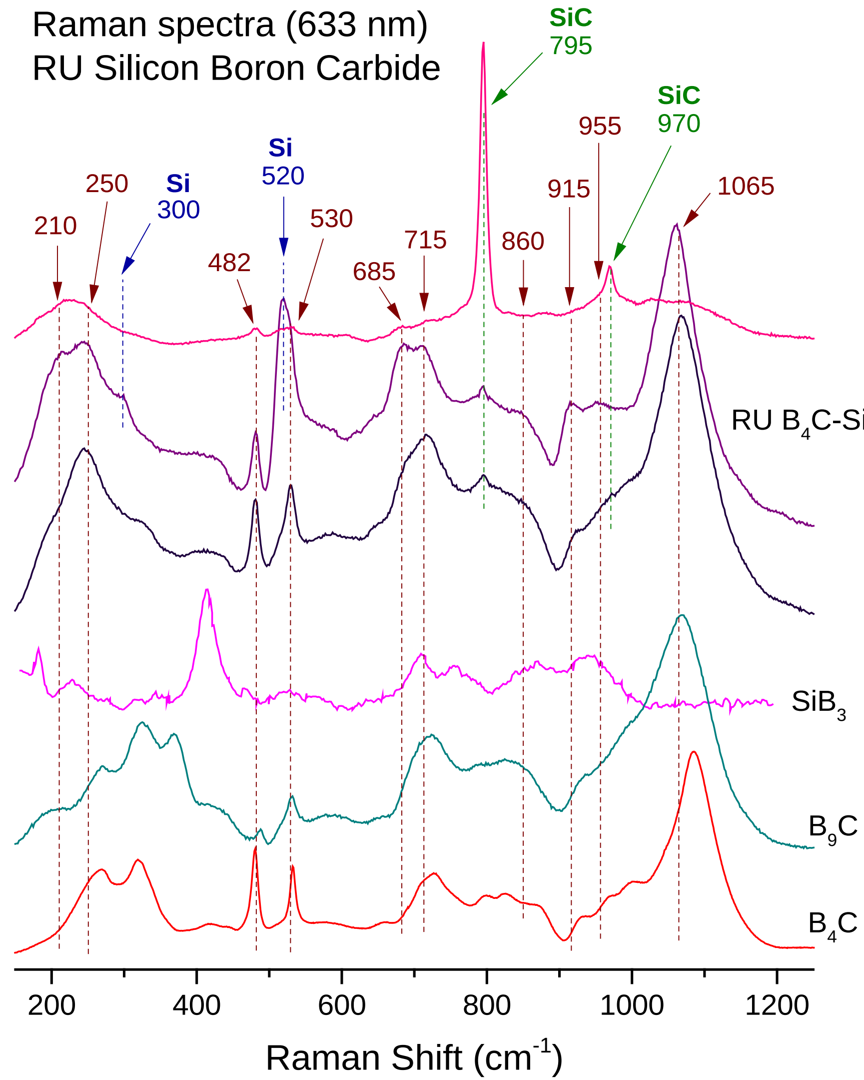
Sample 2



Raman spectra (633 nm)
Reaction Bonded B_4C-Si



Raman spectra (633 nm)
RU Silicon Boron Carbide



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Scaling Up

- Scaling up the production of boron carbide using rapid carbothermal reduction is the next step.

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Conclusions

- By employing rapid carbothermal reduction it is possible to synthesize highly pure submicron boron carbide with little to no detectable free carbon.
- Using pressure assisted sintering, RCR powders can be densified to 100% theoretical densities at 1900°C with short hold times.
- TEM images show microstructures that are both impurity free and highly twinned.
- The stoichiometry of dense boron carbide can be controlled by adding in varying amounts of amorphous boron during sintering.
- Preliminary results show that incorporation of Si into the boron carbide lattice is possible.

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