2021 DOE/FE Spring R&D Project Review Meeting

Ceramic-based Ultra-High-Temperature Thermocouples in Harsh Environments

DE-FOA-0002193

Dr. Yucheng Lan[1], Dr. Maohong Fan[2], Dr. Hertanto Adidharm[2]

MORGAN STATE UNIVERSITY

[1] Department of Physics and Engineering, Morgan State University

UNIVERSITY OF WYOMING

[2] Department of Chemical Engineering, University of Wyoming

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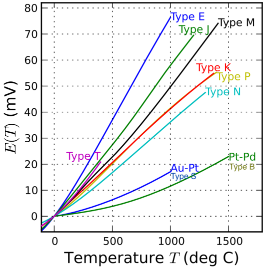
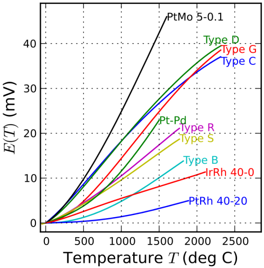
NATIONAL ENERGY TECHNOLOGY

U.S. DEPARTMENT OF ENERGY

Background: Thermocouples





Type	Combination*	T
E	chromel – constantan	-50 – 740
J	Fe – constantan	-40 - 750
K	chromel – alumel	-200 - 1350
M	82%Ni / 18%Mo – 99.2%Ni / 0.8%Co	1400
N	Nicrosil / Nisil	-270 – 1300
T	copper – constantan	-200 – 350

*: by weight. T: Temperature range ($^\circ\mathrm{C}$).

Type	Combination*	T
B	70%Pt / 30%Rh – 94%Pt / 6%Rh	50 - 1820
R	87%Pt / 13%Rh – Pt	0 - 1600
S	90%Pt / 10%Rh – Pt	630 - 1600
C	95%W/5%Re – 74%W/26%Re	2329
D	97%W/3%Re – 75%W/25%Re	2490
G	W – 74%W/26%Re	2,300
P	55%Pd/31%Pt/14%Au – 65%Au/35%Pd	500 – 1400

*: by weight. T: Temperature range ($^\circ\mathrm{C}$).

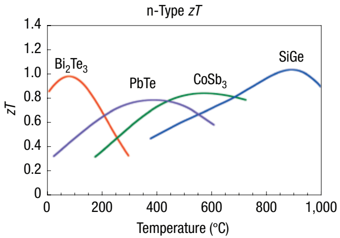
Background: High-Temperature Thermocouple Assemblies

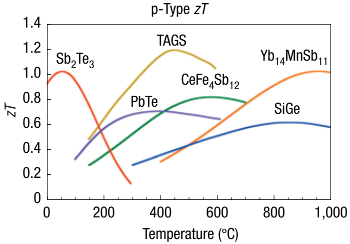
- Cost. Noble metals, such as Pt and Rd and Rh, are used.
- Slow responsive. Protection tubes are used.
- Bulky. Protection tubes are used.
- Low sensitive.

Background: Seebeck Coefficient and Semiconducting Thermoelectric Materials

$$S = \frac{8\pi^2 \kappa_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

- S is Seebeck efficient.
- κ_B is the Boltzmann constant.
- m^* is the effective mass the carrier.
- T is temperature.
- e is the unit charge.
- h is the Planck's constant.
- n is the carrier concentration.





Snyder and Toberer, Nat. Mater. **7** (2008) 105; M. Cutler, *et al.*, Phys. Rev. **133** (1964) A1143.

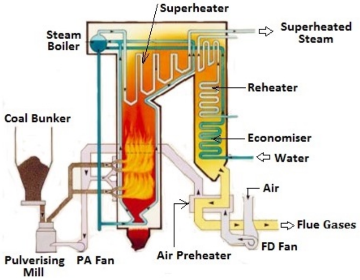
Project: Goals and Potential Significance of Results

A new kind of semiconducting thermocouples working harsh environment with

- High stability at high temperature. Heat resistance.
- Resistance to oxidization, erosion, and shock. Erosion resistance, oxidization resistance , and Erosion resistance
- Simple structure and easy maintenance.
- High sensitivity and high *emf* output.
- Low Cost.

Project: Relevancy to Fossil Energy

Bowen Steam Plant. A coal-fired power station in Georgia.



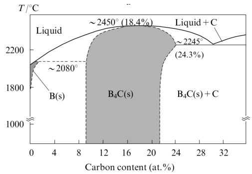
Pulverized coal-fired boiler in thermal-power-plants.

- Coal combustion at $1,300 - 1,700\ ^\circ\mathrm{C}$.
- Coal-fired thermal power plant: emit CO_2, SO_2, NO_x, solid waste under high temperature / high pressure.
- Overall coal plant efficiency: $32 - 42$ %. Efficiency: $35 - 38$ % at $570\ ^\circ\mathrm{C}$ and 170 bar, 42 % at $600\ ^\circ\mathrm{C}$ and 220 bar, 48 % at $600\ ^\circ\mathrm{C}$ and 300 bar.

Thermal sensors work under harsh environment to control temperature accurately. The proposed thermocouples will be good substitutes.

coalhandlingplants.com; brighthubengineering.com; D. Shindell *et al.*, Atmos. Chem. Phys. **10** (2010) 3247.

Achievements 1: BxC Amorphous Borides



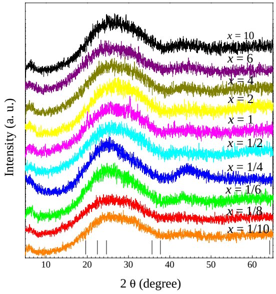
Phase diagram of B-C.

$$2\,B_2O_3 + 4\,C \longrightarrow B_4C + 3\,CO_2$$
$$\text{with } \Delta H_{calculated} = 1,148\ \mathrm{kJ/mol}$$

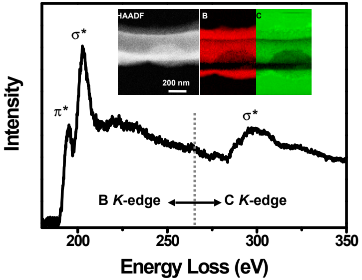
$$26\,B_2O_3 + 47\,C \longrightarrow 4\,B_{13}C_2 + 39\,CO_2$$
$$\text{with } \Delta H_{calculated} = 14,702\ \mathrm{kJ/mol}$$

Chemical reaction of amorphous boron carbide (B_xC) compounds.

Achievements 1: BxC Amorphous Borides



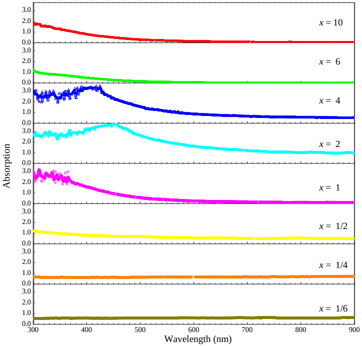
X-ray diffractions indicating amorphous state.



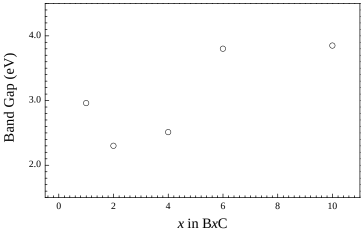
EELS spectrum and mapping indicating uniform B/C distribution.

Crystallographic structure of amorphous boron carbide (B_xC) compounds.

Achievements 1: BxC Amorphous Borides



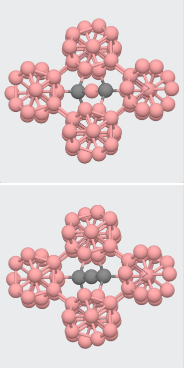
UV-vis spectra.



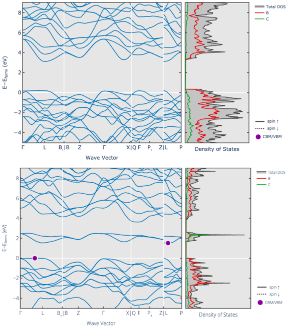
Band gap of B_xC.

Optical properties of amorphous boron carbide (B_xC) compounds.

Achievements 1: BxC Amorphous Borides

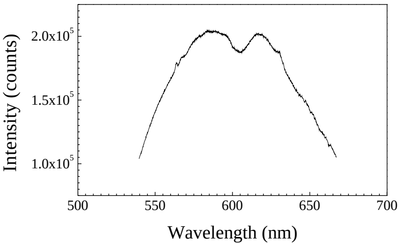


Simulated $B_{13}C_2$ (top) and B_4C (bottom) structure.

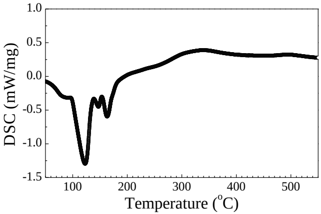


Calculated band-gaps of $B_{13}C_2$ (top) and B_4C (bottom) phase.

Achievements 1: BxC Amorphous Borides



Photoluminescence spectra.



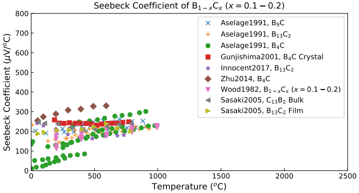
Differential scanning calorimetry.

Other properties of amorphous boron carbide (B_xC) compounds.

Journal of Alloy Compounds **861** (2021) 157951

Achievements 1: BxC Amorphous Borides

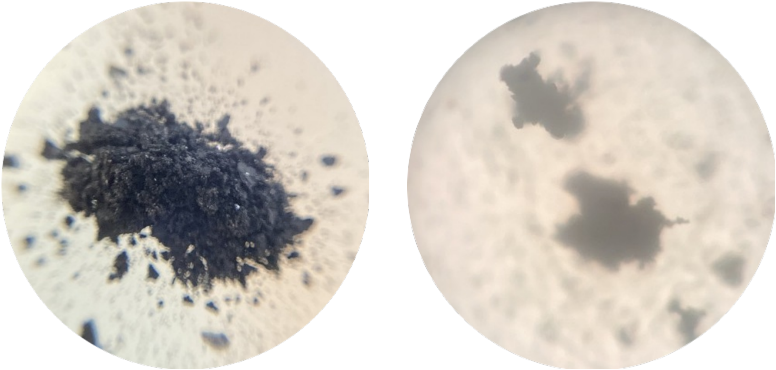
Fabricated B_xC disk.



Expected Seebeck coefficient at high temperatures.

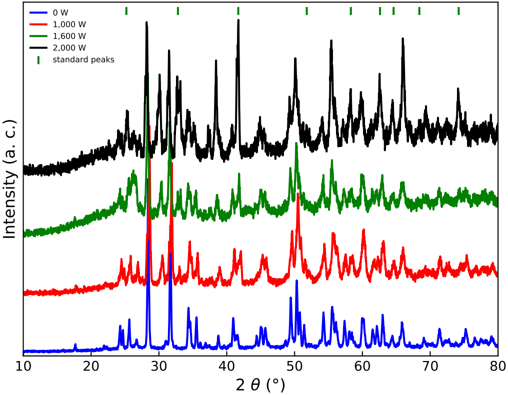
Bulks of amorphous boron carbide (B_xC) compounds.

Achievements 2: *n*-type Ceramic



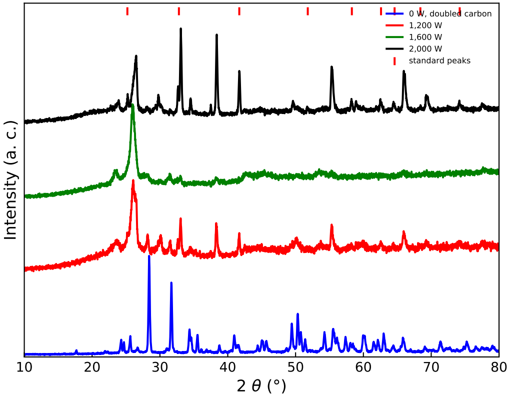
Optical images of synthesized powders.

Achievements 2: *n*-type Ceramic



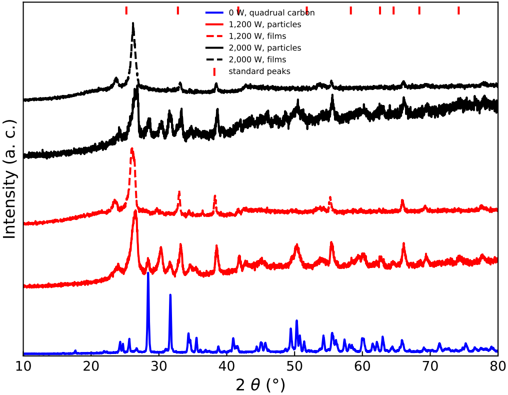
X-ray diffraction patterns of synthesized powders prepared with regular carbon content under various power. Less AB_2 phase was produced.

Achievements 2: *n*-type Ceramic



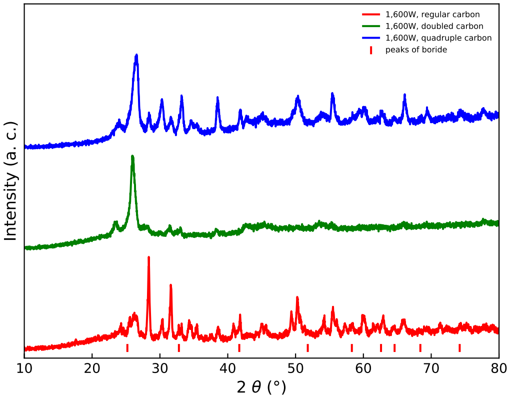
X-ray diffraction patterns of *n*-type AB_2 powders synthesized with doubled carbon content under various power. The content of AB_2 phase increases with power.

Achievements 2: *n*-type Ceramic



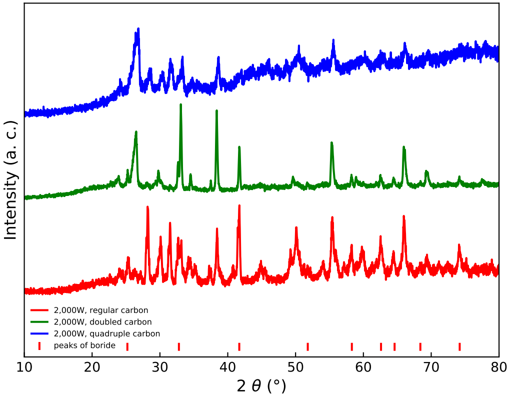
X-ray diffraction patterns of synthesized powders prepared with quadruple carbon content under various power. AB_2 phase was produced.

Achievements 2: *n*-type Ceramic



X-ray diffraction patterns of synthesized powders prepared with various carbon content at 1600 W.

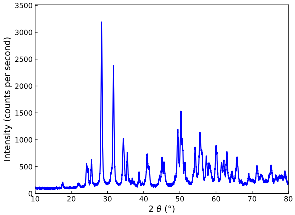
Achievements 2: *n*-type Ceramic



X-ray diffraction patterns of synthesized powders prepared with various carbon content at 2000 W. High carbon content benefits the synthesis of AB_2.

Achievements 2: *n*-type Ceramic

Precursor:



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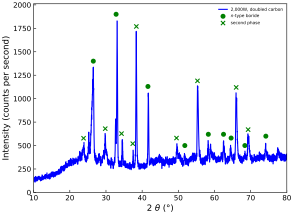
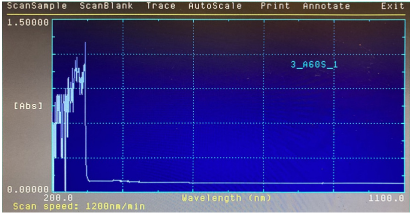
AB_2:

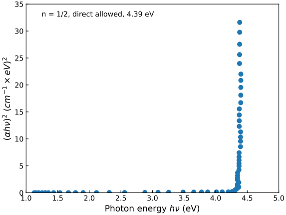


n-type AB_2 phase was synthesized from precursors.

Achievements 2: *n*-type Ceramic



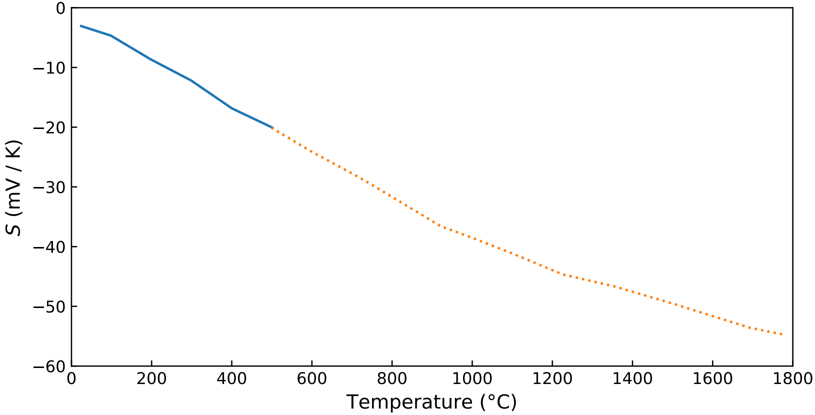
UV-vis spectrum of a typical sample.



Tauc-plot of UV-vis spectrum.

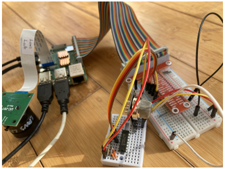
Optical properties of synthesized AB_2 ceramic powders. The band-gap of the synthesized ceramic is 4.39 eV at room temperature.

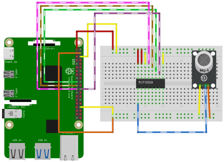
Achievements 2: *n*-type Ceramic



Predicated Seebeck coefficient S of *n*-type AB_2 ceramic at high temperatures up to $2,000\ ^\circ\mathrm{C}$.

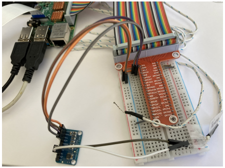
Achievements 3: Sensors

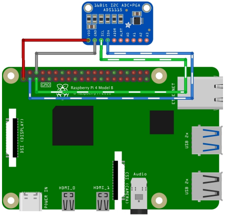





```python
# Importing modules
import spidev # To communicate with SPI devices
from time import sleep  # To add delay
import numpy as np # calculate concentration

# Start SPI connection
spi = spidev.SpiDev() # Created an object
spi.open(0,0)

# Read MCP3008 data
def analogInput(channel):
    spi.max_speed_hz = 5000
    adc = spi.xfer2([1,(8+channel)<<4,0])
    data = ((adc[1]&3) << 8) + adc[2]
    return data

# Below function will convert data to voltage
def Volts(data):
    volts = data / float(1023) * 3.3
    volts = round(volts, 2) # Round off to 2 decimal places
    return volts

```

Gas sensors.






```python
import RPi.GPIO as GPIO
import cmd
import logging
import smbus
import time

# ADS1115 + hardware constants
I2C_BUS = 1
DEVICE_ADDRESS = 0x4B
POINTER_CONVERSION = 0x0
POINTER_CONFIGURATION = 0x1
POINTER_LOW_THRESHOLD = 0x2
POINTER_HIGH_THRESHOLD = 0x3
```

Thermocouples.

Accomplishments

1. M. Tucker, *et al.*, Boron Carbide Amorphous Solid with Tunable Band Gap, Journal of Alloy Compounds, **861** (2021) 157951.
2. Y. C. Lan, *et al.*, Seebeck Coefficient of Boride at Ultra-High Temperatures Over 2000 Celsius, 2020 MRS Fall Meeting.
3. Y. C. Lan, *et al.*, Electron Diffraction of Boron Monoarsenide (submitted).
4. PI as Guest Editor of a Special Issue for Frontiers in Chemistry: Borides, Carbides, and Nitrides Compounds in Renewable Energy (Frontiers Media) (IF = 4.155 in 2017 - 2018).

Disclaimer and Acknowledgment

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