Synthesis and Characterization of Calcium Hexaboride (CaB_6) Nanowires

NSF- REU 2007 at UIC

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Overview: Project Goals

- Department of Energy (DOE)
  - Use of hydrogen as an energy carrier
  - Basic Energy Sciences Advisory Committee (2003)

    - Research and development of hydrogen production, storage, and usage
- Use of Hydrogen as an Energy Carrier:
  - alternative energy strategy
  - reduce greenhouse gas emissions and dependence on foreign energy sources

Hydrogen Storage – Complex Metal Borohydrides $Ca(BH_4)_2$

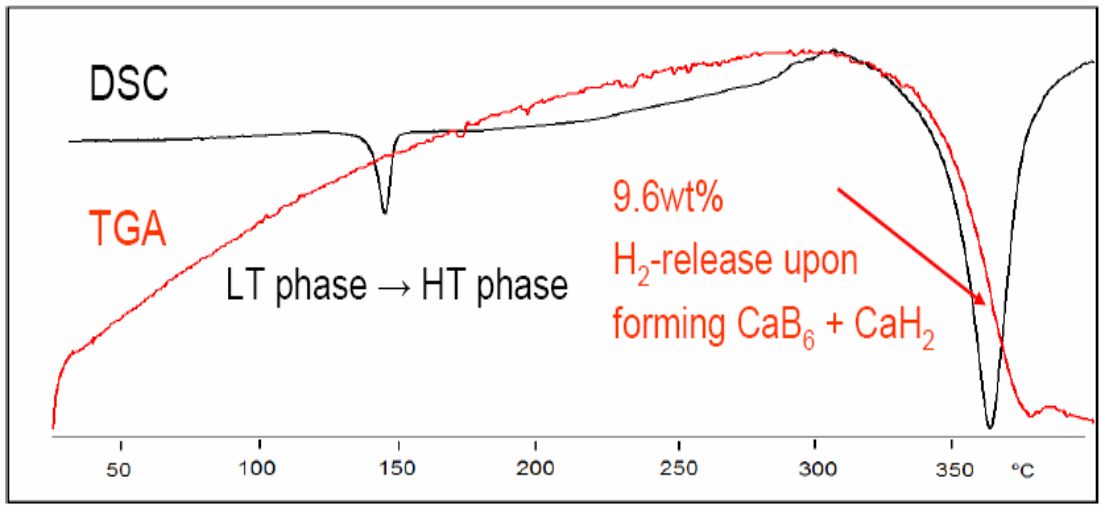
- Thermodynamical stability of Metal Borohydrides
- Boron: lightweight and forms complex hydrides
  - Nanowires increase diffusion rate
  - Favorably high surface to volume ratio of nanowires
- High gravimetric densities of Hydrogen in Metal Borohydrides
  - theoretically 9.6 weight% Hydrogen in $Ca(BH_4)_2$

Gas Release Upon Phase Transition

Desorption Reaction for $Ca(BH_4)_2$ at 350°C

$3Ca(BH_4)_2 \rightarrow 2CaH_2 + CaB_6 + 10H_2$

TGA and DSC of $Ca(BH_4)_2$ as prepared by solid-state synthesis



Ronnebro *et al.*, 2007 Hydrogen Program Review available at

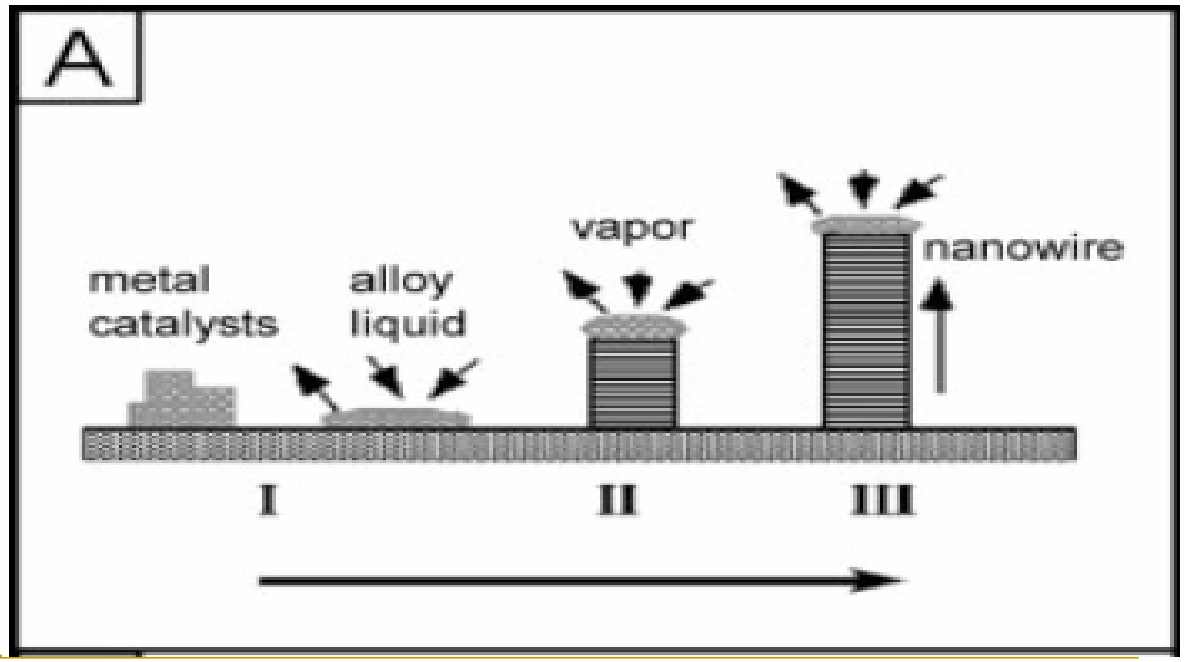
Adsorption Reaction for CaB_6 and CaH_2

$CaB_6 + 2CaH_2 + H_2 \rightarrow Ca(BH_4)_2$

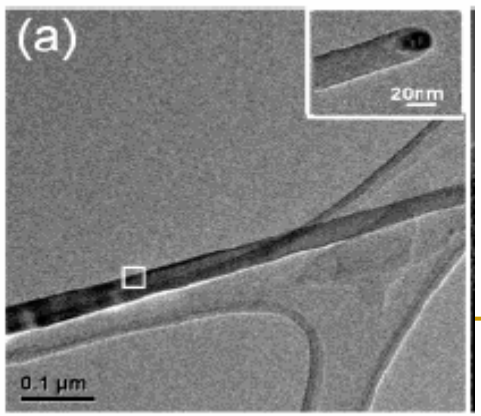
- at 400°C and 700 bar with 80% Yield

Vapor Liquid Solid Mechanism

1) Solid substrate with catalyst
   - forms liquid alloy upon heating
2) Gaseous reactant dissolves onto catalyst alloy
3) Supersaturation of liquid droplet
4) Growth of nanowire at solid-liquid interface by precipitation



Xia *et al.*, Advanced Materials. Vol. 15 (5), 368, 2003



Xu, T., *et al.* Nanoletters. Vol. 4 (10) , 2052, 2004

Synthesis of CaB_6 Nanowires

- **Temperature** in 900-1025°C range
- **Pressure** about 175-180 mTorr under Argon flow
- **Wafer** (SiO_2 substrate) with randomly layered CaO
  - Thermally evaporated Nickel catalyst for coating
- **Gas introduction**:

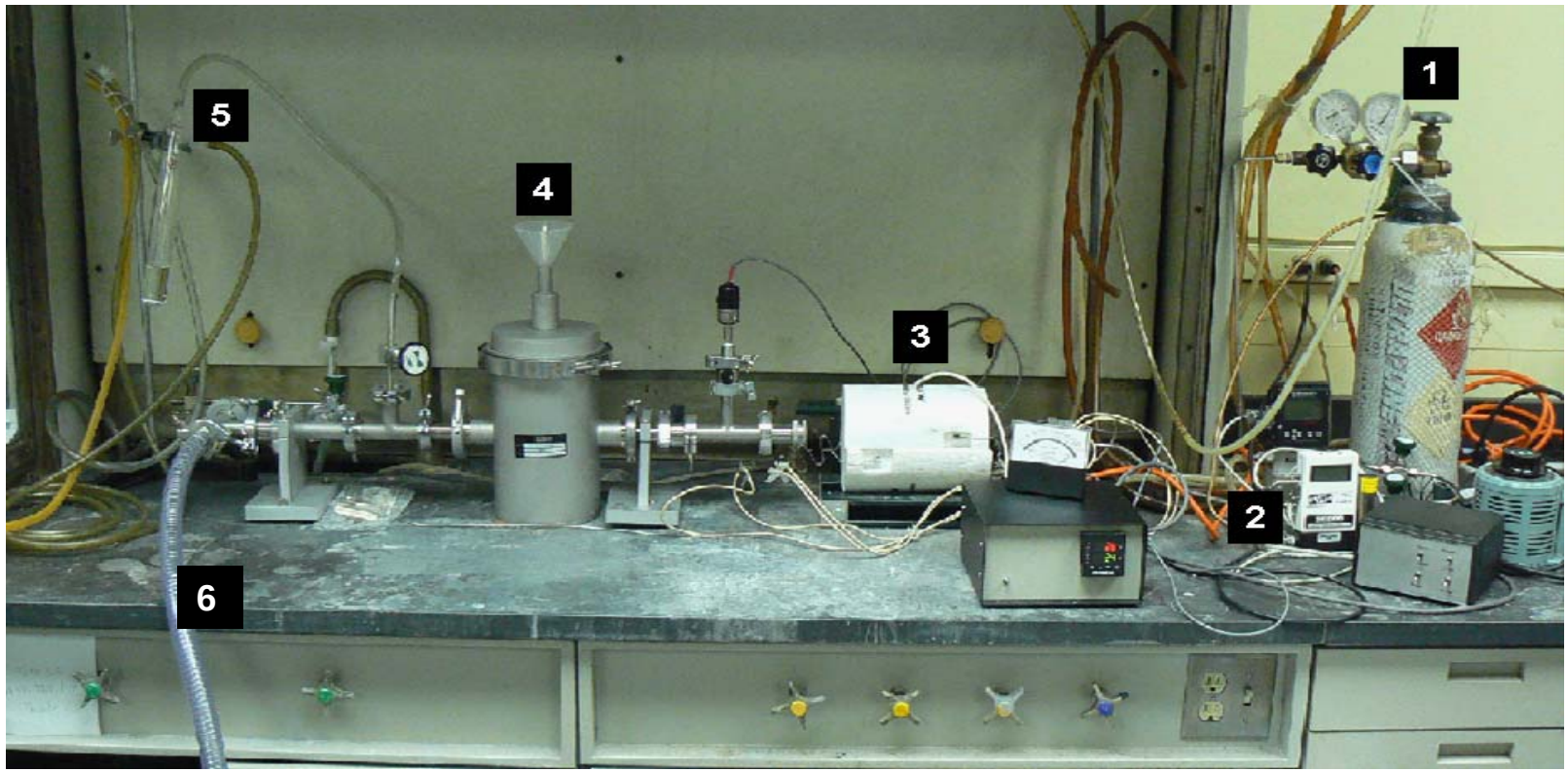
  1) Argon gas inflow for 55 minutes

  2) Diborane (B_2H_6) gas (1.08% in Argon) for 20 minutes

  3) Cooled under the flow of argon for 3 hours

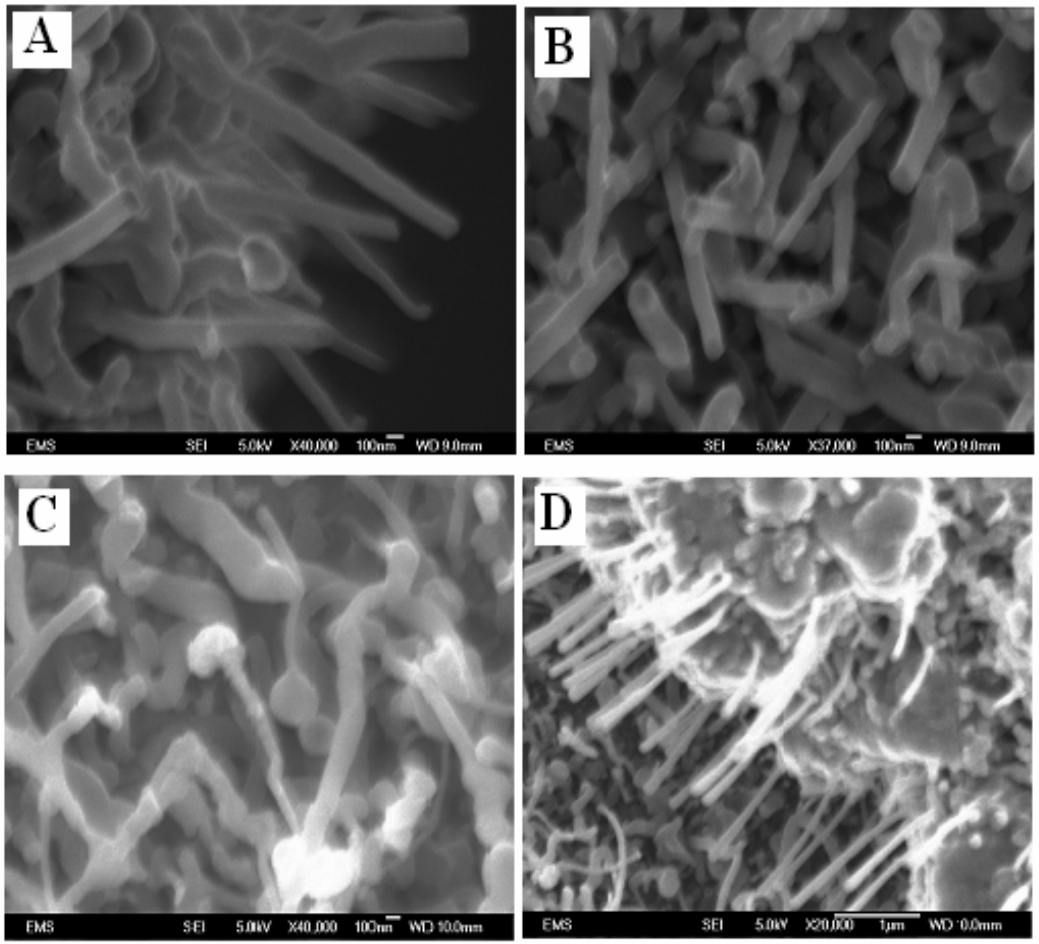
$CaO(s) + 3\ B_2H_6\ (g) \rightarrow CaB_6\ (s) + byproducts$

Low Pressure Chemical Vapor Deposition Apparatus

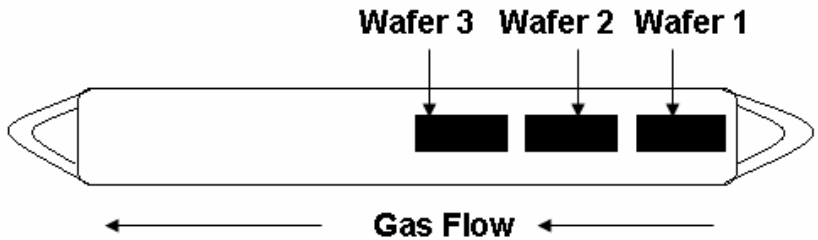


1) Diborane Gas Source
2) Flow meter Controller
3) Ceramic Heating Chamber
4) Liquid Nitrogen Trap
5) Bubbler Tube
6) Connection to Mechanical Pump

Observed Nanowire Morphologies

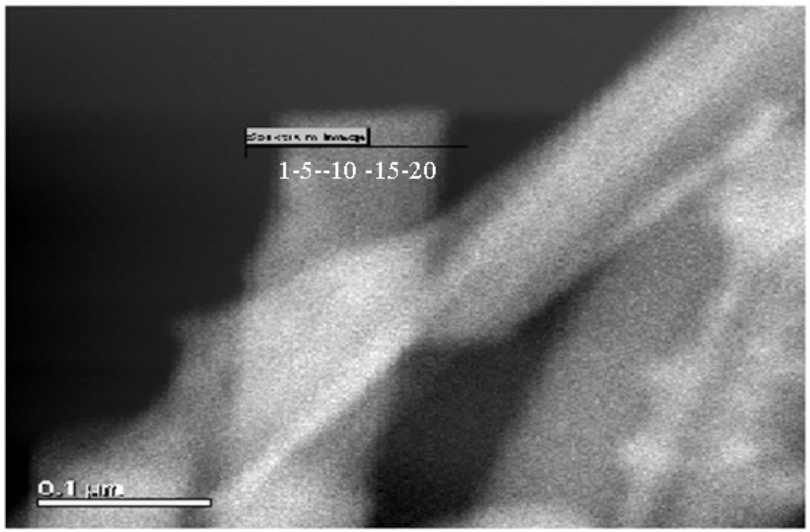


- Different nanowire morphologies across Wafers
- **Potential Explanations**:
  1) Different temperatures experienced across Wafers
  2) Different amounts of gaseous introduction experienced

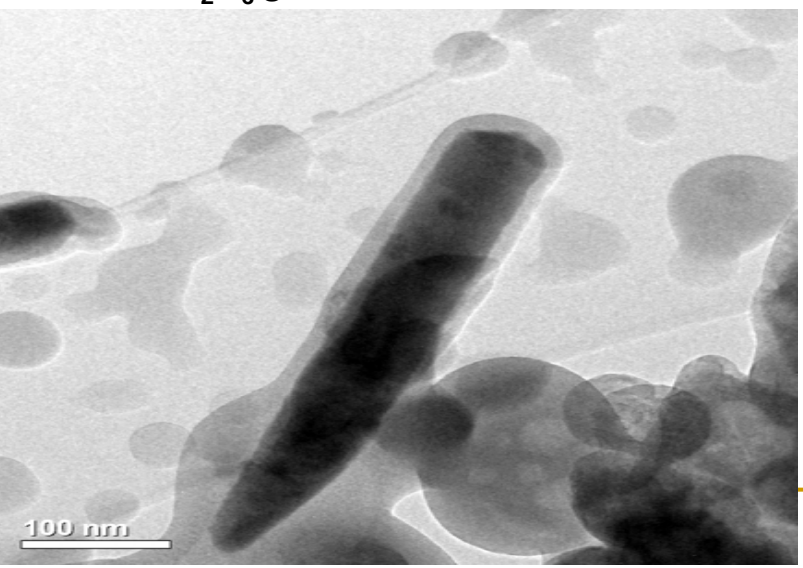


- SEM images of Wafer 1: Figures A and B
- SEM images of Wafer 2: Figures C and D

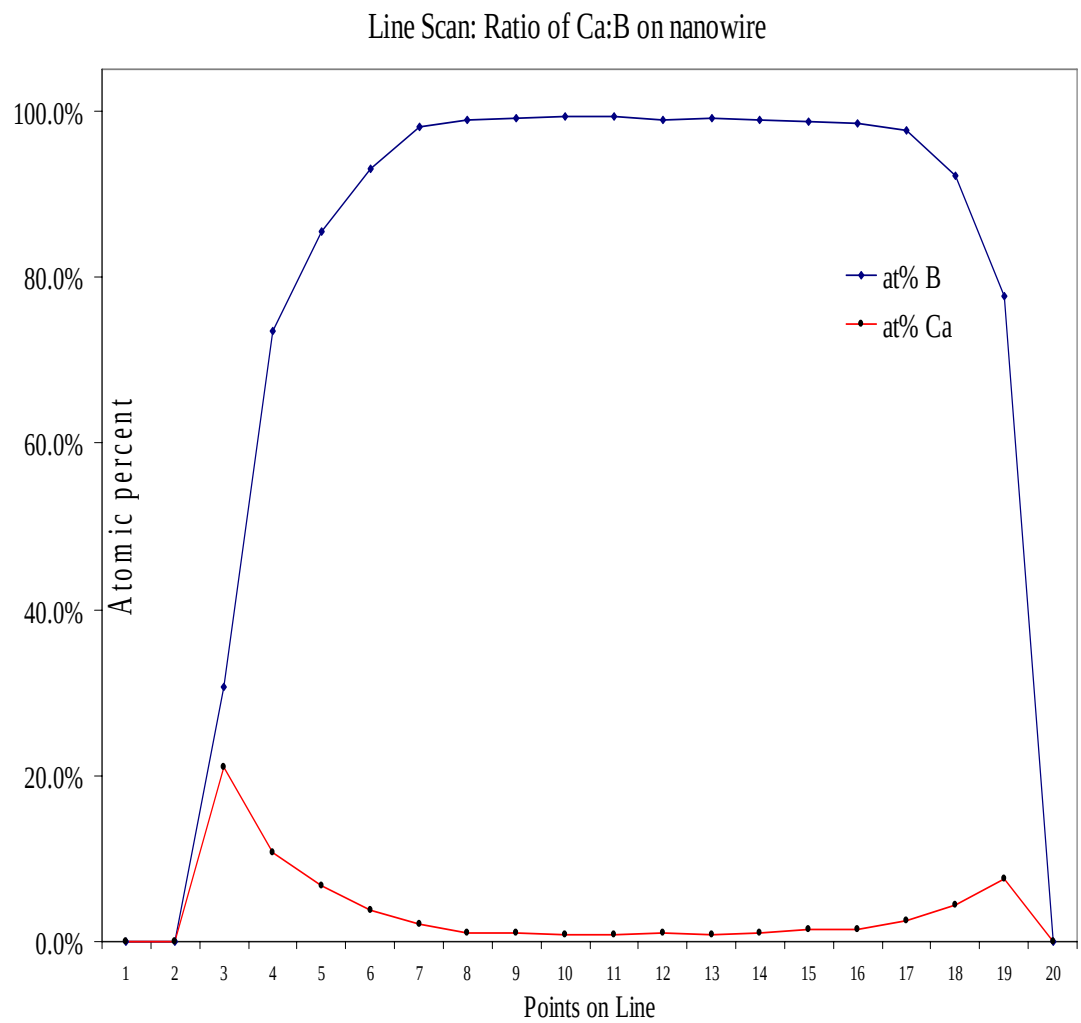
TEM and Electron Energy Loss Spectroscopy Data



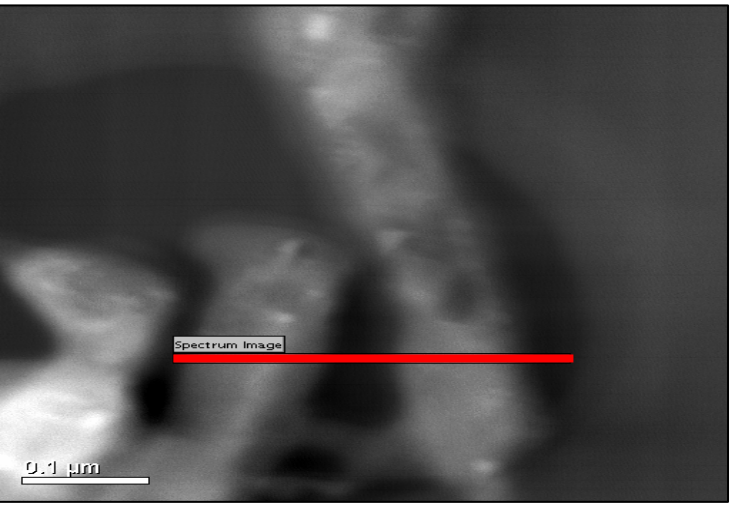
TEM image of nanowire using 10.8 mg Ni with 20 sccm B_2H_6 gas flow rate at 900°C.

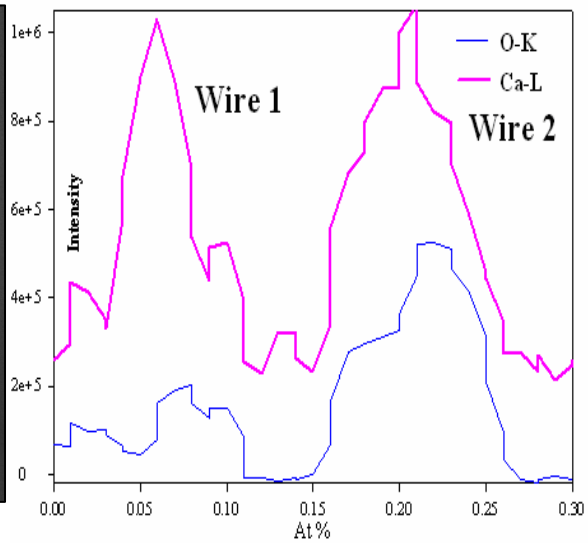


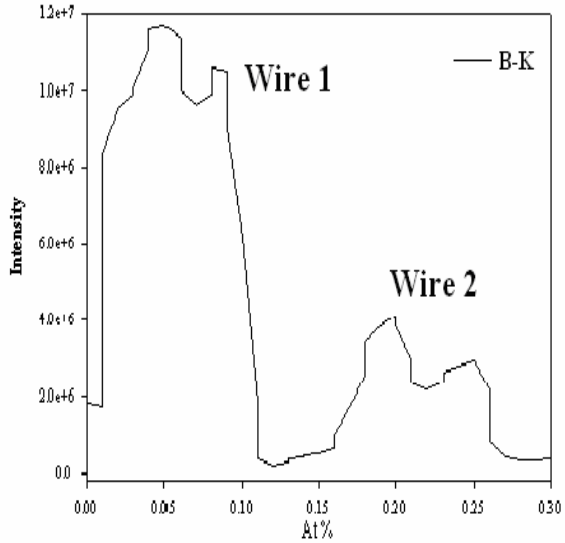
TEM image of nanowire with core and shell structure



EELS Collected Data of Two Nanowires







- Synthesis performed at 925°C with 20 sccm B_2H_6, using 2.7 mg Ni
- TEM image of two distinct nanowires from sample (Right)
- EELS collected data from line scan of 2 nanowires (Left)
  - Detected relative atomic percentages of Ca, O, and B
  - Varying elemental composition of nanowires across same sample
  - Suggests reaction resulted in a mixture of different nanowires

Future Works

- Continue Synthesis and Characterization of CaB_6 nanowires and other metal hexaboride nanowires
- Vary reaction time along with temperature and flow rate
- Perform FTIR studies of reversible hydrogen storage materials
  - Initial steps of Calcium Borohydride dehydrogenation
  - Initial steps of Calcium Hexaboride Hydrogenation

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