Boron Carbides:
Unconventional High-Temperature Thermoelectrics

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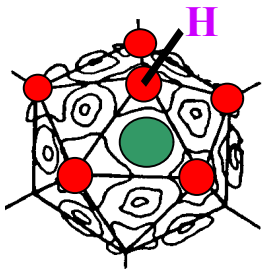
Three topics:

- Sandia uses thermoelectric power sources: RTG's
- Novel contributions to boron carbides' thermoelectric properties
- Implications for boron carbide quantum wells

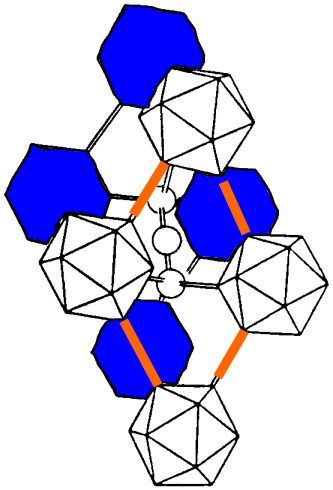
Boron Carbides' Distinctive Structures

Based on twelve-atom icosahedral units



Borane molecule $(B_{12}H_{12})^{2-}$ illustrates unconventional internal bonding

- Each **boron** has **6 nearest neighbors**
  - **5 within icosahedron**
  - **1 external (H)**
- **"Electron-deficient"** internal bonding
  - 26 electrons to fill bonding orbitals
  - **Bonding electrons are delocalized**
  - Charge densities **peak at triangle centers**
- **Strong bi-electron affinity** – $(B_{12})^{2-}$

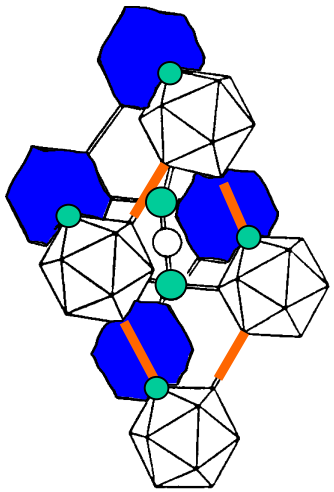


Bonds **between** boron carbides' **icosahedra** are **strong, covalent bonds**

- Very high melting temperatures (> 2400 K)
- Extreme hardness, high stiffness

D. Emin, Physics Today, January 1987

Boron Carbides' Nonstoichiometry: High Carrier Densities



- **Ideal**, "stoichiometric" boron carbide, $\mathbf{B_{12}C_3}$, **would be an insulator**

  $(B_{11}C)^-$ icosahedra, $(CBC)^+$ chains

- **Real boron carbides** have a wide single-phase region $\mathbf{B_{12+x}C_{3-x}}$ **, 0.07 < x < 1.7**

Charge carriers result when B replaces C

x is large, so carrier densities are large

(≈.1 to 1 carrier per unit cell, or ≈ $10^{21}/cm^3$)

Boron Carbides As Thermoelectrics

- Covalently bonded, light elements – high stiffness, high sound velocity

Expect high thermal conductivity

- High carrier density, ≈ $10^{21}/cm^3$, from nonstoichiometry

Expect very low Seebeck coefficient

YET

Boron carbides' Seebeck coefficients are large

Boron carbides' thermal conductivities are low

Boron carbides have long been known as good high-temperature thermoelectrics

1980's – studied by JPL for high-temperature thermoelectric generation

Sandia/JPL collaboration, then Sandia program:
aimed at understanding the "anomalies"

Boron Carbides' Hopping-Type Electronic Transport

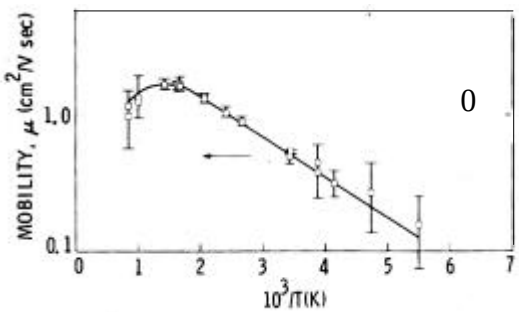
- **DC conductivities**:

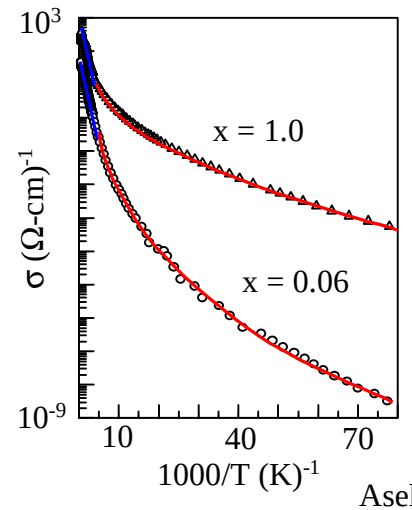
  Non-Arrhenius at **low T**, **Arrhenius** at **high T**

  High carrier densities ***suggest low mobilities***

- **Hall mobilities** are **low, thermally activated**

(C. Wood, and D. Emin,
Phys. Rev. B 29, 4582 1985.)





Aselage, Emin, McCready,
Phys. Rev. B 64, 054302 (2001)

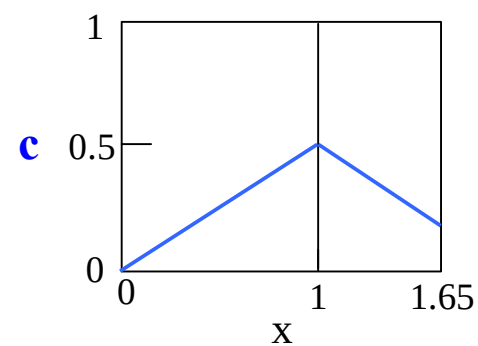
Carriers localize on icosahedra, move by thermally assisted hopping

Carriers are confined to icosahedral units, 1.7 Å radius

- Spin densities from low-T e.s.r and susceptibility << carrier densities

Carriers form singlet pairs, "bipolarons"

- One consequence of pairing:
  carrier density **c** varies non-monotonically with composition

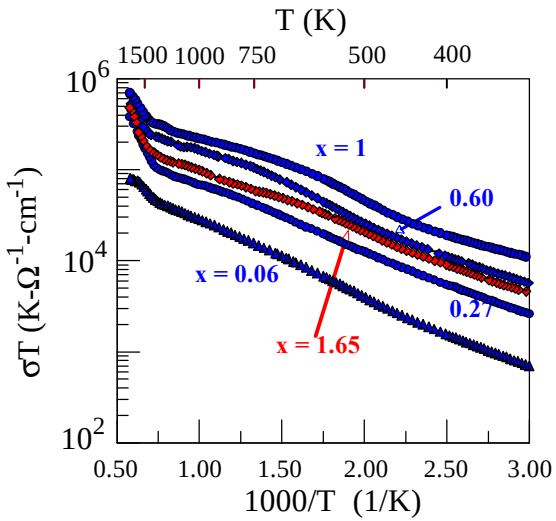


Boron Carbides' High-Temperature Conductivities

Systematic study of many well-characterized hot-pressed samples with compositions that span the single-phase region

- High-temperature, adiabatic hopping of small (bi)polarons:

$$s\,T = \frac{Nc(1-c)q^2a^2n}{k_B}\exp\left(-\frac{E_a}{k_BT}\right)$$



Aselage, Emin, McCready, Phys. Rev. B 64, 054302 (2001)

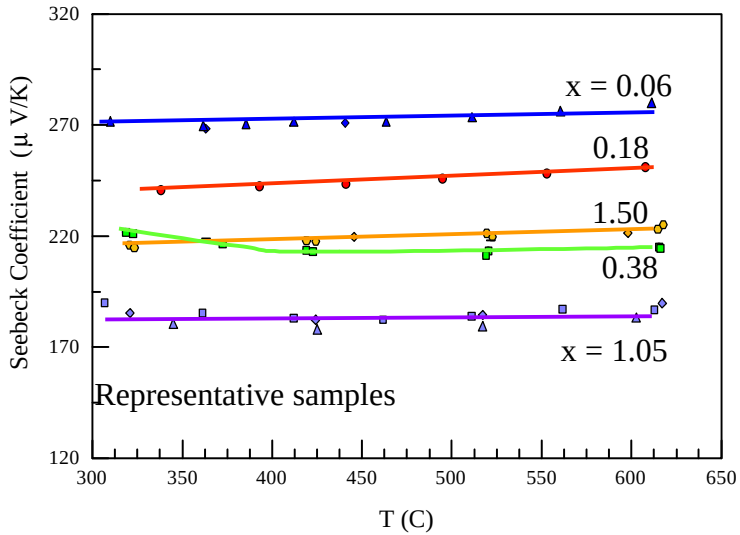
- **E_a » 0.16 eV for all carbon concentrations**

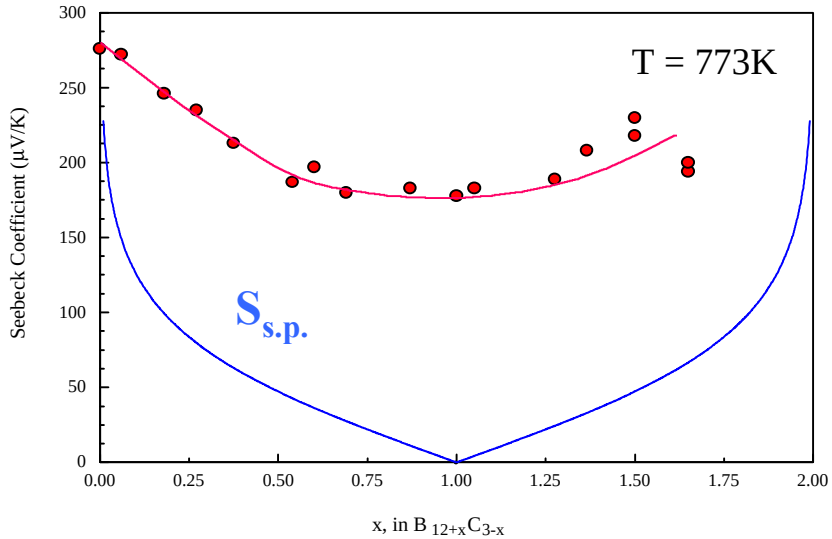
- Conductivity **pre-exponential factor**:
  - **Peaks near x =1**
  - Has **non-monotonic carbon-concentration dependence**
  - **Magnitudes consistent** with carrier densities

Boron Carbides' High-Temperature Seebeck Coefficients

Standard high-temperature treatment for small polarons : $S_{s.p.} = \frac{k_B}{q} \ell n\left(\frac{1-c}{c}\right)$, ($k_B T >> W, \Delta$)

D. Emin, "Seebeck Effect",
Wiley Encyclopedia of Electrical and Electronics Engineering, in press.





"Expected" Results

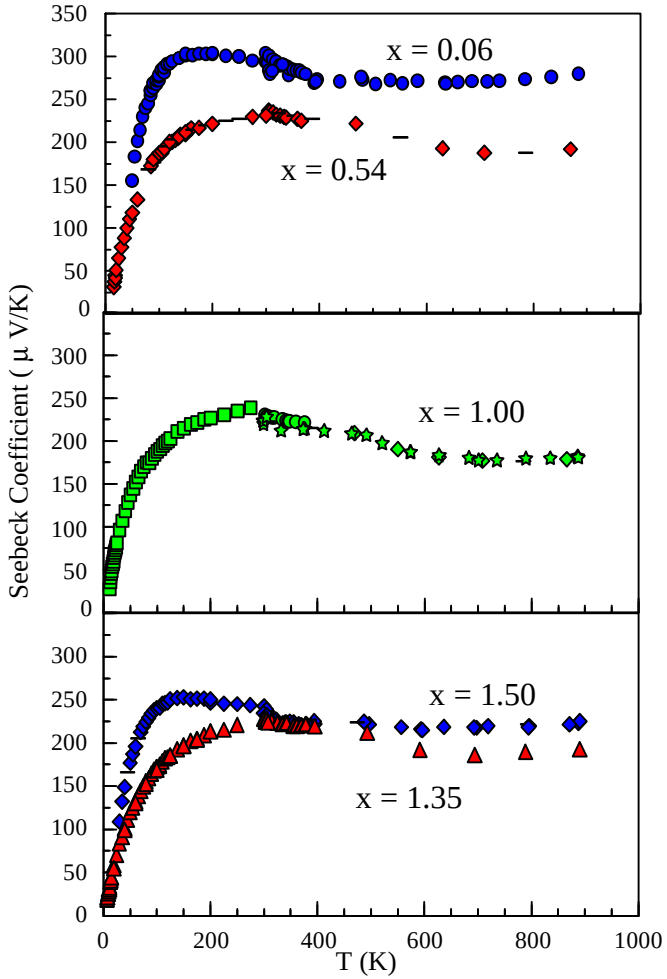
- Series of **parallel, T-independent curves**
- **Magnitude shifts with carrier density** (carbon concentration)

"Anomalous" Results

- **Large** (≈175 μV/K) **contribution beyond $S_{s.p.}$**
- Contribution is **independent of carrier density**

Seebeck Coefficients' Unusual Temperature Dependence

T-dependence and **carrier-density-insensitivity**
consistent with enhancement from **carrier-induced softening**

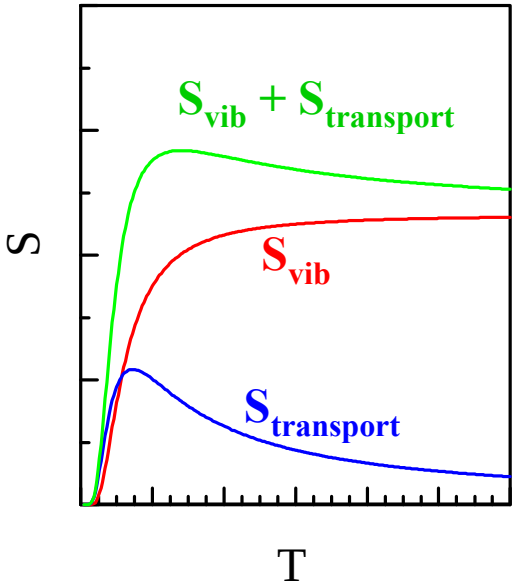


Aselage, Emin, McCready, Duncan, PRL, 81, 2316 (1998)
Aselage, Emin, McCready, Phys. Rev. B 64, 054302 (2001)

- **Carrier-induced softening**:
  Carriers confined to **multi-atom sites** (not point ions)
  Carriers "slosh" around as sites' **atoms vibrate**
  Sloshing **lowers local vibrational frequencies**

  Emin, PRL 72, 1052 (1994); Emin, Phys. Rev. B 61, 6069 (2000)

- **Two Seebeck coefficient contributions**:
  S_{vib} - (increase in vibrational entropy)/q
  $S_{transport}$ - (net vibrational energy transported)/qT

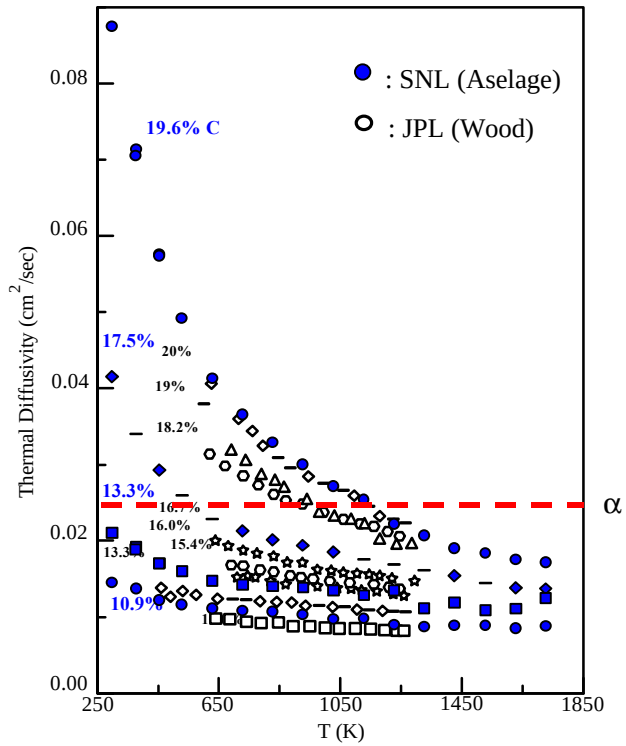


Emin, Phys. Rev. B 59, 6205 (1999)

Boron Carbides' Surprisingly Low Thermal Diffusivities

- With **decreasing carbon concentration**
  - Thermal diffusivities diminish
  - Magnitude falls below "minimum"
  - Temperature dependence changes,
    Crystal-like → Glass-like

- **Vibrational disorder increases**
  - B for C substitutions
  - Increased carrier density and softening



$$\alpha_{min} = \frac{1}{3} v_s a$$

- Glass-like thermal diffusivities can result from incoherent energy transfer between localized vibrational modes

Summary

- Boron carbides are surprisingly good high-temperature thermoelectrics
  (ZT ≈ 0.3 at 1000°C, Z continues to increase with increasing T)

- Novel contributions enhance the thermoelectric properties
  - High densities of ***localized*** charge carriers
  - Thermally activated mobilities increase with temperature
  - Large, carrier-induced softening enhancement of Seebeck coefficients
  - Slow, incoherent vibrational energy transfer – vibrational disorder