Synthesis and Thermoelectric Properties of Type I Ba-Al-Cu-Si Clathrates

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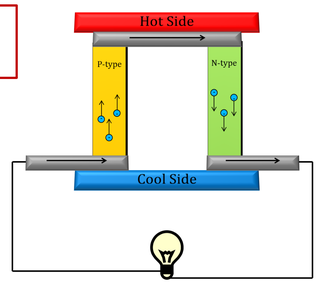
Thermoelectric (TE) Effect and Material Issues

- TE materials convert waste heat to electricity
- Efficiency of TE material is given by figure of merit ZT

$$ZT = \frac{\sigma S^2 T}{\kappa}$$

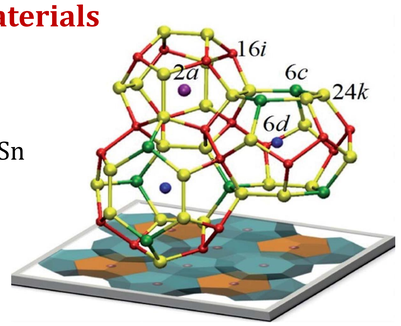
σ=electrical conductivity
S=Seebeck coefficient
T=temperature
κ=thermal conductivity

- TE materials with ZT>2 required
- Challenges of increasing ZT stem from interdependence of σ, S, and κ
- Highest ZT materials tend to be heavily doped semiconductors



Clathrates as potential TE materials

- Cage structure with guest atoms surrounded by host atoms
- Type I clathrate unit cell: G_8H_{46}
- Guests: Ba, Na, K Hosts: Si, Ge, Sn
- Low κ, high σ and high S
- ZT = 1.35 for $Ba_8Ga_{16}Ge_{30}$[1]
- ZT = 0.4 for $Ba_8Al_{16}Si_{30}$[2]

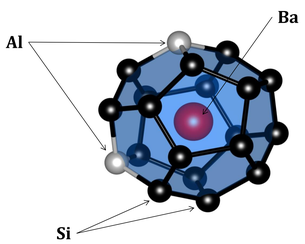


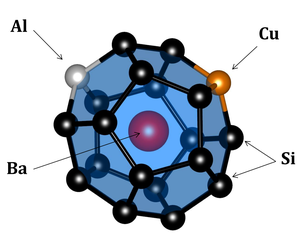
1. Saramat et al. *J. Applied Physics* **99,** 2 (2006) 2. Anno et al. *J. Materials Science* **48**, 7 (2013)

Tuning thermoelectric properties of Si clathrates

- Guest atoms stabilize the structure but also contribute excess charge carriers; host atoms can be substituted to compensate
- Incorporating different guest/host elements enables tuning of thermoelectric properties

Compound	Guest (valency)	Host (valency)	Charge Counting	Net Charge
Ba_8Si_{46}	Ba (2)	Si (4)	8 Ba atoms donate 16 excess electrons	16 electrons
$Ba_8Al_{16}Si_{30}$	Ba (2)	Al (3) Si (4)	8 Ba - donate 16 electrons 16 Al – 16 deficient electrons	0
$Ba_8Al_8Cu_3Si_{35}$	Ba(2)	Al(3) Cu(1) Si(4)	8 Ba - donate 16 electrons 8 Al – 8 deficient electrons 3 Cu- 9 deficient electrons	1 excess hole



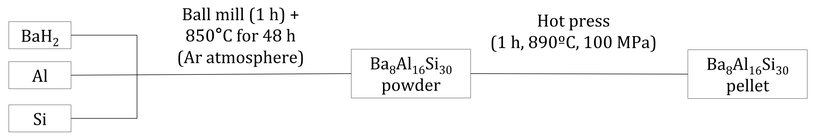


Objectives

- **Develop synthesis technique for phase pure $Ba_8Al_{16}Si_{30}$ and $Ba_8Al_8Cu_3Si_{35}$ clathrates**
- **Identify parameters for hot pressing dense pellets**
- **Perform TE characterizations on clathrate pellets**

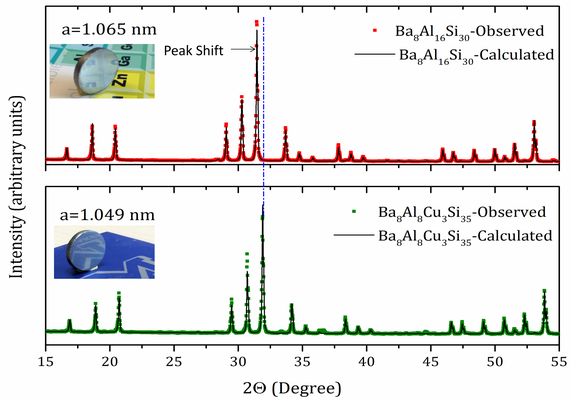
Powder metallurgy synthesis of clathrates

- Polycrystalline clathrate samples were synthesized from stoichiometric quantities of BaH_2, Al, Cu, and Si
- Using BaH_2 as Ba source allowed for ball milling of precursors for homogeneous mixing

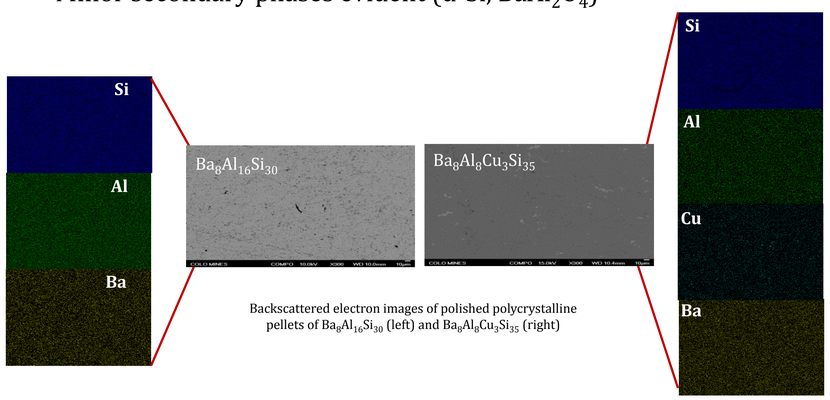


Phase & Composition analysis using XRD and SEM

- X-ray diffraction (XRD) confirmed that our synthesis technique resulted in >98 weight % phase pure samples
- Calculated X-ray pattern for $Ba_8Al_8Cu_3Si_{35}$ agrees with experimental data



- Energy dispersive spectroscopy (EDS) elemental maps show homogeneous distribution of Ba, Al, Si, Cu
- Minor secondary phases evident (d-Si, $BaAl_2O_4$)

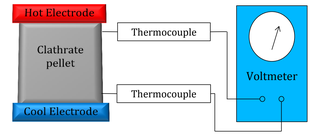


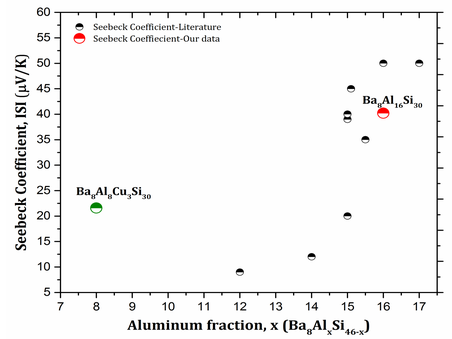
Backscattered electron images of polished polycrystalline pellets of $Ba_8Al_{16}Si_{30}$ (left) and $Ba_8Al_8Cu_3Si_{35}$ (right)

Atomic Percentages from EDS

Target Composition	Composition from EDS				Density (% theoretical) g/cm³
	Ba At % (theoretical)	Al At % (theoretical)	Si At % (theoretical)	Cu At % (theoretical)	
$Ba_8Al_{16}Si_{30}$	16.5 (14.8)	26.75 (29.6)	56.75 (55.5)	--	3.20 (97%)
$Ba_8Al_8Cu_3Si_{35}$	15.31 (14.8)	14.84 (14.8)	65.47 (64.8)	4.36 (5.55)	3.45 (96%)

Seebeck measurements of BaAlCuSi clathrates





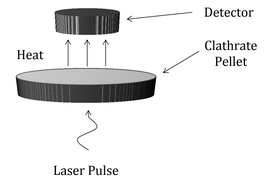
$Ba_8Al_{16}Si_{30}$
- S = -40.2 μV/K
- Comparable to literature[2,3,4] values of x>15

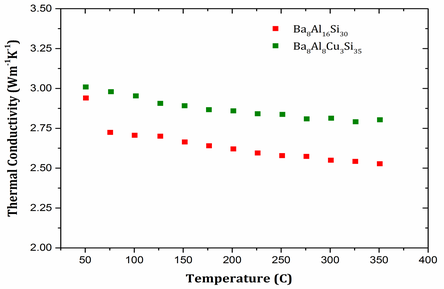
$Ba_8Al_8Cu_3Si_{35}$
- S = -21.6 μV/K
- Expected to be p-type but measurements suggest n-type
- Possible deviation from target Al:Cu ratio or different valancy of Cu

2. Anno et al. *J. Materials Science* **48**, 7 (2013)
3. Anno et al. *J. Electronic Materials* **42**, 7 (2013) 4. Tsujii et al. *J. Solid State Chemistry* **184**, 5 (2011)

Thermal conductivity of BaAlCuSi clathrates

- Netzsch LFA457 was used to measure thermal diffusivity
- κ is the product of thermal diffusivity, specific heat, and density





Accomplishments

- Large-scale synthesis of phase pure type I BaAlCuSi clathrate
- Doped BaAlSi clathrates with Cu for the first time
- BaAlCuSi clathrates showed promising TE performance

Future directions

- Investigating different ratios of Al and Cu for efficient TE performance
- Exploring Zn as a host element

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