Ytterbium-Substituted Clathrate Thermoelectrics: Deflection of Phonons Through 'Rattling'

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Abstract:

Clathrate or 'cage and rattler' thermoelectric materials are promising candidates for high-efficiency thermoelectricity, offering low thermal conductivities. Barium germanide clathrates have been synthesized in previous studies with moderate efficiencies. Six bulk samples of barium germanide were synthesized, substituting small amounts of ytterbium into the barium stoichiometry. Upon x-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and thermoelectric analysis, the ytterbium substitution was unsuccessful in increasing thermoelectric properties. The presence of secondary phases that sequestered ytterbium prevented the substitution of the Yb ions into the Ba clathrate sites.

Summary of Research:

The stoichiometry of the germanide clathrate samples is $Ba_{8-x}Yb_xGa_{16}Ge_{30}$, where x is 0, 0.2, 0.4, 0.6, 0.8, and 1.0 in samples 1-6, respectively. The type-I clathrate metal shot was used as the precursor for synthesis, with the barium weighed in a glove box to minimize oxidation. The metal was combined and melted in an arc furnace, forming ingots around 6 g in mass. The ingots were broken and pulverized in a ball mill, then the powder was sieved down to 52 µm and 2 g was packed into a die for spark plasma sintering (SPS). The SPS sintered at 840°C and 30 MPa for 30 min. After bulk synthesis, the samples were polished and sectioned for analysis.

Thermoelectric analysis was performed using a Netzsch LFA Hyperflash and an Ulvac-Riko ZEM2. EDS was performed using a scanning electron microscope (SEM).

The data were inconsistent in establishing a trend between Yb content and thermoelectric efficiency, ZT, as shown in Figure 4. Similarly, the lattice thermal conductivity in Figure 3 shows no consistent trend with Yb content. The EDS image in Figure 2 provides an explanation for this inconsistency. The sequestration of Yb in specific regions, likely YbO_2, prevented any Yb from substituting into the Ba sites and consistently changing the structure.

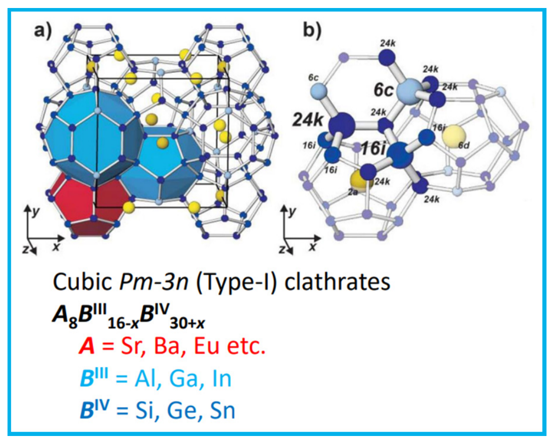

Figure 1: Barium and ytterbium rattler atoms are held in the alternating tetrakaidecahedron and decahedron cages in the Pm-3n structure, which are made up of the germanium and gallium atoms.

Conclusions and Future Steps:

The mechanism for the decrease in thermal conductivity is inconsistent between samples, due to the formation of ytterbium and ytterbium oxide secondary phases. At low grain size, these phases impede phonon motion, but at large grain size they increase thermal conductivity. Minimal Yb substitution occurred, failing to reproduce the high ZT and solubility limit of 0.7 reported in [11].

Future research can explore the magnetic properties of these samples to identify the valence state of the Yb ions to explain the changes in conductivity. Additionally, samarium germanide clathrates are a similar material with promising clathrate properties.

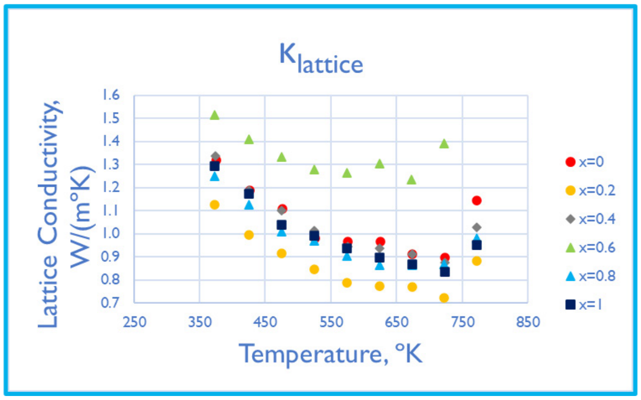

Figure 2: EDS image of the x=0.4 sample, isolating the Yb atomic signal. White regions show significant Yb sequestering and inhomogeneity.

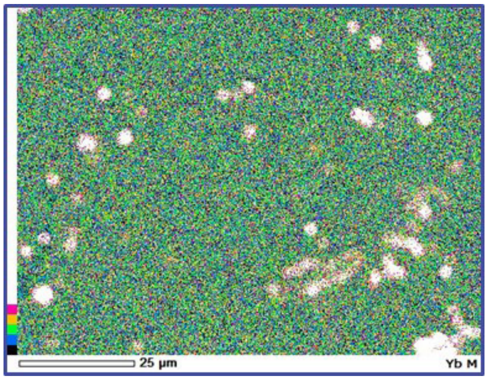

Figure 3: Lattice thermal conductivity of all 6 samples, calculated using the Wiedemann-Franz law to remove the electronic thermal conductivity contribution.

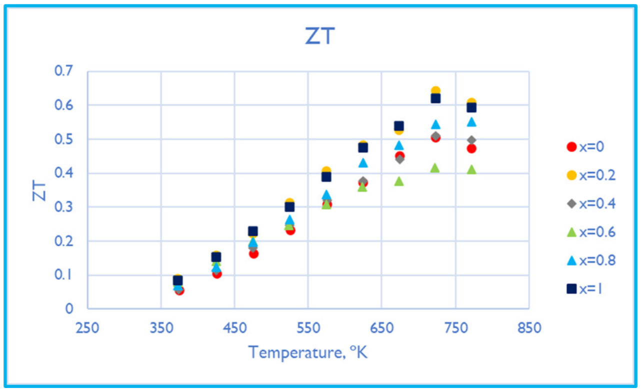

Figure 4: Thermoelectric efficiency of all six samples.

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