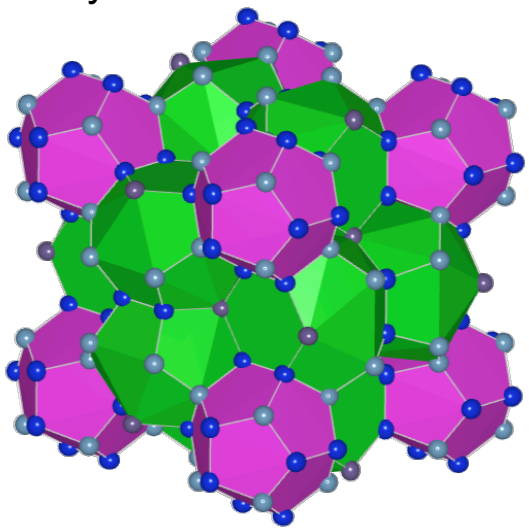
Tuning thermoelectric materials at the atomic level, guest-host interactions are important

The clathrate-type semiconductor, $Ba_8Al_xSi_{46-x}$, provides a controlled system to explore the role of the interactions between the guest atoms, barium in this case, and the host atoms, Al and Si, because the Al-content can be varied over a large range. We have used neutron diffraction to explore the detailed structural changes of the crystal structure of $Ba_8Al_xSi_{46-x}$ as a function of Al content using the HB-2A Neutron Powder Diffractometer at the High Flux Isotope Reactor, Oak Ridge National Laboratory (ORNL). The Ba atomic displacements increase with increasing cage size, but appear to be primarily dependent on the host framework site occupancies, specifically that displacement increases in the direction of host framework sites with the largest Al content. Differences in the physical properties, specifically thermal conductivity, have been linked to the displacement of the atom in the large cage. These new findings emphasize the importance of site occupancies in the framework sites nearest to the guest atom in the large cage. This correlation will help guide the search for new clathrate-type thermoelectric phases with improved physical properties. Thermoelectric materials are used in devices to generate power from waste heat or alternatively in devices to provide solid-state refrigeration. This research was from a collaboration between University of California – Davis and ORNL scientists.



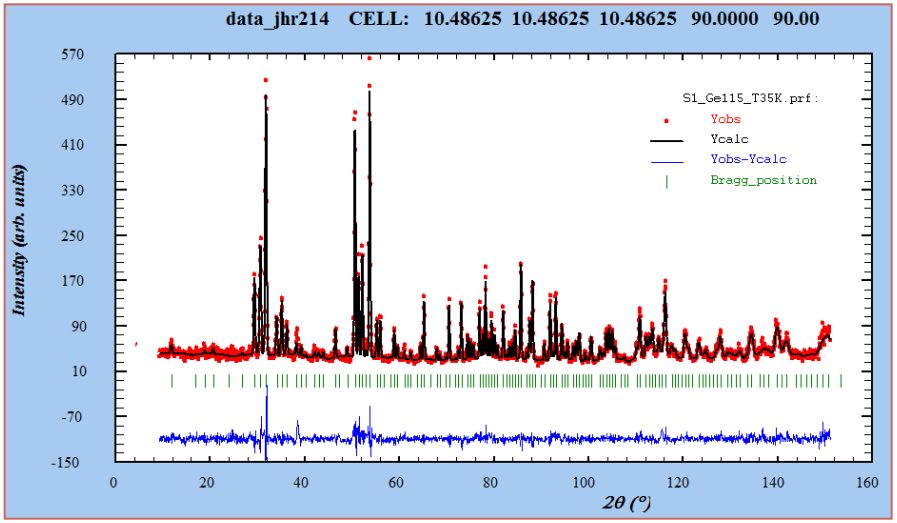
This clathrate crystal structure (at right) consists of a host framework of tetrahedrally linked Al and Si atoms (show as three differently colored balls), which form polyhedral cages (green and purple) that enclose one Ba atom in each.

Roudebush, J.H., C. de la Cruz, B.C. Chakoumakos, S.M. Kauzlarich, Neutron Diffraction Study of the Type-I Clathrate $Ba_8Al_xSi_{46-x}$: Site occupancies, cage volumes and the interaction between the guest and host framework. *Inorganic Chemistry*, in press.

Experimental

Synthesis:
Direct melting of elements
small batches (~1 g), arc welding
Annealing
Powder X-ray diffraction
Mix homogeneous samples
Mechanical mill (5 min)

Composition – Microprobe analysis



5.5 – 151 ° 2θ, λ= 1.5385 Å

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