

The Structure and Thermoelectric Properties of New Clathrate Compounds

Douglas P. Savin

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Thermoelectric materials are used for small-scale cooling and power generation applications. The limited use of thermoelectrics on a large scale is a result of the low efficiency of currently available materials.^{1,2} In the search for more efficient thermoelectric materials, one of the obstacles to overcome is the lowering of efficiency by thermal conduction.

One class of compounds currently being investigated toward this end is the semiconducting clathrates. These are compounds formed by the inclusion of atoms in large voids of a crystal lattice of different atoms. The clathrate-I structure, A_8X_{46} , is the focus of the current discussion and is shown in Figure 1A.³ The A atoms are electropositive and are located within the cages formed by the X atoms. Figure 1B shows the two distinct cage structures present, as well as labels for the different sites.³

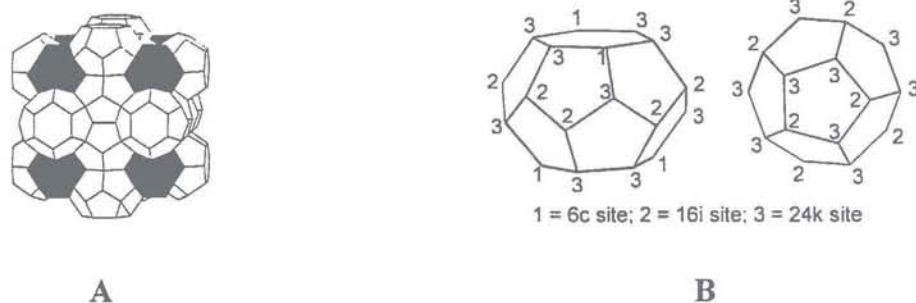


Figure 1

Several binary and pseudo-binary clathrates have been studied. Among them are K_8Sn_{44} , Cs_8Sn_{44} , and $K_{1.6}Cs_{6.4}Sn_{44}$.^{4,5} These have been described as Zintl phases with defect structures in which Sn atoms are missing from one-third of the 6c sites.⁴ Temperature dependent thermal conductivity measurements of Cs_8Sn_{44} resemble those of crystalline insulators, with the lattice thermal conductivity, $\kappa_{\text{lattice}} \propto 1/T$.⁵ Crystallographic refinements for this compound show a large isotropic atomic displacement parameter (ADP) for the 24k site, implying a lack of rigidity in the polyhedra.⁵ In addition, the Cs atoms in the tetrakaidecahedra (A2 site) also exhibit large ADPs.⁵ This has little effect on the temperature dependence of the thermal conductivity, however.⁵ In contrast to the above compounds, the binary clathrate Na_8Si_{46} has also been studied but does not have a defect structure.^{6,7}

Unlike most binary clathrates, ternary clathrates are not defect structures. ADPs for all framework atoms are similar in magnitude, suggesting a rigid cage. The guest atoms within the tetrakaidecahedra show large ADPs, indicating that the ion is “rattling” in the cage.⁸⁻¹⁰ The maximum displacements are observed in the directions parallel to the hexagonal faces of the cage. $\text{Cs}_8\text{Zn}_4\text{Sn}_{42}$ exhibits a $\kappa_{\text{lattice}} \propto 1/T^{0.45}$ dependence.⁵

Studies of clathrates with different guest atoms in the same framework suggest that the cation has little effect on cage size,⁹ supporting the idea of a rigid framework. It was also found that small cations reduce κ_{lattice} more than large cations in the same cage structure.¹¹ This suggests an increase in the “rattle” for smaller ions.

The temperature dependence of the ADPs reveals interesting characteristics of the clathrates. For $\text{Cs}_8\text{Sn}_{44}$, a large low temperature ADP was observed for Sn in the 24k site, suggesting large static disorder caused by the missing 6c Sn atoms.⁵ The same type of ADPs were seen for the electropositive atoms in the tetrakaidecahedra of $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$.¹² $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ possesses a $\kappa_{\text{lattice}}(T)$ characteristic of an amorphous solid.

Experiments have been done to elucidate the effects of non-stoichiometric elemental compositions and doping on thermoelectric parameters. Small deviations from the ideal stoichiometry led to large changes in electric properties.¹³ The same is true of doping. Indeed, one doped clathrate synthesized this year was found to exhibit p-type semiconducting behavior and is the first reported example of a p-type clathrate.¹⁴ This demonstrates the high degree of doping that can be achieved in semiconducting clathrates.¹⁴ In addition, greater efficiency is achieved in a thermoelectric device with n-type and p-type couples as opposed to n-type and metal couples.

Clathrates with glasslike κ_{lattice} values may become the thermoelectric materials of the future, but for this to occur the electronic properties must be optimized. Optimization through doping must be explored. This will undoubtedly produce more p-type clathrate compounds to compliment the wealth of n-type clathrates.

References

- 1) Blake, N. P.; Mollnitz, L.; Kresse, G.; Metiu, H. "Why Clathrates are Good Thermoelectrics: A Theoretical Study of $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$," *J. Chem. Phys.* **1999**, *111*, 3133-3144.
- 2) Kuznetsov, V. L.; Kuznetsova, L. A.; Kaliazin, A. E.; Rowe, D. M. "Preparation and Thermoelectric Properties of $\text{A}_8^{\text{II}}\text{B}_{16}^{\text{III}}\text{B}_{30}^{\text{IV}}$ Clathrate Compounds," *J. Appl. Phys.* **2000**, *87*, 7871-7875.
- 3) Bobev, S.; Sevov, S. C. "Clathrates of Group 14 with Alkali Metals: An Exploration," *J. Solid State Chem.* **2000**, *153*, 92-105.

- 4) Zhao, J.-T.; Corbett, J. D. "Zintl Phases in Alkali-Metal-Tin Systems: K_8Sn_{25} with Condensed Pentagonal Dodecahedra of Tin. Two A_8Sn_{44} Phases with a Defect Clathrate Structure," *Inorg. Chem.* **1994**, *33*, 5721-5726.
- 5) Nolas, G. S.; Chakoumakos, B. C.; Mahieu, B.; Long, G. J.; Weakley, T. J. R. "Structural Characterization and Thermal Conductivity of Type-I Tin Clathrates," *Chem. Mater.* **2000**, *12*, 1947-1953.
- 6) Tse, J. S.; Uehara, K.; Rousseau, R.; Ker, A.; Ratcliffe, C. I.; White, M. A.; MacKay, G. "Structural Principles and Amorphouslike Thermal Conductivity of Na-Doped Si Clathrates," *Phys. Rev. Lett.* **2000**, *85*, 114-117.
- 7) Ramachandran, G. K.; McMillan, P. F.; Diefenbacher, J.; Gryko, J.; Dong, J.; Sankey, O. F. " ^{29}Si NMR Study on the Stoichiometry of the Silicon Clathrate Na_8Si_{46} ," *Phys. Rev. B* **1999**, *60*, 12294-12298.
- 8) Nolas, G. S.; Weakley, T. J. R.; Cohn, J. L. "Structural, Chemical, and Transport Properties of a New Clathrate Compound: $Cs_8Zn_4Sn_{42}$," *Chem. Mater.* **1999**, *11*, 2470-2473.
- 9) Schujman, S. B.; Nolas, G. S.; Young, R. A.; Lind, C.; Wilkinson, A. P.; Slack, G. A.; Patschke, R.; Kanatzidis, M. G.; Ulutagay, M.; Hwu, S.-J. "Structural Analysis of $Sr_8Ga_{16}Ge_{30}$ Clathrate Compound," *J. Appl. Phys.* **2000**, *87*, 1529-1533.
- 10) Chakoumakos, B. C.; Sales, B. C.; Mandrus, D. G.; Nolas, G. S. "Structural Disorder and Thermal Conductivity of the Semiconducting Clathrate $Sr_8Ga_{16}Ge_{30}$," *J. Alloys Compd.* **2000**, *296*, 80-86.
- 11) Cohn, J. L.; Nolas, G. S.; Fessatidis, V.; Metcalf, T. H.; Slack, G. A. "Glasslike Heat Conduction in High-Mobility Crystalline Semiconductors," *Phys. Rev. Lett.* **1999**, *82*, 779-782.
- 12) Nolas, G. S.; Weakley, T. J. R.; Cohn, J. L.; Sharma, R. "Structural Properties and Thermal Conductivity of Crystalline Ge Clathrates," *Phys. Rev. B* **2000**, *61*, 3845-3850.
- 13) Nolas, G. S.; Cohn, J. L.; Slack, G. A.; Schujman, S. B. "Semiconducting Ge Clathrates: Promising Candidates for Thermoelectric Applications," *Appl. Phys. Lett.* **1998**, *73*, 178-180.
- 14) Lattner, S.; Bu, X.; Blake, N.; Metiu, H.; Stucky, G. "Gallium Antimonide-Doped Germanium Clathrate—A *p*-Type Thermoelectric Cage Structure," *J. Solid State Chem.* **2000**, *151*, 61-64.