The Relationship Between Structure and Thermoelectric Properties of Skutterudites

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State of the art thermoelectric materials are extremely inefficient and are currently only used in very specialized areas such as the cooling of electronics and the supplying of power for deep space probes.[1] Recent interest in the field of thermoelectric materials is due to the need for a replacement of current cooling technology and new power sources. For thermoelectric materials to be used for these purposes, their efficiency must be increased. An efficient thermoelectric material is one that has a low resistivity, a low thermal conductivity, and a high thermopower, which is defined as V/T.[2]

One class of compounds that has received great attention recently for its thermoelectric properties is the skutterudites, which have the general formula AB_3, where A is Co, Ir, or Rh; and B is As, P, or Sb. The skutterudite unit cell is shown in figure 1. This structure is made up of a simple cubic lattice of A atoms, each of which has octahedral coordination to six B atoms. These AB_6 octahedra are corner sharing with six other octahedra and form a structure which is a distorted form of the ReO_3 structure. Within each unit cell are two large holes, that are each surrounded by twelve B atoms.[4] One of these holes are shown in figure 2. These holes range in

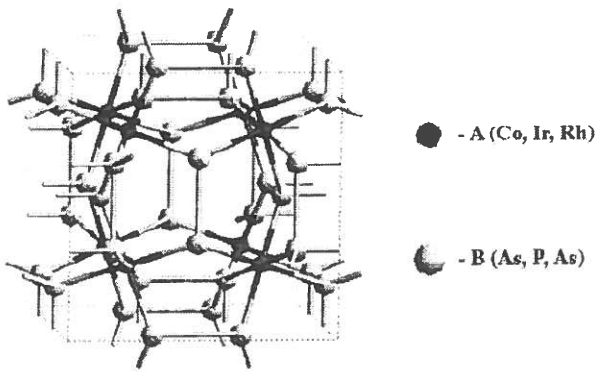

Figure 1

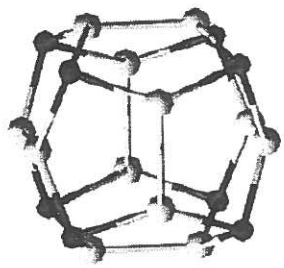

Figure 2

size from 2.526 Å in CoP_3 to 4.080 Å in $IrSb_3$.[5] Most of these compounds have resistivities and thermopowers that are comparable to the best thermoelectric materials known, such as Bi_2Te_3 -Sb_2Te_3 and SiGe. The efficiency of skutterudites, however, is much lower due to their large thermal conductivity.[5,6]

In 1977, Jeitscko showed that skutterudites could be synthesized in which the large hole is filled with an atom. These filled skutterudites have the formula TM_4P_{12} where T is a lanthanide,[7] an alkaline earth metal,[8] or a transition metal;[9] M is Fe, Ru, or Os; and B is P, As, or Sb. This structure is made up of a polyanionic skutterudite framework that contains a cation in the large hole. These compounds can be prepared by high temperature[7] and high pressure techniques.[10] Recently, thin films have also been prepared by depositing modulated thin films

of the elemental reactants by evaporation and then annealing at low temperatures.[11] This new technique has provided an easy route to many filled skutterudite compounds.[11,12]

These filled skutterudites are particularly interesting due to the fact that in many cases the cation is much too small for the hole that it sits in. X-ray and neutron diffraction have shown that these atoms have extremely large mean-square atomic displacements.[13,14] The displacement of the cation has been shown to increase as the size of the hole increases and as the size of the filling cation decreases.[8,13] Two localized vibrational modes of the filling atom have also been identified using heat capacitance measurements and inelastic neutron scattering.[15,16]

Relative to the unfilled skutterudites, filled skutterudites show a dramatic reduction in thermal conductivity.[17,18] Thermoelectric measurements have also shown a relationship between the size of the filling atom and the thermal conductivity of the material.[18,19] As the radius of the filling atom decreases, the mean square atomic displacement increases, and there is a corresponding decrease in thermal conductivity. This structure-property relationship may provide a new tool in the search for more efficient thermoelectric materials.

The filled skutterudites that have been measured are still too inefficient for practical use.[1] Work currently under way includes the measurement of thermoelectric properties of other filled skutterudite compounds, and the optimization of these properties by partial filling.[20] Further studies are also needed to clarify the nature of the bonding interactions between the filling atom and the surrounding framework. Finally, it may be interesting to see if using a mixture of different filling atoms can be used to lower the thermal conductivity further, and to see if this structure-property relationship can be seen in other compounds such as clathrates.

References

1. Winder, E. J.; Ellis, A. B. "Thermoelectric Devices: Solid-State Refrigerators and Electrical Generators In the Classroom," *J. Chem. Educ.* **1996**, 73, 940-946.

2. Sales, B. C "Electron Crystals and Phonon Glasses: A New Path To Improved Thermoelectric Materials," *MRS Bulletin* **1998**, 23, 15-21.

3. Stetson, N. J.; Kauzlarich, S. M.; Hope, H. "The Synthesis and Structure Of Two Filled Skutterudite Compounds: $BaFe_4Sb_{12}$ and $BaRu_4Sb_{12}$," *J. Solid State Chem.* **1991**, 91, 140-147.

4. Sales, B. C.; Mandrus, D.; Chakoumakus, Keppens, V.; Thompson, J. R. "Filled Skutterudite Antimonides: Electron Crystals and Phonon Glasses," *Phys. Rev. B.* **1997**, 56, 15081-15089.

5. Morelli, D .T.; Caillat, T.; Fleurial, J. -P.; Borshchevsky, A.; Vandersande, J.; Chen, B.; Uher, C. "Low-temperature Tansport Properties of p-type $CoSb_3$," *Phys. Rev. B.* **1995**, 51, 9622-9628.

6 Slack, G. A.; Tsoukala, V.G. "Some Properties Of Semiconducting $IrSb_3$," *J. Appl. Phys.* **1994**, 76, 1665-1671.

7. Jeitschko, W.; Braun, D. "$LaFe_4P_{12}$ With Filled $CoAs_3$-Type Structure and Isotypic Lanthanoid-Transition Metal Polyphosphides," *Acta Crystallagr. Sect. B.* **1977**, B33, 3401-3406.

8. Evers, C. B. H.; Boonk, L.; Jeitschko, W. "Alkaline Earth Transition Metal Antimonides AT_4Sb_{12} (A = Ca, Sr, Ba; T = Fe, Ru, Os) With $LaFe_4P_{12}$-Structure," *Z. Anorg. Allg. Chem.* **1994**, 620, 1028-1032.

9. Sellinschegg, H.; Stuckmeyer, S. L.; Hornbostel, M. D.; Johnson, D. J. "Synthesis Of Metastable Post-Transition-Metal Iron Antimony Skutterudites Using the Multilayer Precursor Method," *Chem. Mater.* **1998**, 10, 1096-1101.

10. Shirotani, I.; Adachi, T.; Tachi, K.; Todo, S.; Nozawa, K.; Yagi, T.; Kinoshita, M. "Electrical Conductivity and Superconductivity Of Metal Phosphides With Skutterudite-Type Structure Prepared At High Pressure," *J. Phys. Chem. Solids* **1996**, 57, 211-216.

11. Hornbostel, M. D.; Hyer, E. J.; Thiel, J.; Johnson, D. C. "Rational Synthesis Of Metastable Skutterudite Compounds Using Multilayer Precursors," *J. Am. Chem.Soc.* **1997**, 119, 2665-2668.

12. Hornbostel, M. D.; Hyer, E. J.; Edvalson, J. H.; Johnson, D. C. "Systematic Study Of New Rare Earth-Iron-Antimony Skutterudites Synthesized Using Multilayer Precursors," *Inorg. Chem.* **1997**, 36, 4270-4274.

13. Braun, D. J.; Jeitschko, W. "Preparation and Structural Investigations Of Antimonides With the $LaFe_4P_{12}$ Structure," *J. Less-Common Met.* **1980**, 72, 147-156.

14. Chakoumakos, B. C.; Sales, B. C.; Mandrus, D.; Keppens, V. "Disparate Atomic Displacements in Skutterudite-Type $LaFe_3CoSb_{12}$, a Model For ThermoelectricBehavior," *Acta Crystallagr. Sect. B.* **1999**, B55, 341-347.

15. Nolas, G. S.; Kendziora, C. A. "Raman Spectroscopy Investigation Of Lanthanide-Filled and Unfilled Skutterudites," *Phys. Rev. B.* **1999**, 59, 6189-6192.

16. Keppens, V.; Mandrus, D.; Sales, B. C.; Chakoumakos, B. C.; Dai, P.; Coldea, R.; Maple, M. B.; Gajewski, D. A.; Freeman, E. J.; Bennington, S. "Localized Vibrational Modes In Metallic Solids," *Nature* **1998**, 395, 876-878.

17. Morelli, D. T.; Meisner, G.P. "Low Temperature Properties Of the Filled Skutterudite $CeFe_4Sb_{12}$," *J. Appl. Phys.* **1995**, 77, 3777-3781.

18. Sales, B. C.; Mandrus, D.; Williams, R. K. "Filled Skutterudite Antimonides: A NewClass Of Thermoelectric Materials," *Science* **1996**, 272, 1325-1328.

19. Nolas, G. S.; Slack, G. A.; Morelli, D. T.; Tritt, T. M.; Ehrlich, A. C. "The Effect Of Rare-Earth Filling On the Lattice Thermal Conductivity Of Skutterudites," *J. Appl. Phys.* **1996**, 79, 4002-4008.

20. Nolas, G. S.; Cohn, J. L.; Slack, G. A. "Effect Of Partial Void Filling On the Lattice Thermal Conductivity Of Skutterudites," *Phys. Rev. B.* **1998**, 58, 164-170.