Disorder in Clathrate Materials for Thermoelectric Applications

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Introduction

Thermoelectric devices are widely used in portable solid-state refrigerators. However, there is considerable interest in the development of new materials for these devices as improvements in efficiency may lead to economically viable, environmentally friendly alternatives to chlorofluorocarbon (CFC) based refrigeration and/or as competitive power generation sources. The materials that are currently used were developed by Ioffe in the 1950s.[1] Interest in the subject was heightened about ten years ago by two new ideas,[2] i) the concept of "minimum thermal conductivity", the thermal conductivity that a crystalline lattice would have if it were amorphous, and ii) the "phonon-glass, electron-crystal" (PGEC) concept.

The application of these concepts, to the development of new materials, has led to interest in semiconductors with open structures (zeolite like) that possess cavities big enough to allow the introduction of smaller atoms that can "rattle." Such materials are promising due to their characteristically low thermal conductivities. Of particular recent interest are semiconducting compounds with structures related to those of the clathrate hydrates.[3-6] A large family of clathrates with frameworks constructed from the group IV elements Si, Ge, and Sn exists. There are two dominant structure types for these materials, both of which are cubic: type-I, with typical composition A_8B_{46}, and type-II, with typical composition $A_{24}B_{136}$, where A is an alkali or alkaline-earth atom and B is Si, Ge or Sn. The framework atoms B are often partly substituted by other elements in order to meet the bonding requirements of the structure, examples are compounds such as $Sr_8Ga_8Ge_{16}$ and $Cs_8Cd_4Sn_{42}$ have received attention. The dynamics of the atoms in the "cages" of these clathrates play an important role in determining the thermal conductivity of these materials and the distribution of any "dopant" atoms in the framework can affect their electronic properties.

The crystallographic atomic displacement parameters (ADPs) of the atoms in the cages can provide information regarding the "rattling" of atoms in the cavities. However, for specimens that are only available in powder form, there can be problems in determining accurate ADPs. We have started to explore very high-energy x-rays as a method for eliminating the systematic errors (absorption and extinction) that typically lead to inaccurate ADP estimates in powder x-ray diffraction. Our initial experiments examined the type-II clathrate $Cs_8Na_{16}Ge_{136}$.

The distribution of dopant atoms in the clathrate frameworks can be determined crystallographically if there is sufficient scattering contrast between the elements that comprise the framework. Unfortunately, many of the clathrates of interest for thermoelectric applications are made up of elements that are not readily distinguished from one another by normal x-ray and in some cases neutron diffraction. We report the results of a resonant scattering study on $Cs_8Cd_4Sn_{42}$ where we determine the distribution of Cd over the available framework sites.

Methods and Materials

Powder diffraction data were recorded for $Cs_8Na_{16}Ge_{136}$ at several temperatures between 20 and 298K using 80 keV x-rays from a doubly bent Si(111) Laue monochromator. A triple-axis geometry with a Si(111) analyzer crystal was employed. All the data were analyzed using the Rietveld method. Single-crystal diffraction data were also collected at several temperatures in the range 100 – 298K using Mo Kα radiation so that the ADPs derived from the powder diffraction data could be compared with those from the single-crystal measurements.

Powder diffraction data were recorded for a specimen of $Cs_8Cd_4Sn_{42}$ at 80 keV, just below the Cd K-edge and just below the Sn K-edge. The lower energy data were obtained using a Kohzu 311 double-crystal monochromator. A triple-axis geometry with a Si(111) analyzer crystal was employed for all of these measurements. The three data sets were analyzed as part of a single refinement using the Rietveld method. The resonant scattering factors used in the analysis were determined from transmission absorption measurements on the compound.

Results and Discussion

The ADPs derived from the high-energy powder diffraction measurements on $Cs_8Na_{16}Ge_{136}$ were generally in good agreement with those obtained from the single-crystal data. However, the agreement was not quite as good as would be expected given that both absorption and extinction, the two typical major sources of error, are negligible at 80 keV. A complete discussion of our data analysis and conclusions will be presented elsewhere, but it is clear that high-energy powder diffraction offers a viable alternative to neutron powder diffraction when reasonably accurate ADPs are needed and only powder samples are available.

The resonant scattering measurements on the $Cs_8Cd_4Sn_{42}$ facilitated a precise determination of the cadmium distribution in the framework. No constraints on the chemical composition or site occupancies were applied during the data analysis. The refined chemical composition was extremely close to that expected based on our chemical analysis, and no evidence for any framework vacancies could be found. A complete discussion of our data analysis and conclusions will be presented elsewhere.

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