Resonant Powder Diffraction Study of Gallium Distribution in the Type I Clathrates $Sr_8Ga_{16}Ge_{30}$ and $Sr_4Eu_4Ga_{16}Ge_{30}$

Y. Zhang,[1] G. S. Nolas,[2] P. L. Lee,[1] A. P. Wilkinson[3]
[1]Synchrotron Radiation Instrumentation Collaborative Access Team (SRI-CAT),
Advanced Photon Source, Argonne National Laboratory, Argonne, IL, U.S.A.
[2]Department of Physics, University of South Florida, Tampa, FL, U.S.A.
[3]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA, USA

Introduction

In recent years, there has been an intense search for new thermoelectric materials [1, 2]. Slack has proposed that a good material for thermoelectric applications should combine the electronic properties of a crystal (high charge carrier mobility) with the thermal transport properties of a glass (poor heat transport) [3, 4]. These seemingly contradictory requirements can be found in some clathrates with "rattling" guest species inside their cavities [5-7].

The clathrates have structures similar to the type I and type II gas hydrates [8], but the host frameworks are made up of group 13 and 14 elements and alkali, alkaline, earth, or rare earth atoms as the guests [7]. Previous studies indicate that the type I clathrates $Sr_8Ga_{16}Ge_{30}$ and $Sr_4Eu_4Ga_{16}Ge_{30}$ are good candidates for thermoelectric applications (see Fig. 1) [9-11].

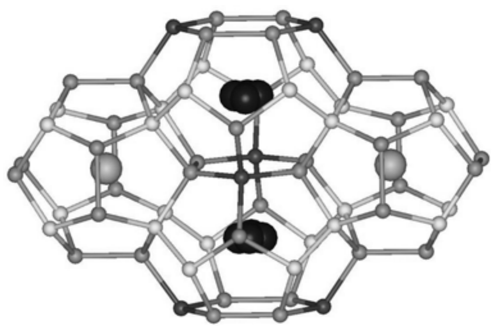

FIG. 1. The $Sr_8Ga_{16}Ge_{30}$ structure. In the framework, the black atoms occupy the 6c sites, the light gray atoms occupy the 16i sites, and the dark gray atoms occupy the 24k sites. In the cavities, the gray atoms are at the Sr(1) 2a sites and the black atoms are at the Sr(2) 24k sites.

Little is known about the static disorder of gallium and germanium in their frameworks because of the lack of x-ray scattering contrast between gallium and germanium. Neutron diffraction provides only 10% contrast. Electronic structure calculations for $Sr_8Ga_{16}Ge_{30}$ suggest that the lowest energy arrangement of the framework components in this compound is nonrandom [12]. However, the neutron diffraction results suggest a random distribution of gallium and germanium in $Sr_8Ga_{16}Ge_{30}$. Compared with neutron and conventional x-ray diffraction, resonant x-ray scattering can provide considerably more contrast in the case of gallium and germanium.

Methods and Materials

X-ray data were acquired at the SRI-CAT 1-BM beamline. Data sets recorded near the Ga and Ge K edges were employed for the examination of $Sr_8Ga_{16}Ge_{30}$, and data sets recorded at the Ga, Ge, and Sr K edges were used to study $Sr_4Eu_4Ga_{16}Ge_{30}$. Transmission absorption spectra were obtained at the Ga, Ge, and Sr K edges from thin samples supported on tape. All diffraction patterns were collected at room temperature by using a flat-plate geometry with a Si(111) double-crystal sagitally focusing monochromator, a Si(111) analyzer crystal, and an Oxford Cyberstar detector. The program GSAS was employed for the Rietveld refinements (Fig. 2).

Results and Discussion

The refinement for $Sr_8Ga_{16}Ge_{30}$ [a = 10.73637(4) Å, Pm-3n] shows a strong preference of gallium for the 6*c* site [75.9(4)% occupancy] and a weaker preference for the 24*k* site [43.2(3)% occupancy], with only 23.8(3)% occupancy of the 16*i* site. These occupancy values are comparable to those previously suggested on the basis of electronic structure calculations. The stoichiometry from the refinement [$Sr_8Ga_{18.74(9)}Ge_{27.26(9)}$] is only slightly different from what was expected ($Sr_8Ga_{16}Ge_{30}$), which provides confidence in the results from the refinement.

The results from our analysis of $Sr_4Eu_4Ga_{16}Ge_{30}$ [10.72768(1) Å] also strongly suggest a nonrandom distribution of gallium. The refined gallium occupancies for the 6*c* [69.7(6)%], 16*i* [18.0(5)%], and 24*k* [30.9(4)%] sites are similar to those seen for $Sr_8Ga_{16}Ge_{30}$, but there is a slight deficiency of Ga at the 24*k* site in $Sr_4Eu_4Ga_{16}Ge_{30}$ compared with $Sr_8Ga_{16}Ge_{30}$. The refined stoichiometery ($Sr_{4.53(3)}Eu_{3.47(3)}$ $Ga_{14.48(13)}$ $Ge_{31.52(13)}$) is in satisfactory agreement with what was expected ($Sr_4Eu_4Ga_{16}Ge_{30}$).
Our observation that gallium atoms have a strong preference for the occupation of 6*c* sites in both $Sr_8Ga_{16}Ge_{30}$ and $Sr_4Eu_4Ga_{16}Ge_{30}$ is consistent with recent theoretical predictions and experimental observations of other type I clathrates that have no scattering contrast

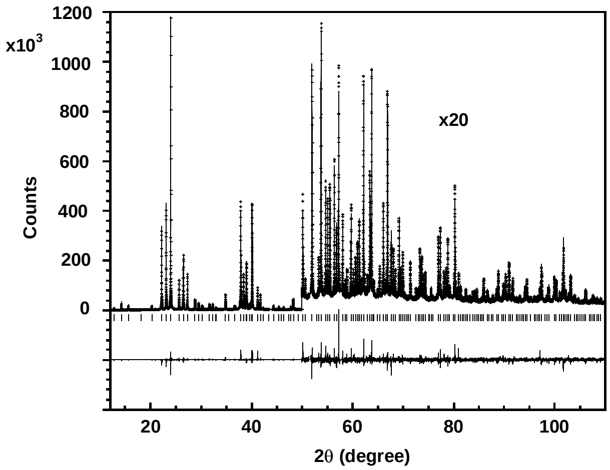

FIG. 2. The Rietveld fit to the 10.367-keV diffraction data for $Sr_8Ga_{16}Ge_{30}$. Dots are the observed counts, continuous line is the best fit. The difference (obs - calc) is shown at the bottom of the plot, along with tag marks indicating the expected peak positions.

difficulties, but it is contrary to the reported neutron diffraction studies of $Sr_8Ga_{16}Ge_{30}$ and $Eu_8Ga_{16}Ge_{30}$ [11]. A more complete account of this work has recently been published [13].

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