Synchrotron X-ray structure refinement of Zn$_4$Sb$_3$

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Abstract

The structure of the thermoelectric Zn$_4$Sb$_3$ is refined using synchrotron X-ray powder diffraction data collected at wavelengths both near to and relatively far from the Zn adsorption edge. In agreement with earlier studies, the compound crystallized in a trigonal structure, space group $R \bar{3} c$ with $a = 12.2406(3)\text{Å}$, $c = 12.4361(3)\text{Å}$ at room temperature, and there are three primary sites in the asymmetric unit. Each site contains only one atomic species, in contrast to many previous studies. The primary Zn (36f) site is slightly less than fully occupied, whereas the two Sb sites (18e and 12c) are fully occupied. In addition, several Zn interstitial sites (36f) with low occupancies (>5%) are also present. The results are in agreement with the model proposed by Snyder [1], as opposed to that originally proposed by Mayer [2] and more recently by Mozharivskyj [3]. The refined site occupancies yield an overall stoichiometry which is consistent with that measured experimentally. The presence of interstitial Zn can be understood in terms of charge balance requirements and is likely responsible for the exceptionally low thermal conductivity of this material.

Keywords
Zinc antimonide, Zn$_4$Sb$_3$, crystal structure, structural disorder, Rietveld refinement, Zintl phase.

Introduction

The development of efficient thermoelectric devices for both space and terrestrial applications requires the discovery of materials with a high thermoelectric figure of merit, $zT$, defined as $\alpha^2\sigma/\kappa$, where $\alpha$ is the Seebeck coefficient, $\sigma$ the electrical conductivity and $\kappa$ the thermal conductivity. Of known thermoelectrics, the compound Zn$_4$Sb$_3$ has attracted recent attention because it has the highest reported value of $zT$ at moderate temperatures (reaching almost 1.3 at 400°C) [4,1]. This behavior is a result of the particularly low thermal conductivity of Zn$_4$Sb$_3$, being lower by as much as a factor of 4,1. This behavior is a result of the particularly low thermal conductivity of Zn$_4$Sb$_3$, being lower by as much as a factor of

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In this study we have reexamined the structure of ‘Zn$_4$Sb$_3’ in an attempt to resolve the continuing controversy regarding its crystal-chemical nature. By making use of anomalous scattering of Zn at two wavelengths ($\lambda = -5.7$ and -1.3 for the two data sets) we can distinguish mixed occupancy from vacancies.

Experimental Procedure

The powder sample was obtained by direct reaction of the constituent elements from the melt. For this zinc (99.9999%) and antimony (99.999%) shots were combined in a 57.5:42.5 atomic ratio and processed in a silica ampoule.

High-resolution X-ray powder diffraction data were recorded at room temperature in $\theta$–2$\theta$ reflection geometry at NSLS beamline X3B1. The sample was side-drifted onto a quartz zero-background holder, rocked $10^\circ$ at each point in order to improve sampling statistics. In two separate data collections, X-rays of wavelength 1.14985 and 1.28788 Å were selected by a double-crystal Si(111) monochromator. High resolution was achieved by analyzing the diffracted beam with a Ge(111) crystal placed before the NaI scintillation counter. Data were collected from 16.000° to 77.765° 2$\theta$ and 18.000° to 89.990° 2$\theta$, respectively, for the two wavelengths using a step size of 0.005° and counting time of 5 sec. The incoming beam was monitored by an ion chamber and the recorded data normalized for its fluctuations and decay.

Rietveld refinement was performed simultaneously for the two datasets using the program GSAS [8] with EXPGUI interface [9]. The presence of elemental Zn was detected in the diffraction data and this second phase was included in the model refinement. In addition, a peak of unknown origin at $d = 1.805$ Å was observed in both histograms and thus the region about this peak was omitted from the analysis.
Refinement Procedure and Results

The initial parameters for the refinement of the structure of Zn₄Sb₃ were taken from Mayer [2], which contains at its core one Zn 36f site and two Sb sites: Sb(1) on an 18e site and Sb(2) on a 12c site, Table 1. The key question to be addressed was the atomic occupancy factors, in particular the possible incorporation of Zn on the Sb(1) site and the existence of additional 36f sites for Zn. Accordingly, the lattice constants, atomic coordinates of the three primary sites, and all profile parameters were refined early in the analysis and fixed at their optimal values for subsequent comparisons of structural models that differed primarily in terms of site occupancies.

Table 1. Structure of Zn₄Sb₃ as originally reported by Mayer [2] and used as the starting point for the present refinements.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(1)</td>
<td>36(f)</td>
<td>0.0794</td>
<td>0.2437</td>
<td>0.4037</td>
</tr>
<tr>
<td>Sb(1) [+Zn]</td>
<td>18(e)</td>
<td>0.3554</td>
<td>0</td>
<td>0.1365</td>
</tr>
<tr>
<td>Sb(2)</td>
<td>12(c)</td>
<td>0</td>
<td>0</td>
<td>0.1365</td>
</tr>
</tbody>
</table>

Refinement of the Sb occupancies showed these sites to be fully occupied with occupancy factors typically settling at values just above 1, without improvement in the refinement statistics. Because Zn is a lighter element than Sb, its presence on the Sb(1) site would result in an apparent reduction in the occupancy on this site. Thus, we can immediately conclude that the model proposed by Mayer [2], with partial (11%) Zn occupancy on the Sb(1) site does not describe the true structure of Zn₄Sb₃.

With the occupancies of the Sb atoms fixed at one and their isotropic thermal displacement parameters optimized and then fixed, the Zn occupancy factor was probed. Because of the high correlation between occupancy factor and thermal displacement parameter, these terms were adjusted cautiously. In all cases, the occupancy factor dropped substantially below 1 (to 0.915) and resulted in a slight but statistically significant improvement in the refinement. As would be expected, the isotropic thermal displacement parameter for this atom also decreased substantially from a highly unreasonable value to one that was about a factor of three greater than that of the Sb atoms.

In the final step, Zn interstitial atoms were introduced at sites determined from our previous single crystal diffraction study, reported in Snyder et al. [1]. Doing so improved the refinement statistics considerably, and the three sites displayed statistically significant occupancy factors. Again, because of the high correlation between occupancy and thermal displacement parameters, these terms were varied cautiously and in the final cycles of the refinement the three interstitial atoms were assigned a fixed isotropic displacement parameter that corresponded to the average value that was obtained upon varying the three terms independently. The excellent fit to the experimental diffraction data obtained from this model supports the proposal that Zn exists at interstitial positions within the ‘core’ structure of Zn₄Sb₃.

Table 2. Comparison of refinement statistics for the models of ‘Zn₄Sb₃’ and the stoichiometries implied. The full occupancy model is as proposed by Mayer [2]; the vacancy model [3] assumes the Zn site to be 91.5% occupied; and the three interstitial model assumes, in addition, vacancies on the primary Zn site, that three Zn interstitial sites exhibit 3.6-6.5% occupancy, Table 3.

<table>
<thead>
<tr>
<th>Model</th>
<th>(R_F) (%)</th>
<th>(\chi^2)</th>
<th>3.6-6.5% occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full occupancy</td>
<td>12.31</td>
<td>5.218</td>
<td>3.60</td>
</tr>
<tr>
<td>Zn vacancy</td>
<td>12.22</td>
<td>5.136</td>
<td>3.30</td>
</tr>
<tr>
<td>Three interstitial</td>
<td>11.62</td>
<td>4.648</td>
<td>3.88</td>
</tr>
</tbody>
</table>

Table 3. Final refinement statistics and crystallographic data for the three interstitial site model of Zn₄Sb₃.

<table>
<thead>
<tr>
<th>Space Group</th>
<th>(R_F) (no. 62)</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>(Z)</th>
<th>(V) (Å³)</th>
<th>(R_p \times 100)</th>
<th>(R_w \times 100)</th>
<th>(R_F^2 \times 100) [Hist1]</th>
<th>(R_F^2 \times 100) [Hist2]</th>
<th>(\chi^2)</th>
<th>(Zn(1) x)</th>
<th>(Zn(1) y)</th>
<th>(Zn(1) z)</th>
<th>(Zn(1) U_{iso})</th>
<th>(Zn(1)) occupancy</th>
<th>Zn(2) (U_{iso})</th>
<th>Zn(3) (U_{iso})</th>
<th>Zn(4) (U_{iso})</th>
<th>Zn(2) (U_{iso})</th>
<th>Zn(3) (U_{iso})</th>
<th>Zn(4) (U_{iso})</th>
</tr>
</thead>
<tbody>
<tr>
<td>R̃c</td>
<td>12.233 Å</td>
<td>12.428 Å</td>
<td>10</td>
<td>1613.693(4)</td>
<td>3.14</td>
<td>11.62</td>
<td>16.57</td>
<td>11.78</td>
<td>4.648</td>
<td>Zn(1) x</td>
<td>0.07999(9)</td>
<td>0.24318(9)</td>
<td>0.40152(9)</td>
<td>0.35645(4)</td>
<td>0.00751(14)</td>
<td>0.13656(5)</td>
<td>0.00733(18)</td>
<td>0.0607(19)</td>
<td>0.0364(21)</td>
<td>0.0649(21)</td>
<td></td>
</tr>
</tbody>
</table>

1 with remaining coordinates as given in Table 1.
2 with fixed isotropic displacement parameter of 0.085 and fixed atomic coordinates as given in [1]: Zn(2) at 0.1574, 0.4207, 0.0715; Zn(3) at 0.242, 0.460, 0.200; Zn(4) at 0.126, 0.2367, 0.276.
Figure 1. Measured (black) and calculated (red) X-ray diffraction data for the three interstitial site model of Zn$_4$Sb$_3$, Table 3; (a) $\lambda = 1.14985$ Å and (b) $\lambda = 1.28788$ Å. Difference curve shown in blue and phase peak positions in magenta.
The full occupancy model corresponds to that in which the three primary sites are fully occupied and mixed occupancies are not permitted. The vacancy model corresponds to that proposed by Mozharivskyj [3] in which the two Sb sites are fully occupied by Sb only, but the Zn site occupancy takes on the refined value of 0.915. The three interstitial model corresponds to that in which the three primary sites are stoichiometrically required, surely results from the close proximity of the interstitial sites to the primary site, Figure 2. This work was funded by the NSF through Caltech’s Center for the Science and Engineering of Materials (MRSEC program). NSLS beamline X3 was partially supported by the Department of Energy under grant no. DE-FG02-86ER 45231. The National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

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