

DISORDERED ZINC IN THERMOELECTRIC MATERIAL Zn_4Sb_3 WITH PHONON-GLASS AND ELECTRON-CRYSTAL PROPERTIES

By converting waste heat into electricity, thermoelectric generators could be an important part of the solution to today's energy challenges. The compound Zn_4Sb_3 is one of the most efficient thermoelectric materials known. Its high efficiency results from the extraordinarily low thermal conductivity in conjunction with the electronic structure of a heavily doped semiconductor. The efficiency of a thermoelectric generator depends on the thermoelectric figure of merit zT , where z is defined as $z = S^2\sigma/\kappa$ (S is the Seebeck coefficient, σ the electrical conductivity, and κ is the thermal conductivity). S and σ in Zn_4Sb_3 are not exceptionally high, and the power factor ($S^2\sigma$) is only half that of optimally doped $(Bi, Sb)_2Te_3$ [1]. It is the extremely low lattice contribution to the thermal conductivity, which gives Zn_4Sb_3 a very high zT . Previous structural studies have been unable to explain the unusual properties [2]. We have determined the maximum entropy method (MEM) electron density (ED) from synchrotron X-ray powder diffraction data, and Bader topological analysis [3] of the MEM density reveals that the origin of the remarkable physical properties is additional interstitial zinc atoms [1]. The discovery of glass-like interstitial sites uncovers a highly effective mechanism for reducing thermal conductivity. The analysis also leads to the identification of Sb^{3-} ions and Sb_2^{4-} dimers, and this shows that Zn_4Sb_3 is a Zintl semiconductor with ideal stoichiometry $Zn_{13}Sb_{10}$ [4].

Accurate diffraction studies of high symmetry inorganic solids containing heavy atoms are very challenging. Systematic errors such as absorption, extinction, anomalous scattering and twinning can seriously compromise the level of structural detail that can be extracted from the data. To overcome these problems we have used high energy synchrotron X-ray powder diffraction on a minute sample (0.2 mm capillary) at beamline **BL02B2**. The accuracy of the diffraction data is critical when MEM analysis is used, since the MEM has no "filter" to remove systematic discrepancies in the data [5]. The MEM has in recent years provided insight into the structure and chemical bonding in many interesting solids [6]. However, the limitation of the method has been that visualization of the thermally smeared ED only provides qualitative information. To quantify the electronic features we have used Bader topological analysis [4]. Our results show that important new information can be obtained

by this method, and it greatly enhances the potential for extracting useful chemical and physical information from MEM EDs.

High-resolution synchrotron X-ray powder diffraction data were collected with $\lambda = 0.42061 \text{ \AA}$ ($d_{\min} = 0.626 \text{ \AA}$). The space group is $R-3c$ with $a = 12.22320(4)$, $c = 12.41608(7) \text{ \AA}$. The details of combined Rietveld/MEM analysis of powder diffraction data have been extensively presented in the literature [6]. In Figs. 1 and 2 the crystal structure and the corresponding MEM thermally smeared ED are shown. Interstitial zinc atoms are clearly observed as small secondary maxima in the MEM density. Based on bonding distances there are 18 free Sb^{3-} ions ($Sb1$) and 6 $(Sb2)^{4-}$ dimers ($Sb2$) in the unit cell requiring a total donation of 78 electrons from 39 Zn^{2+} ions for charge balance [1]. This is close to the stoichiometry of the present model, and Zn_4Sb_3 may be considered a Zintl phase. The MEM density provides direct evidence for the Zintl model, and the Sb-Sb dimer does indeed show covalent bonding density, Fig. 2. In contrast, the ED of the other Sb atom is more spherical. Bader topological analysis of the MEM ED establishes six maxima corresponding to two Sb atoms and one Zn atom forming the basic crystal structure, and three Zn interstitials. The positions of the maxima give a quite short Zn-Zn contact of 2.13 \AA . However, since X-ray diffraction measures the average crystal structure, all the

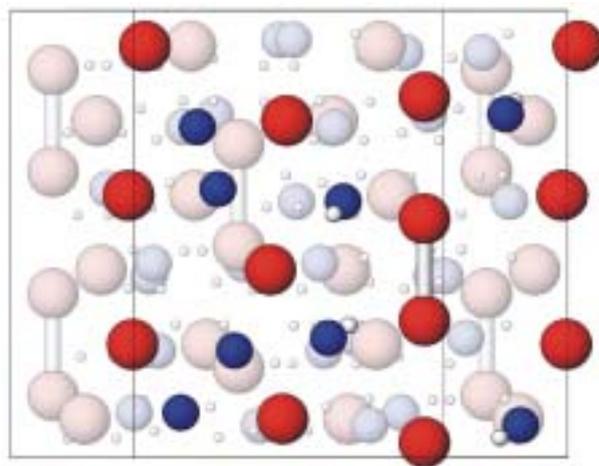


Fig. 1. The crystal structure of Zn_4Sb_3 including three interstitial Zn sites (small spheres). Sb atoms are red, Zn atoms on the main lattice site are blue. Atoms in or near the plane of Fig. 3 are highlighted.

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interstitials are not necessarily present in the same unit cell. Nevertheless, we have refined a model with a restraint of 2.25 Å on the Zn-Zn distances. The restraint distance of 2.25 Å was determined from a series of refinements where the distance restraint on the Zn-Zn contacts was increased in steps between 2.0 to 2.5 Å. A minimum in Rietveld refinement reliability factors was found for 2.25 Å. Hg and Cd dimers are well known but only very recently firm experimental evidence for a Zn dimer was reported with a Zn-Zn distance of 2.30(3) Å [7]. There are other peculiar features in the MEM density. On the “back side” of the Sb dimer we locate a small maximum along the *c*-axis. This non nuclear maximum (NNM) is unlikely to be interstitial atoms, since the Sb sites are fully occupied and the Sb to NNM distance is very short. In Fig. 3 the Bader atomic basins are shown for the different types of atoms. The plot shows that the Sb atoms indeed have very different volumes and charge distributions. The atomic volume of the NNM fits perfectly into a void in the Sb₂ atomic volume along the *c*-axis. The NNM suggests that Zn₄Sb₃ may in fact also have Sb disorder along the *c*-axis. In summary the density contains one partly occupied main Zn site, three Zn interstitials and Sb disorder along the *c*-axis. These are all features which contribute to the drastic reduction of the thermal conductivity.

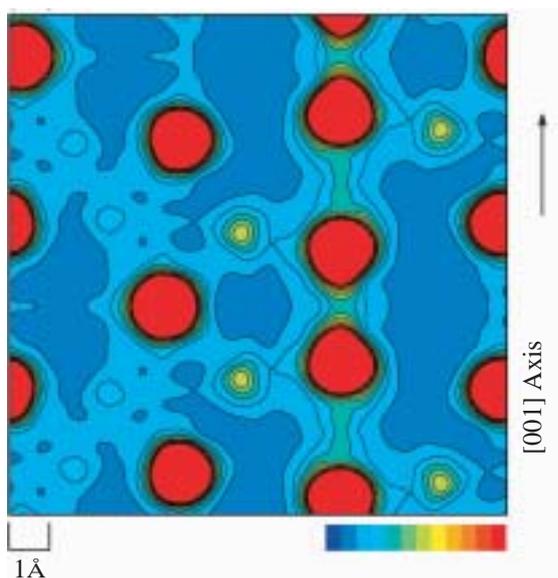


Fig. 2. Contour plot of the MEM density in the Sb₂⁴⁺ dimer region. The contour level is 0.2 e/Å³.



Fig. 3. Atomic surfaces defined by the Bader zero flux condition. The Zn₄Sb₃ structure is viewed nearly along the *c*-axis. The light shiny green basins along the *c*-axis correspond to the “dimer” Sb atom. At the top of the Sb dimer a non nuclear maxima (blue) fits exactly into the void. The red basin is the main Zn atom, the purple basins the interstitial Zn atoms, and the matt green basin is the Sb³⁻ ion.

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