

The Structure of α - Zn_4Sb_3 : Ordering of the Phonon-Glass Thermoelectric Material β - Zn_4Sb_3

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The β -modification of Zn_4Sb_3 is considered as a state-of-the-art thermoelectric material.¹ The key to the high thermoelectric performance lies in the exceptional thermal conductivity, which is as low as that for glasslike materials.² Although β - Zn_4Sb_3 was already discovered in the late 1960s³ and subsequently structurally characterized,⁴ the nature of its peculiar thermal conductivity behavior remained unknown. Very recently Snyder et al.⁵ and Cargoni et al.⁶ provided a plausible reason for this phenomenon when identifying a high degree of intricate disorder in the Zn substructure of β - Zn_4Sb_3 . Structural disorder on the atomic level is one means to effectively damp heat-carrying phonons.^{7,8} Naturally, thermal conductivity is lowest in amorphous glasses, but on the other hand the low electron mobility inherent to glasses is not appropriate for a thermoelectric material. As a matter of fact, the ideal material is a “phonon glass—electron crystal”⁹ and β - Zn_4Sb_3 seems to fulfill these contradictory demands.

At around 260 K β - Zn_4Sb_3 transforms to a low-temperature α -form¹⁰ whose structure hitherto evaded solution.¹¹ Clearly, knowledge of the α - Zn_4Sb_3 structure and the mechanism of the $\alpha \leftrightarrow \beta$ phase transition would give invaluable additional insight into the nature of the complicated disorder in β - Zn_4Sb_3 . In this work we report on the complex crystal structure and electronic structure of the low-temperature phase α - Zn_4Sb_3 . Surprisingly, α - Zn_4Sb_3 turns out to be completely ordered, and the order—disorder $\alpha \leftrightarrow \beta$ phase transition appears to be reversible. We show further that the composition of both forms of Zn_4Sb_3 is actually $\text{Zn}_{13}\text{Sb}_{10}$ ($\text{Zn}_{3.9}\text{Sb}_3$) and that with this composition the electronic structure of both phases corresponds to that of a narrow-gap semiconductor, which actually is prerequisite for a thermoelectric material.^{7,8} We consider these findings as an essential step toward a complete understanding of the remarkable thermoelectric properties of this material. Such an understanding must eventually provide a key for optimizing performance of Zn_4Sb_3 , for example by doping, and possibly develop it into a technological material.

A well-shaped crystal was selected from a β - Zn_4Sb_3 sample,¹² and single-crystal X-ray diffraction data were collected first at 300 K. Indexing yielded the R-centered hexagonal unit cell of β - Zn_4Sb_3 ($a = 12.204(2)$ Å, $c = 12.411(2)$ Å). Subsequently the measurement was performed at 150 K. Now the diffraction pattern exhibited pronounced superstructure reflections along the reciprocal $[011]^*$ directions in the rhombohedral cell, quadrupling this direction. A monoclinic C-centered unit cell was obtained ($a = 32.536(5)$ Å, $b = 12.237(2)$ Å, $c = 10.862(2)$ Å, $\beta = 98.77(3)^\circ$) which agrees well with the cell reported by Mozharivskiy et al.¹¹ Group—subgroup considerations and extinction conditions give only one centrosymmetric possibility, triclinic $C\bar{1}$. The cell is metrically monoclinic (indeed, trigonal) due to pseudomerohedry. A structure solution was found, yielding 20 unique Sb atoms and 26 fully

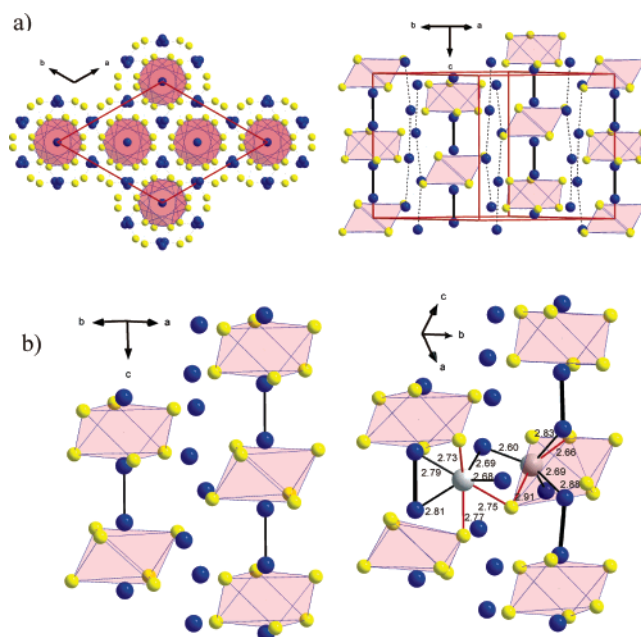


Figure 1. Comparison between the structures of α - and β - Zn_4Sb_3 . Yellow and blue spheres denote Zn and Sb atoms, respectively. (a) Idealized framework $\text{Zn}_{36}\text{Sb}_{30}$ of β - Zn_4Sb_3 shown along the [001] (left part) and approximately [110] (right part) directions. This framework consists of channels built from Zn_2Sb_2 diamonds (thin lines in the upper figure) and stuffed by linear chains of Sb2 atoms (cf. Supporting Information). All Zn atoms are situated at corners of isolated octahedra (pink). Short distances between linear chain forming Sb2 atoms (2.82 Å) are indicated with bold lines. The broken lines between Sb1 atoms forming spirals along the c direction are merely a guide for the eye. (b) Smaller section of the idealized framework of rhombohedral β - Zn_4Sb_3 along [110] (left-hand side) depicted together with a corresponding segment of the α - Zn_4Sb_3 ($\text{Zn}_{13}\text{Sb}_{10}$) structure (right-hand side). Additional Zn atoms in α - Zn_4Sb_3 (a pair) are represented by large gray spheres. Their coordination environment is highlighted.

occupied, unique Zn atoms.¹³ When diffraction data were re-collected at 300 K, the superstructure reflections clearly visible at 150 K had disappeared, and the rhombohedral unit cell of β - Zn_4Sb_3 was retained.

The idealized structure of β - Zn_4Sb_3 is depicted in Figure 1a. It contains three distinct atomic positions (36 Zn, 18 Sb1, and 12 Sb2 in space group $R\bar{3}c$) and can be described as consisting of channels formed by the Zn and Sb1 atoms running along the [001] direction. The channels are centered by chains of Sb2 atoms, which are located on the three-fold axes. The chains of Sb2 atoms display alternating short (2.84 Å) and long (3.38 Å) contacts. Each Sb2 atom is additionally coordinated to three Zn atoms and attain a tetrahedral environment (see Figure 1, Supporting Information). Thus, pairs of Sb2 atoms become situated between Zn_6 octahedra. These octahedra, which involve all Zn atoms in the structure, are

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not structural entities in terms of bonding but provide a convenient object for describing the structure of both, α -Zn₄Sb₃ and β -Zn₄Sb₃.

The cell content of the idealized β -Zn₄Sb₃ structure amounts to just Zn₃₆Sb₃₀ (Zn_{3,6}Sb₃), which implies a significant deviation from the nominal composition. Recently discovered disorder in β -Zn₄Sb₃ manifests in the framework Zn position, which displays a considerable occupational deficiency (0.89–0.90) and in the occurrence of three weakly occupied (by around 0.06) general positions representing interstitial Zn atoms. The composition obtained from the refined occupancies in refs 5 and 6 is Zn_{3,83}Sb₃ and Zn_{3,84}Sb₃, respectively. The C-centered unit cell of triclinic α -Zn₄Sb₃ contains 104 Zn and 80 Sb atoms, and thus the composition of α -Zn₄Sb₃ is Zn₁₃Sb₁₀ (Zn_{3,9}Sb₃). Since it is unconceivable that the composition can change reversibly during our single crystal X-ray investigation first at 300 K, then at 150 K, and finally again at 300 K, the actual composition of β -Zn₄Sb₃ has to be the same as that of α -Zn₄Sb₃, i.e., Zn_{3,9}Sb₃, which is close to the reported values in refs 5 and 6. The volume per formula unit Zn₁₃Sb₁₀ of α -Zn₄Sb₃ at 150 K and β -Zn₄Sb₃ at 300 K are virtually the same (533.8 and 533.6 Å³, respectively). With respect to the idealized (i.e., fully occupied) Zn₃₆Sb₃₀ framework of rhombohedral β -Zn₄Sb₃ the unit cell of α -Zn₄Sb₃ contains eight additional atoms. These extra atoms occupy two unique sites (Zn24 and Zn26 in the CIF). They are distributed “pairwise” between rows of Zn₆ octahedra (i.e., the channels in β -Zn₄Sb₃) and coordinated by six (4 Sb + 2 Zn) and seven (4 Sb + 3 Zn) neighboring atoms, respectively (Figure 1b). The additional Zn atoms distort the closest situated octahedra heavily but leave those more distant quite unperturbed. We note that, while the Zn substructures of α - and β -Zn₄Sb₃ deviate strongly locally, the Sb substructures differ only fractionally. It is puzzling that the heavily disordered Zn substructure in β -Zn₄Sb₃ orders completely in α -Zn₄Sb₃ and that the $\alpha \leftrightarrow \beta$ transition, taking place at rather low temperatures, appears to be reversible.

First-principles electronic structure calculations were carried out for α -Zn₄Sb₃ (Zn₁₃Sb₁₀) and the idealized Zn₃₆Sb₃₀ framework of β -Zn₄Sb₃.¹⁴ In the density of states (DOS) for α -Zn₄Sb₃ the Fermi level is exactly situated at a narrow band gap of 0.3 eV separating valence and conduction band (Figure 2, Supporting Information). This phase appears to be electron precise. Formally, the Zintl–Klemm concept could be applied and Zn₁₃Sb₁₀ rewritten as (Zn²⁺)₁₃(Sb¹³⁻)₆(Sb₂⁴⁻)₂. Then the Sb substructure is described as consisting of isolated Sb³⁻ ions and Sb₂⁴⁻ dumbbells. The ionic description, however, is not recognized in the band structure, rather Zn₁₃Sb₁₀ corresponds to a heteroatomic polarized framework structure. This is analogous to III–V semiconductors (e.g., GaAs, InSb) with the diamond structure, but the Zn–Sb framework is more electron poor and thus displays localized multicenter bonding and a much higher complexity. The shape of the DOS for the idealized framework of β -Zn₄Sb₃ is strikingly similar to that of α -Zn₄Sb₃; however, the narrow band gap is now located above the Fermi level. The framework Zn₃₆Sb₃₀ lacks exactly six electrons for a complete filling of the valence band—and a filled valence band has to be the actual electronic structure of β -Zn₄Sb₃ according to its physical properties, which corresponds to that of a narrow gap semiconductor. Thus, to explain the peculiar phonon glass–electron crystal behavior of β -Zn₄Sb₃ interstitial, phonon-damping Zn atoms behave electronically like two-electron donors to a rigid electronic structure provided by the idealized rhombohedral framework Zn₃₆Sb₃₀.

There remain many questions to be answered before the nature of the exceptional thermoelectric performance of β -Zn₄Sb₃ is completely understood. However, we believe that the recently reported structural disorder in β -Zn₄Sb₃^{5,6} together with our crystal and electronic structure characterization of α -Zn₄Sb₃ represents a milestone which will trigger massively further research. The important issue of the actual composition of the phases is now settled (Zn₁₃Sb₁₀). The next step is to connect unambiguously the glasslike thermal conductivity of β -Zn₄Sb₃ to the occurrence of disorder by thermal conductivity measurements during the $\alpha \leftrightarrow \beta$ phase transition. Further, the exact nature of this remarkable reversible order–disorder transition has to be revealed. A detailed investigation of the structural and transport property changes during the $\alpha \leftrightarrow \beta$ transition is currently underway.

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Supporting Information Available: An X-ray crystallographic file in CIF format. A figure showing the local coordination environment of the atoms in Zn₃₆Sb₃₀ and a figure showing the DOS for triclinic Zn₁₃Sb₁₀ and rhombohedral Zn₃₆Sb₃₀. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) β -Zn₄Sb₃ was prepared from a reaction mixture Zn₄Sb₃ (total amount 0.5 g), which was pressed into a pellet and heated to 923 K in an evacuated quartz tube. Subsequently, the sample was slowly cooled (at a rate of 5 K/h) to 723 K and then quenched in water. The obtained product was single-phase β -Zn₄Sb₃, which was characterized by X-ray diffraction patterns taken on a Guinier powder camera (Cu K α) and by compositional analysis with energy-disperse spectroscopy in a JEOL 820 scanning electron microscope (average Zn content: 56.5 at %).
- (13) The crystal structure of α -Zn₄Sb₃ was determined at 150 K using a Stoe IPDS single-crystal X-ray diffractometer (rotating anode Mo K α). Data collection and integration were carried out using the supplied Stoe software. Structure solution and refinement were done using JANA2000 according to the strategy described in the Supporting Information. The obtained unique 26 Zn and 20 Sb positions are fully occupied (within a few esd's). Due to a number of large correlations between anisotropic thermal displacement parameters of different Sb atoms (remind the high (rhombohedral) symmetry of the rigid Sb atom substructure) we chose to carry out the final refinement with only isotropic thermal displacement parameters for all Sb atoms. α -Zn₄Sb₃ (Zn₁₃Sb₁₀): triclinic, C1, $a = 32.536$ (5) Å, $b = 12.237$ (2) Å, $c = 10.852$ (2) Å, $\beta = 98.77$ (3)°, $V = 4270$ (1.5) Å³, $Z = 8$, $T = 150$ K, $\rho_{\text{calc}} = 6.43$ g/cm³, $\mu = 13.35$ mm⁻¹, R1 refined against $F = 0.044$, wR2 = 0.052.
- (14) Electronic structure calculations were performed in the framework of the frozen core all-electron Projected Augmented Wave (PAW) method, as implemented in the program VASP.¹⁵
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