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Thermoelectric properties of the clathrate-I $\text{Ba}_8\text{Ge}_{43}\square_3$

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Abstract

The clathrate-I $\text{Ba}_8\text{Ge}_{43}\square_3$ (space group $Ia\bar{3}d$, no. 230, $a = 21.307(1)$ Å) has been synthesized as single phase and characterized by X-ray powder diffraction and metallographic analysis. Electrical and thermal transport measurements have been performed in the temperature range 5 - 673 K. $\text{Ba}_8\text{Ge}_{43}\square_3$ displays a metal-like electrical resistivity at low temperatures turning into semiconducting-like behavior above 300 K.

I. Introduction

Intermetallic clathrates are considered to be promising candidates for thermoelectric applications at high temperatures.¹ The crystal structure of the most common clathrate-I type can be described as a three dimensional host framework of 4-connected, covalently bonded atoms (e.g., Ga, Si, Ge, Sn) forming 20- and 24-atom cages encapsulating electropositive atoms (e.g., Na, K, Rb, Cs, Sr, Ba, Eu). The interaction between cage atoms and host framework is a key property for understanding the thermoelectric properties of these compounds. So far, the highest thermoelectric figure of merit for a clathrate compound was reported for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ with $ZT \approx 1.35$ at 900 K.² In comparison, the binary archetype, $\text{Ba}_8\text{Ge}_{43}\square_3$,^{3,4} displays only very low ZT values with 0.06 at 693 K.⁵ However, a complete characterization of $\text{Ba}_8\text{Ge}_{43}\square_3$ is important to identify the most promising clathrates among the variety of possible compositions.

$\text{Ba}_8\text{Ge}_{43}\square_3$ was originally predicted to show metallic behavior according to the 8- N rule,^{3,4} because only 12 of the 16 valence electrons related to the Ba atoms are necessary to satisfy electronic requirements of 12 Ge anions surrounding three vacancies. Experimentally, it was found that the compound shows semiconducting behaviour.^{5,6} The apparent discrepancy to the simple valence rules has been tentatively ascribed to an ordering of the framework vacancies resulting in modifications of the electronic band structure near the Fermi level.⁵ On the other hand, investigations on the ternary system $\text{Ba}_{8-x}\text{Eu}_x\text{Ge}_{43}$ ($x < 0.6$) revealed metallic behavior for the whole homogeneity range.⁷ Here we present detailed transport properties measurements of $\text{Ba}_8\text{Ge}_{43}\square_3$ including electrical resistivity, thermopower and thermal conductivity in the 5 - 673 K temperature range. In order to exclude the influence of grain boundary and impurity effects on the transport properties, we developed a preparation route to single-phase polycrystalline samples.

II. Experimental

Polycrystalline samples were synthesized from stoichiometric amounts of Ba (Chempur, 99.9 %) and Ge (Chempur, 99.9999 %) in an argon-filled glove box. $\text{Ba}_8\text{Ge}_{43}\square_3$ is thermodynamically stable in the temperature range 770 - 810°C and could not be obtained as a pure phase by quenching of sealed reaction containers.⁴ To avoid the peritectoid decomposition below 770°C, the elements were placed in a glassy carbon crucible, heated to the melt with an induction furnace and quenched between two steel plates in less than one second to room temperature. The reaction product consists typically of a circular plate of ~ 10 mm in diameter and ~1 mm in thickness. The single-phase character of the samples was confirmed by metallographic analysis (Fig. 1) and X-ray powder diffraction, which shows a relatively narrow half-width of the reflections up to $2\theta = 120^\circ$ (Fig. 2). All reflections were indexed within the space group $Ia\bar{3}d$ ($a = 21.307(1)$ Å), and no reflections of impurity phases were observed. The sample composition was determined to be $\text{Ba}_{8.0(1)}\text{Ge}_{43.0(1)}$ according to WDXS results. Within the experimental accuracy of the measurements, the reaction product is homogeneous.

Electrical and thermal transport properties were measured on parallelepipeds ($1 \times 2 \times 8$ mm³) cut from the as-cast sample over 5 - 350 K by means of a 4-point and a steady-state method, respectively (Physical Properties Measurement System, Quantum Design). Due to heat losses towards higher temperatures, the thermal conductivity has only been investigated up to 150 K. High-temperature electrical resistivity and thermopower on a second sample were simultaneously determined in the 300 - 673 K temperature range by a standard steady-state method (ZEM 3, Ulvac-Riko).

III. Results and discussion

Electrical resistivity and thermopower of $\text{Ba}_8\text{Ge}_{43}\square_3$ at low temperatures are depicted in Figures 3a and 3b, respectively. The first essential outcome of these measurements is the observation of a metal-like electrical resistivity below 280 K. The resistivity values are two orders of magnitude lower than those previously reported,⁵ and corroborate the high quality of the samples. The thermopower exhibits a rather complex behavior with two sign changes from n-type to p-type near 90 K (Fig. 3b) and from p-type to n-type slightly above 300 K (Fig. 4). Such behavior might indicate multi-band conduction with differing temperature-dependent mobilities of electrons and holes. The low values ranging between -5 and $+10 \mu\text{V K}^{-1}$ are consistent with the metallic character of $\text{Ba}_8\text{Ge}_{43}\square_3$ below 280 K.

Above 300 K, the temperature dependences of electrical resistivity and thermopower substantially differ from those expected in a metallic system (Figure 4a and 4b). The electrical resistivity decreases with temperature indicating semiconducting behavior. The thermopower displays a linear temperature dependence in the whole temperature range to reach a value close to $-40 \mu\text{V K}^{-1}$ at 673 K. Both features suggest that a transition from metal-like to semiconducting-like behavior sets in near room temperature. The absolute values of low- and high-temperature measurements are slightly different, but in fair agreement considering different methods and uncertainties of the geometry factor of the specimen ($\sim 10\text{-}20\%$). Measurements of the Hall effect, which would help to understand the complex temperature behavior of the thermopower are currently in progress.

The temperature dependence of the thermal conductivity shows a pronounced maximum near 25 K indicating a crystal-like character of the thermal transport (Fig. 5). This is in contrast to the glass-like temperature dependence observed in p-type $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$,^{8,9} but it is consistent with transport properties reported for other ternary clathrate-I compounds

containing framework vacancies.¹⁰

Conclusion

The clathrate-I $\text{Ba}_8\text{Ge}_{43}\square_3$ has been synthesized as single-phase material. The transport properties reflect a metal-like to semiconducting-like transition near room temperature. The observed metal-like conductivity at low-temperatures shows the applicability of the valence rules for the prediction of conduction behavior. The observed semiconducting-like behavior above room temperature is in good agreement with the previously reported result.⁵ The origin of the observed transition, however, must await further structure investigations to determine, whether or not an intimate link between possible crystal structure modifications and this electronic transition exists.

Acknowledgements

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- ¹⁰ G. S. Nolas, T. J. R. Weakley, J. L. Cohn, *Chem. Mater.*, 11, 2470 (1999).

Figure captions

Figure 1: Optical microscopy image of splat-cooled $\text{Ba}_8\text{Ge}_4\text{Sb}_3$ (bright field contrast).

Figure 2: X-ray powder diffraction pattern of $\text{Ba}_8\text{Ge}_4\text{Sb}_3$. All reflections can be indexed with the cubic lattice parameter $a = 21.307(1)$ Å, no additional reflections are detected. The baseline corresponds to the residuals of a Rietveld refinement based on the reported structure model.⁴

Figure 3: Electrical resistivity $\rho(T)$ (a) and thermopower $S(T)$ (b) of $\text{Ba}_8\text{Ge}_4\text{Sb}_3$ at low temperatures.

Figure 4: Electrical resistivity $\rho(T)$ (a) and thermopower $S(T)$ (b) of $\text{Ba}_8\text{Ge}_4\text{Sb}_3$ above 300 K.

Figure 5: Thermal conductivity $\kappa(T)$ of $\text{Ba}_8\text{Ge}_4\text{Sb}_3$ at low temperatures.

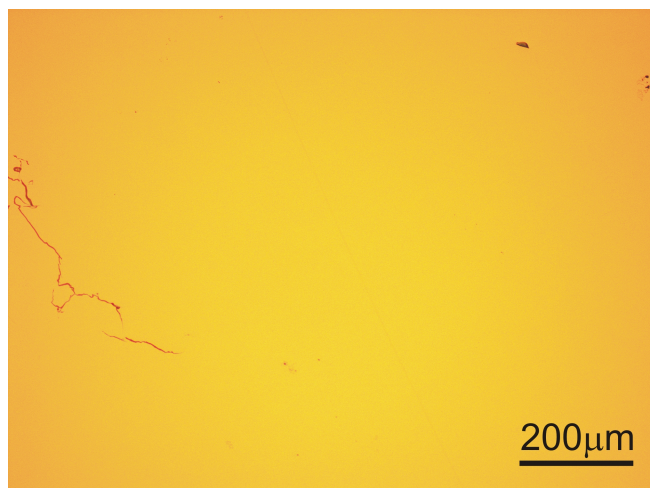


Figure 1

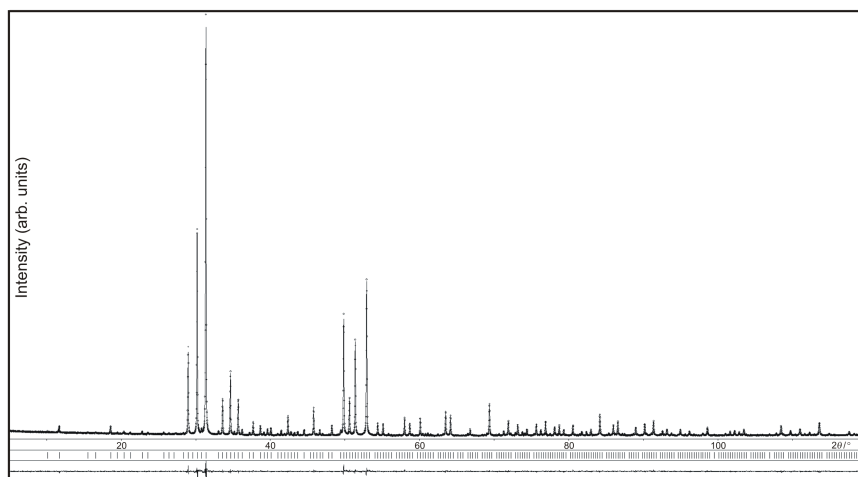


Figure 2

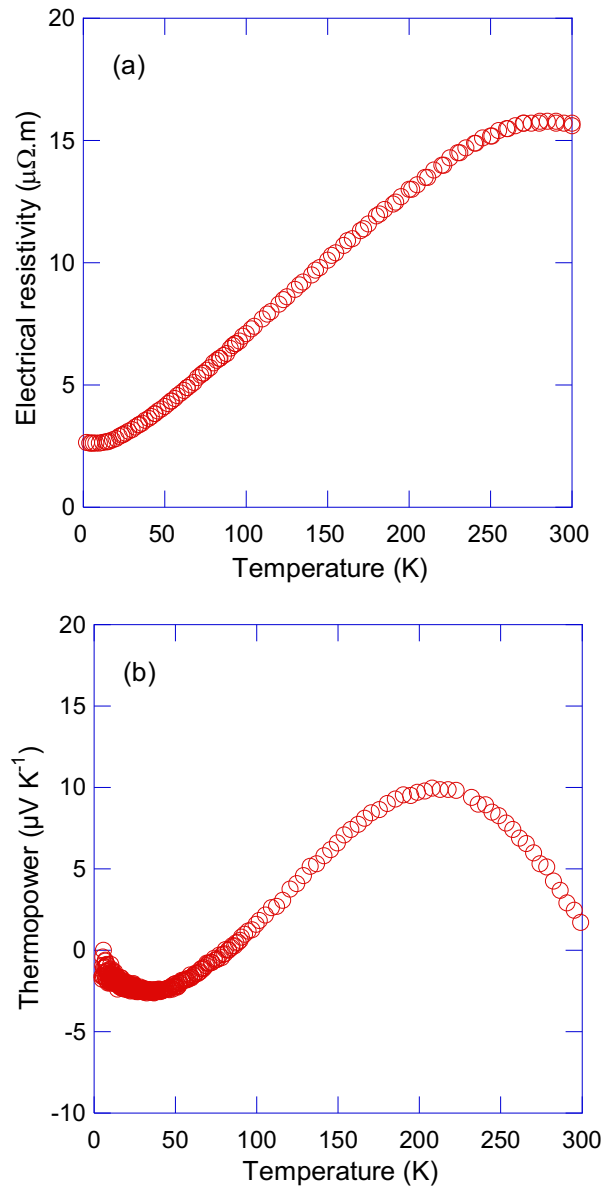


Figure 3

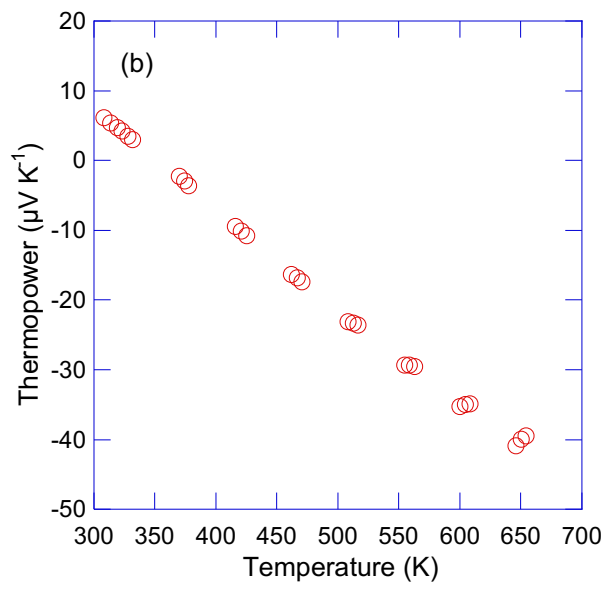
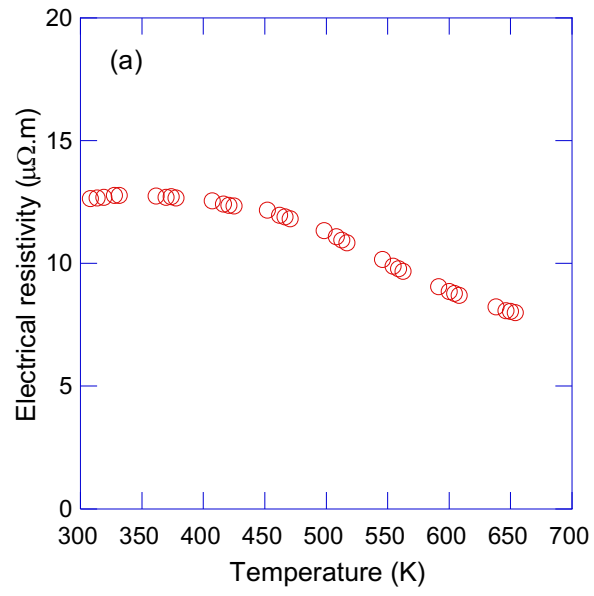


Figure 4

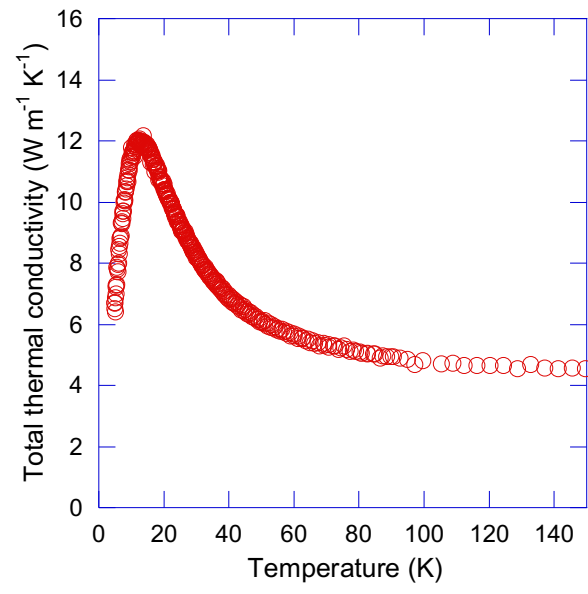


Figure 5