High temperature thermoelectric properties of Czochralski-pulled $Ba_8Ga_{16}Ge_{30}$

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Abstract

High temperature thermoelectric properties have been measured on a Czochralski pulled $Ba_8Ga_{16}Ge_{30}$ crystal. Complete transport properties obtained in the temperature range from 273K to 1150K. The physical properties are reproducible even after thermal cycling. The Seebeck coefficient reveals the sample to be an *n-type* conductor with a maximum value of -148 µV/K at 1073K. The electrical resistivity shows the characteristics of a heavily doped semi conductor, and it goes through a maximum at 1073 K with a value of 1.7 mΩ-cm. The thermal conductivity goes through a minimum of 1.25 W/m-K around 900K, and *ZT* reaches a maximum of 0.9 at 1000 K.

Introduction

The interest in thermoelectric clathrates has escalated since Nolas *et al.* identified $Sr_8Ga_{16}Ge_{30}$ as a promising candidate for thermoelectric power generation at elevated temperatures [1]. Nolas *et al.* estimated a ZT value above 1 at T > 700K. Despite the promising thermoelectric properties at high temperatures only few studies of transport properties at elevated temperatures have been carried out on the type I clathrates with $X_8III_{16}IV_{30}$ (X = Eu, Sr and Ba, III = group 13 elements and IV = group 14 elements) [2-4]. High temperature properties of $Sr_8Ga_{16}Ge_{30}$ were measured by Kuznetsov *et al.*, who found a ZT of ~0.6 at 800K [2]. A somewhat lower value than the initial estimates by Nolas *et al.* Better performance was observed in $Ba_8Ga_{16}Si_{30}$ and $Ba_8Ga_{16}Ge_{30}$ where ZT values of 0.87 at 870K and 0.7 for at 700K were measured [2]. Fujita *et al.* investigated a large number of samples with stoichiometry $Sr_8Ga_xGe_{46-x}$ [3]. The maximum *ZT* was found for x = 16.5 at 800 K at a value of 0.62 in good agreement with Kuznetsov *et al.* [2].

Saramat *et al.* recently presented data from a large crystal of $Ba_8Ga_{16}Ge_{30}$ grown by the Czochralski method [4]. A number of samples were cut from the pulled rod and investigated. The sample with the best thermoelectric properties was reported to have a record high *ZT* of 1.35 at 900K. From extrapolation to 1100K it was expected that a *ZT* of 1.63 could be reached from Czochralski grown crystals [4]. The high *ZT* values of $Ba_8Ga_{16}Ge_{30}$ places the clathrate type I compounds among the most promising bulk materials for thermoelectric application.

The unique properties of the type I clathrates are related to the structural features. The structure can be illustrated by host structure build of group 13 and 14 elements, with the guest atom alkali or alkali earth elements residing in the large voids created by the host structure, Figure 1. The guest atoms serve as phonon scattering centers, thereby lowering the thermal conductivity of the clathrates. By controlling the stoichiometry of the group 13 and 14 elements in the host structure, it is possible to control the dominating charge carrier type and the number of charge carriers [5].
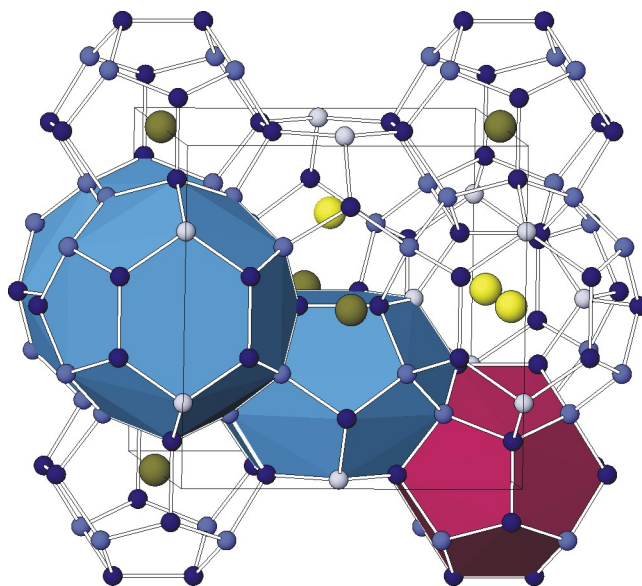

Figure 1: The clathrate type I structure. The polygons show the shape of the cages: The large tetrakaidecahedral cage is shown in light blue, whereas the dodecahedral cage is dark red. The guest atoms are shown as light yellow spheres for those which reside in the large cage and dark yellow for the guests in the small cage. The host structure atoms are blue.

Synthesis

Conventional synthesis: Pure elements of barium (99.2%), gallium (99.999%), and germanium (99.9999%) were weighed in relative ratios of 8:16:29.5. The elements were placed in a glassy-carbon crucible and sealed under argon in a steel bomb. The bomb was heated to 1050°C in a tube furnace and left there for four hours before cooling to room temperature. The product was washed in HCl for 24 hours to remove impurities. A powder diffraction pattern revealed the sample to single phase $Ba_8Ga_{16}Ge_{30}$, within the detection limits of the diffraction measurement.

Czochralski pulling: A sample was prepared using the Czochralski pulling method. The melt was prepared by the conventional method described above. The product from the conventional synthesis was placed in glassy carbon crucible, inside an induction furnace. The furnace chamber was filled with He to a background pressure of ~6 atm. A piece from a previously Czochralski pulled crystal of $Ba_8Ga_{16}Ge_{30}$ was used as a seeding crystal. The crystal was pulled with a speed of 10 mm/h. The resulting rod is seen in Figure 2a. The samples for the measurements of the thermoelectric properties were cut with a diamond saw from the bottom of the shown rod. They were disc shaped (typically 1-2 mm thick) and obtained from 8 mm long cylinder.
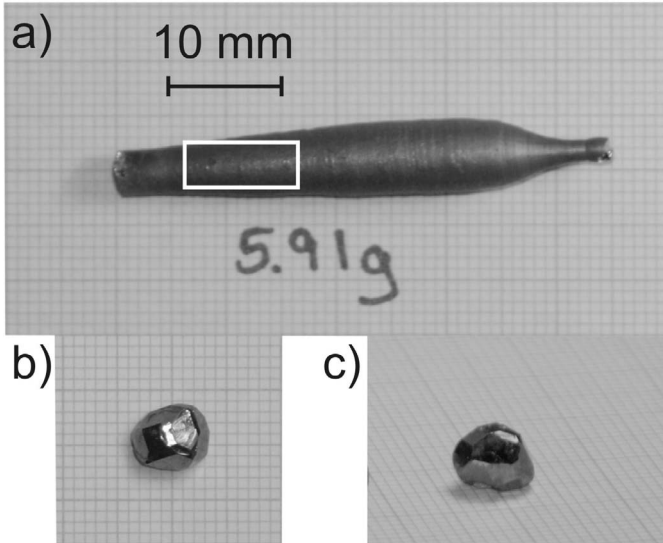
Figure 2: The synthesised samples. a) the Czochralski pulled rod. The white square marks the region from where the sample was extracted. b) and c) are the flux grown samples before cutting from two different angles.

Flux growth: A large single crystal (~1 g) of $Ba_8Ga_{16}Ge_{30}$ was grown by taking conventionally prepared material and adding 75 weight% of gallium. The material was sealed in an evacuated quartz tube and placed in a tube furnace. The sample was heated to 950°C and slowly cooled to room temperature (1 °C/h). Figure 2b and c show the resulting nicely facetted single crystal. The sample was cut into a bar shape for measurements of the thermoelectric properties.

Measurements of transport properties:

The high temperature measurement of the thermoelectric properties of the flux grown crystal failed due to extrusions of gallium. Droplets or liquid gallium was observed to form on the surface of the sample. Whether the gallium is extruded from the grain boundaries or from the bulk of the sample is unknown. The gallium extrusion prevented the measurement of the physical properties and it may present a general problem for clathrates grown from Ga flux. However, the Czochralski pulled crystal did not give any problems with the measurements of the physical properties. All measurements were performed in dynamic vacuum (10^{-5} torr).

Electrical resistivity: A slice of the of the Czochralski pulled $Ba_8Ga_{16}Ge_{30}$ sample was studied using the van der Pauw technique (giving resistivity perpendicular to growth direction) with a current of 100 mA using a special high temperature apparatus. The Hall coefficient was measured in the same apparatus with a constant magnetic field value of about 1 T. The resistivity along the growth direction was measured using a 4 point technique, and comparable results were obtained. The data were measured both during heating and cooling and identical values were observed. An additional heating cycle was done in order to check reproducibility and verify that no sample changes had taken place. Figure 3 shows the resistivity and thermopower.
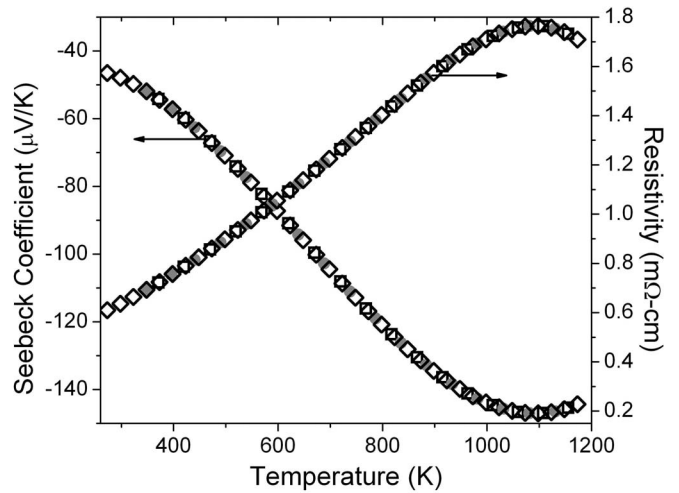
Figure 3: The Seebeck coefficient (*left axis*) and the electrical resistivity (*right axis*) as function of temperature. The *open squares* are from the first heating cycle, whereas the *open diamonds* are from the second heating cycle. The *grey spheres* are from the cooling.

Seebeck Coefficient. The Seebeck coefficient (*S*) was measured using a high temperature light pulse technique using W/Nb thermocouples [6]. Data were recorded both during heating, and cooling, as well as a second heating cycle. The data are shown in Figure 3.

Thermal conductivity. The thermal diffusivity was measured for several samples using a laser flash technique. The thermal conductivity (κ) is given in Figure 4.
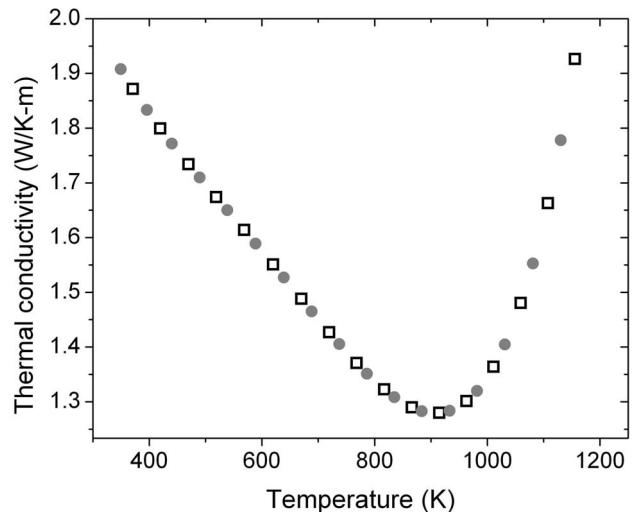
Figure 4: The thermal conductivity shown as function of the temperature. The *open squares* were obtained during heating and the *grey circles* during cooling.

The heat capacity was estimated using the model of Dulong and Petit, $C_p = 3\ k_B$, for each atom. The thermal conductivity (κ) was then calculated from the heat capacity, the density, and the experimental thermal diffusivity values [7]. Data were acquired both during heating and cooling. Using a constant heat capacity for the entire temperature

range is not entirely justified. The approximation can underestimate the thermal conductivity by 10-15%. [8] However the presented thermal conductivities are in good agreement with the thermal conductivities reported by Samarat et al. [4], where high temperature heat capacity data were measured.

Results

Electrical resistivity: The electrical resistivity in Figure 3 reveals a temperature profile of the Czochralski pulled $Ba_8Ga_{16}Ge_{30}$ crystal resembling that of a heavily doped semiconductor. Thus, the resistivity increases with increasing temperature, but goes through a maximum at 1073 K. The melting temperature is at ~1240 K. The measurements of the Hall coefficient revealed the sample to be an *n-type* conductor. The carrier density was calculated from the Hall coefficient R_H, assuming a scattering factor of 1.0 in a single carrier scheme, by $n = 1/R_H e$, where *n* is the density of free electrons and *e* the charge of the electron. The carrier density was found to be ~$2 \cdot 10^{-21}$ cm^{-3} in the entire temperature range.

Seebeck coefficient: The negative sign of the Seebeck coefficient corroborates that the main charge carriers are the electrons. As in the case of the electric resistivity, the Seebeck coefficient goes through maximum at ~1073 K at a value of -147 µV/K.

Thermal conductivity: The thermal conductivity is observed to decrease with increasing temperature until about 900 K, where it goes through a minimum and starts to increase rapidly. The minimum value found at ~900K is about 1.25 WK^{-1}m^{-1}.

Thermoelectric figure of merit: The thermoelectric figure of merit $ZT = TS^2/\rho\kappa$ is shown in 5. ZT increases with temperature up to 1000 K, where it reaches its maximum value of 0.9. The ZT is possibly overestimated by 10-15% due to the error in the estimate of high temperature heat capacity.
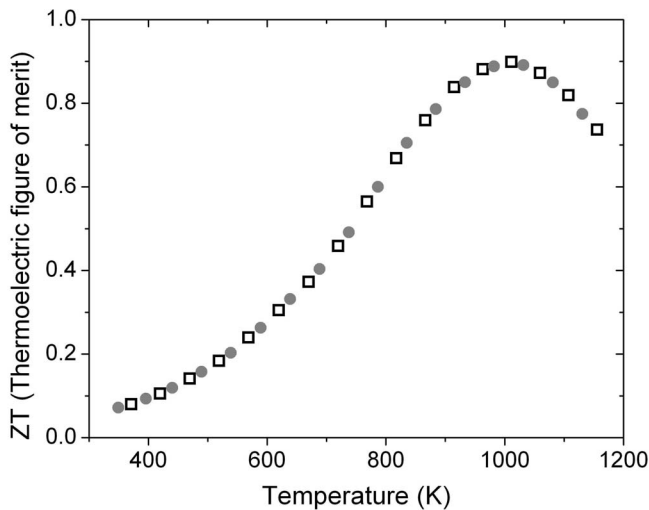
Figure 5: The thermoelectric figure of merit (*ZT*) as function of temperature. The maximum is observed at 1000 K. The *open squares* correspond to heating and the *grey circles* are from cooling.

Discussion

Electrical resistivity: The electric resistivity at room temperature is found to be ~0.64 mΩ-cm, which is in good agreement with Kuznetsov et al [2] and Saramat et al. [3], who obtained ~0.66 mΩ-cm and ~0.67 mΩ-cm, respectively. All these samples show the characteristics of a heavily doped semiconductors. The previously reported electrical resistivities did not observed reach a maximum, because the measurements were limited to 870 K and 1050 K, respectively. The maximum observed in the present data is at ~1100 K. It is interesting to note, that the charge carrier concentration and mobility at room temperature, in the Kuznetsoz sample [2] are $n = 6.8 \cdot 10^{20}$ cm^{-3} and $\mu_H = 14$ cm^2/V-s. The present sample has about three times the charge carrier concentration $n = 2 \cdot 10^{21}$ cm^{-3}, but a lower mobility $\mu_H = 7.8$ cm^2/V-s.

Seebeck coefficient: The room temperature Seebeck coefficient for the present sample is about -46 µV/K, which compares well to values reported by Kuznetsov et al. [2] ($S = -66$ µV/K) and Saramat et al. [4] (-42 to -50 µV/K). These values also compare well with other reported room temperature measurements [9, 10]. The peak in the Seebeck coefficient is observed at different temperatures for the different samples. Kuznetsov et al. [2] report a maximum of -190 µV/K at 740 K, while Saramat et al. [4] observe a maximum at 900 K (S > 250 µV/K). However, some of the Saramat samples appear to have a plateau at 1050 K (the highest measured temperature). The sample presented in this work goes through a maximum at ~1100 K. The different positions of the extrema could be a consequence of different charge carrier concentrations, but unfortunately the charge carrier concentration was not reported by Saramat et al. [4].

Thermal conductivity: The thermal conductivity for the present sample is observed to follow the result obtained by Saramat et al. [4] with a room temperature value of about ~1.8 W/K-m and the minimum at 900 K with a value of ~1.25 W/K-m.

Thermoelectric figure of merit: The differences in the observed maxima in the thermoelectric figure of merit between the various samples are mainly due to the differences in the values of the Seebeck coefficient. The following maximum ZT values were reported: Kuznetsov et al. [2] 0.7 at 700 K, Saramat et al.[4] 1.35 at 900 K and the present work gave 0.9 at 1000 K.

Conclusion

Samples of $Ba_8Ga_{16}Ge_{30}$ have been prepared by the flux method and by Czochralski pulling. The flux grown sample proved to be unsuitable for high temperature applications as gallium is extruded from the sample at elevated temperatures. The Czochralski pulled crystal on the other hand showed promising thermoelectric properties reaching a ZT value of 0.9 at 900 K. The value for the Czochralski pulled crystal is in good agreement with result reported by Saramat et al.[4]. The good agreement between this work and Saramat et al. demonstrates the reproducibility of the Czochralski pulling method for crystal synthesis. Further investigations should be performed to elucidate the reason for the shift in the

temperature of the Seebeck coefficient maximum and to optimize it further. The fact that the clathrate sample is not affected by thermal cycling gives promise for actual high temperature applications.

References

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