



# Electronic and transport properties of polycrystalline $\text{Ba}_8\text{Ga}_{15}\text{Ge}_{31}$ type I clathrate prepared by SPS method

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## ABSTRACT

Samples of germanium  $\text{Ba}_8\text{Ga}_{15}\text{Ge}_{31}$  clathrate of type I were prepared using standard metallurgy methods. The structure, microstructure and phase composition of the prepared samples were analyzed by powder X-ray diffraction XRD and scanning electron microscope SEM combined with energy dispersive X-ray analysis EDX. Scanning thermoelectric microprobe STMP was used to characterize uniformity of Seebeck coefficient distribution at different stages of the material synthesis in order to optimize the synthesis method. Electrical conductivity, Seebeck coefficient and thermal conductivity were measured in the temperature range 20–450 °C. Based on the measured electrical properties and Hall carrier concentration  $n=5-9 \cdot 10^{20} \text{ cm}^{-3}$  at room temperature, electron effective mass  $m^*$  was estimated to be between 2.1–3  $m_0$ . Preliminary FP-LAPW DFT calculations were performed for two chosen high symmetry superstructures  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  and  $\text{Ba}_8\text{Ga}_6\text{Ge}_{40}$  by means of WIEN2K package. Additionally topological analysis of total electron density according to Bader's Quantum Theory of Atoms in Molecules was carried out. The energy band gaps were calculated to be 0.3 eV for  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  and 0.38 eV for  $\text{Ba}_8\text{Ga}_6\text{Ge}_{40}$  which was close to the experimental results for  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ . The observed electrical properties were compared with the electronic band structure calculations, showing good qualitative correlation between the measured transport properties and the theoretical predictions.

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## 1. Introduction

Intermetallic clathrates crystallize in a variety of structure types with characteristic cage-forming polyhedra of framework atoms. Due to the presence of large structural voids which can be filled with loosely bonded guest atoms, clathrates can be regarded as “phonon glass electron crystals” PGEC — a concept of an ideal thermoelectric material proposed by Slack [1]. Majority of these compounds belong to type I clathrates having cubic structure (space group  $Pm-3n$ ) with an ideal unit cell formula  $2X_6Y_46T$ . In this formula T denotes 46 framework atoms (group 14 elements, usually partially substituted by group 13 elements) creating cage structure with 2 small dodecahedral voids and 6 large tetrakaidecahedral voids (X, Y, respectively), which can be filled with alkali and alkaline earth metals. Among this group of compounds a number of materials derived from  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  composition with high maximum thermoelectric figure-of-merit  $ZT_{\text{max}}$  values up to 1.35 [2–4] have been discovered. Chemical bonding between the guest and the host atoms for most of the intermetallic anionic clathrates is predominantly ionic with a complete electron transfer between the guest and the framework

atom [5–7]. Therefore, the majority of intermetallic clathrates fulfill Zintl rule and can be regarded as Zintl compounds. The detailed discussion on applications of the Zintl scheme to intermetallic clathrates can be found in the paper of Shevelkov and Kovnir [8]. The electron balance for type I clathrates according to Zintl rule requires that the number of valence electrons per formula unit equals 184. If the number of valence electrons differs slightly from the Zintl scheme the system becomes either electron rich or electron deficient. Number of electrons per formula unit can be changed easily through the partial substitution of tetravalent framework atoms by trivalent group 13 elements or d-block elements from the groups 10–12. Thus, the type and concentration of charge carriers can be changed continuously and the electronic properties can be tuned from semiconducting to metallic. Huge interchangeability of elements in the host framework of clathrates and quite a wide homogeneity range enables formation of a variety of clathrate compounds and opens many possibilities for optimization of their thermoelectric properties.

According to the Zintl scheme all of the type I germanium clathrates are semiconductors. Depending on guest atom and charge balancing element their energy band gap  $E_g$  is ranging from 0.1 to 0.5 eV [4,9,10]. The experimental energy gap values are usually the estimated values calculated from the temperature dependence of the Seebeck coefficient. The theoretically predicted band gap values are

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generally higher than the reported experimental  $E_g$  both calculated using pseudopotential [11] and full potential DFT method [12] This is contrary to the well known fact that calculations using standard GGA functionals lead usually to underestimation of the energy gap width. Christensen et al. [13] have addressed several possible reasons for this fact, including the presence of vacancies, difficulties in modeling of random atom distribution as well as the difference of temperature assumed in calculations (0 K) and during high temperature resistivity or thermopower measurements. Nevertheless it is still not clear what is the major origin of this discrepancy.

The electronic transport properties of intermetallic clathrates are closely related to the material's stoichiometry. Any deviation from the intended composition results in a large change of electrical resistivity and Seebeck coefficient. Therefore, ensuring homogeneity is an important issue both in basic research and during the search for materials with the best thermoelectric properties. Seebeck coefficient nonuniformity can be a source of circulating currents significantly reducing efficiency of the thermoelectric devices. Sample's inhomogeneity is a known problem in the clathrate literature. It was observed in the case of single crystals that depending on the synthesis method thermoelectric properties varied significantly in different parts of the same crystal [2,14,15]. One of the studies devoted to sample purity and nonstoichiometry was done by Bryan et al. [14]. They have examined purity of a zone refined ingot of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  by means of electron probe microanalysis EPMA, glow discharge mass spectrometry GDMS and XRD with a corresponding examination of transport properties. They have found that the main source of charge carriers are not the impurities but the sample nonstoichiometry. Using the precise EPMA measurement and high resolution XRD the authors concluded that host atom vacancies are present in the samples, but they were not able to exactly determine the vacancy concentration. The methods used in that paper allowed to check the composition just in a few places of the specimen and simultaneously required huge effort and use of destructive methods. Another possibility of sample uniformity checking is use of scanning thermoelectric microprobe [16]. It was used by Christensen et al. [17] for thermoelectric properties screening of Czochralski pulled  $\text{Ba}_8\text{Ga}_{16}(\text{Ge}_{1-x}\text{Si}_x)_{30}$  crystal with graded Si/Ge ratio. Chemical composition of the crystal was examined using energy dispersive X-ray spectroscopy EDX and powder and single-crystal X-ray diffraction (PXRD, SCXRD) showing strong correlation between measured thermopower and Si/Ge ratio. This study has shown big usability of the Seebeck microprobe in thermoelectric material characterization as a fast and nondestructive method. Those results together with our own experience with use of STMP method have encouraged us to apply this method in investigations of polycrystalline type I clathrate synthesis optimization.

The aim of this work was to develop synthesis techniques of polycrystalline samples of the *n*-type germanium type I clathrate. Scanning thermoelectric microprobe STMP was used to characterize sample quality and uniformity of thermoelectric properties at different stages of synthesis in order to optimize the synthesis method.  $\text{Ba}_8\text{Ga}_{15}\text{Ge}_{31}$ , which has carrier concentration close to the optimum for the best thermoelectric properties [18] was selected for the detailed study. Simultaneously, preliminary electronic band structure calculations were carried out to check influence of composition on the electronic and transport properties.

## 2. Experimental

### 2.1. Synthesis and characterization

Four samples (labeled A to D) with the same nominal composition have been prepared at different temperatures and at different times of synthesis and sintering. The polycrystalline

$\text{Ba}_8\text{Ga}_{15}\text{Ge}_{31}$  samples were prepared from pure elements: barium (99.2%), gallium (99.999%) and germanium (99.999%), mixed in stoichiometric ratios with 5% excess of Ba. The elements were loaded into an alumina crucible, covered with alumina lid and closed in quartz tube under argon pressure of 1.5 atm. The crucible was heated in a vertical furnace to 1030 °C samples A, B and 1050 °C samples C, D with a heating rate 5 °C/min and kept at this temperature for 30 min. Next, the temperature was decreased to 800 °C, kept for 1 h and then the furnace was cooled down to the room temperature. The resulting ingot was broken into smaller pieces, ground in an agate mortar and annealed at 820 °C for 3 day in graphitized quartz ampoule. Next, the obtained powder was ground once again and it was hot-pressed. The powders were sintered using spark plasma sintering SPS apparatus. The SPS process was carried under a pressure of 50 MPa in Ar atmosphere (0.1 atm.). The SPS temperatures and times were: 780 °C and 15 min; 830 °C and 15 min; 880 °C and 10 min; 900 °C and 7 min for samples A to D, respectively. The obtained cylindrical samples were 10 mm in diameter and 12 mm in height. Sample density was determined from sample mass and dimensions and confirmed by hydrostatic weighing. The measured relative densities were: 88% for sample A, 97.7% for sample B, 98.2% for sample C and 99.0% for sample D.

Phase composition of the powders after synthesis and of the final polycrystalline samples was analyzed by means of XRD method using X'pert Philips diffractometer with Ni filtered  $\text{CuK}_\alpha$  radiation. Microstructural observations were performed with scanning electron microscope SEM JEOL JSM-840 equipped with EDX probe.

### 2.2. Measurements of electrical and thermal properties

Electrical resistivity  $\rho$  and Seebeck coefficient  $\alpha$  data were collected from room temperature RT up to 450 °C. The resistivity was measured using DC four-probe method. The Seebeck coefficient was determined in steady state conditions of heat flow at two temperature gradients. To improve electrical and thermal contacts a silver paint (TAAB Electrodag 915) was used. Possibility of reaction between the paint and the sample and chemical stability of the sample were examined by performing several measuring cycles to 450 °C. No significant change of the measured resistivity values and Seebeck coefficient was observed. A STMP was used for sample thermoelectric properties uniformity analysis at room temperature. The measured sample area was  $4 \times 4 \text{ mm}^2$  with a spatial resolution of 0.05 mm. Hall effect measurements were carried out at room temperature in a constant magnetic field of 0.7T applied in two opposite directions. Hall coefficient  $R_H$  was determined using 5-wire setup with alternatingly applied DC current. Hall carrier concentration and mobility was calculated assuming single carrier type and Hall scattering factor  $A=1$ . Thermal diffusivity was measured using a laser flash technique up to 500 °C on a Netzsch LFA457 Microflash apparatus. Heat capacity  $c_p$  was measured by means of differential scanning calorimetry DSC (TA Instruments DSC 2010 apparatus) with a sapphire as a reference. The determined heat capacity is  $0.28 \text{ J g}^{-1} \text{ K}^{-1}$  at 67 °C and it is increasing to  $0.30 \text{ J g}^{-1} \text{ K}^{-1}$  at 485 °C. These results are within the range of reported experimental room temperature heat capacity for  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  ( $c_p \cong 0.23\text{--}0.29 \text{ J g}^{-1} \text{ K}^{-1}$ ) [9,19–21], and close to theoretically predicted  $c_v$  value at RT  $c_v = 0.288 \text{ J g}^{-1} \text{ K}^{-1}$  ( $2.82 k_B/\text{atom}$  Nenghabi et al. [22]) and the Dulong–Petit limit of  $c_v = 0.306 \text{ J g}^{-1} \text{ K}^{-1}$ . Thermal conductivity  $\lambda$  was calculated from the measured thermal diffusivity  $D$ , experimental density  $d$  and heat capacity  $c_p$  using equation:  $\lambda = D \cdot c_p \cdot d$ .

### 2.3. Computational details

Band structure and density of states calculations in  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  and  $\text{Ba}_8\text{Ga}_6\text{Ge}_{40}$ , have been performed using WIEN2k FP-LAPW

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