Thermoelectric properties of meltspun Ba$_8$Cu$_5$(Si,Ge,Sn)$_{41}$ clathrates

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**Abstract**

The type-I clathrates Ba$_8$Cu$_5$(Si,Ge,Sn)$_{41}$ show promising thermoelectric (TE) properties. We investigated the influence of Sn substitution for Ge on the TE properties of Ba$_8$Cu$_5$Si$_6$(Ge,Sn)$_{35}$ samples prepared by the fast and economic melt–spinning technique and compared our results with a sample series prepared using the conventional synthesis method of high–frequency melting and hot pressing. All samples crystallize in cubic symmetry with the space group $Pmar{3}n$. Scanning electron microscopy (SEM) together with energy dispersive x-ray spectroscopy (EDX) revealed a maximum solid solubility limit of 0.6 Sn atoms per unit cell. Electrical transport measurements showed metal–like behavior. The negative slope of the Hall resistivity $\rho_H$ points on the dominance of electrons in this material, confirmed by Seebeck coefficient measurements. With increasing Sn content the Cu concentration decreases and vacancies appear. These secondary effects have a stronger influence on electrical transport than the direct influence of the Sn substitution. The electronic transport is dominated by alloy scattering at high temperatures and neutral–impurity scattering at low temperatures. The phononic thermal conductivity is by a factor of two lower than in the hot pressed samples. The dimensionless figure of merit $ZT = 0.43$ at 773 K is reached for the sample with the highest Sn content.

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1. Introduction

Materials with an open crystal structure in which guest atoms can be trapped have attracted attention due to their potential for thermoelectric applications. Clathrates belong into this class of materials, in particular their type–I form. The crystal structure of type–I clathrates is based on two pentagonal dodecahedra and six tetrakaidecahedra so that the unit cell is cubic with space group $Pmar{3}n$ (Ref. [1]). These polyhedra form an $sp^3$ hybridized framework in which guest atoms can be located [2]. Clathrates are considered as phonon glass–electron crystal (PGEC) materials whose electronic properties are similar to good semiconductor/metal single crystals. Their thermal conductivity exhibits low values similar to glasses due to the interaction of acoustic phonons with rattling modes of the guest atoms [3]. Recently it was shown for the type–I clathrates Ba$_8$Ni$_6_{-x}$Ge$_{40+x}$ that the guest atoms are not completely isolated from the host cages. Rather, the rattling modes of the guest atoms hybridize with the framework–derived acoustic phonons over a wide region of the Brillouin zone [4]. Based on these results, a new mechanism of phononic low–pass filtering of acoustic phonons modes was introduced to explain a low lattice thermal conductivity in clathrates [4,5].

Clathrates have potential as TE materials. Especially type–I clathrates with a germanium–based framework have been much investigated due to their good TE performance [6]. The TE performance of a material is given by the dimensionless figure of merit, $ZT = S^2/\rho\kappa$, where $S$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, $\kappa$ is the thermal conductivity, and $T$ is the absolute temperature [7]. In the case of Czochralski–grown $n$–type Ba$_8$Ge–a$_{35}$Cu$_{40}$ single crystals the highest $ZT$ value of 1.35 at 900 K was reported [6]. Clathrates like Ba$_8$Cu$_{35}$Si$_{40}$–, composed of low price elements, have also raise the attention to researchers [8–10]. Ba$_8$Cu$_{35}$Si$_{40}$ for instance showed $ZT = 0.23$ (Ref. [9]) and later on $ZT = 0.5$ was shown for Ba$_8$Cu$_{35}$Si$_{40}$Ge$_{18}$ (Ref. [10]).

In the present study, we investigate polycrystalline samples with the nominal compositions Ba$_8$Cu$_{35}$Si$_{40}$Ge$_{25–x}$Sn$_x$ ($x = 0.6 – 3.0$)
prepared using melt spinning. We expected the partial Ge substitution by heavier Sn to lower the thermal conductivity. Not only the reduction of thermal conductivity by substitution with heavier Sn was successful but as well the change of the electronic structure shifted the maximum of $T_\text{ZT}$ to a lower temperatures [11]. The motivation of this study was to increase the amount of substituted Sn in studied clathrates by forming a metastable phase and therefore enhance TE properties. Melt spinning was selected not only because it has been considered as fast and economic synthesis technique (Ref. [12]) but also it has been previously proved to increased the solid solubility range compared to the conventional synthesis method of high—frequency melting and hot pressing [13].

2. Experimental

2.1. Sample preparation and characterization

A series of samples with nominal compositions $\text{Ba}_x\text{Cu}_y\text{Si}_z\text{Sn}_t$ with $x = 0.6$, 0.8, and 3.0 was prepared using high—purity bulk elements (Ba 99.9%, Cu 99.999%, Si 99.999%, Ge 99.9999%, Sn 99.999%). All elements were melted in a high—frequency furnace prior to the quenching by melt spinning on copper rotating wheel of diameter 300 mm with a speed of 3000 rpm (Ref. [12]). The meltspun (MS) flakes were then powdered in an achat mortar and sintered by spark plasma sintering (SPS) at 1073 K for 15 min under 56 MPa. The whole procedure was undertaken under Ar (99.99%) atmosphere. The samples after SPS are denoted as MS—SPS samples. The relative densities of the MS—SPS samples were calculated from the experimental density measured by the mass and the geometry (with a regular shaped sample), and from the theoretical density, respectively.

The phase constitution of the samples were studied by x-ray powder diffraction (XPD). The XPD data were collected using a HUBER—Guinier image plate system (Cu $K\alpha$, 8° < 2θ < 100°). The lattice parameters of the type—I clathrate phase were calculated by least—squares fits of peaks using Ge as internal standard ($\alpha_{\text{Ge}} = 0.5657906$ nm). The phase compositions were determined using energy dispersive x-ray spectroscopy (EDX) in a Philips XL30 ESEM scanning electron microscope (SEM) operated at 20 kV.

2.2. Physical properties

Physical properties at low temperatures were measured with a Physical Property Measurement System (PPMS) of Quantum Design. The electrical resistivity and the Hall effect were measured in the temperature range $1.8 \text{ K} < T < 300 \text{ K}$ with a 6—point quasi ac technique in a PPMS using a rotor. Hall effect measurements were performed on thin samples. The Hall voltage was measured in magnetic fields up to 9 T at the angles 0° and 180° between the sample and the magnetic field, to eliminate the misalignment voltage.

The Seebeck coefficient $S$ and electrical resistivity $\rho$ above 300 K were measured using a static dc method (ZEM 3, Ulvac—Riko) with four probes. The thermal conductivities $k$ above 300 K were calculated from the thermal diffusivity data $\alpha$ measured by a laser—flash method (Flashline—3000, Anter, USA), the heat capacity of the respective material $C_p$ assuming the Dulong—Petit limit, and the density of the material $D$ using the relation $k = aC_pD$. In the temperature range $1.8 \text{ K} < T < 300 \text{ K}$, the heat capacity was measured using a relaxation—type technique. The sample was thermally attached to the sample holder using thermally conducting Apiezon N grease. The heat capacity of the sample was evaluated by subtracting the Apiezon N contribution from the total signal.

3. Results and discussions

3.1. Phase analysis and structural properties

Fig. 1a shows the cross—section of a MS flake of the sample with $x_{\text{EDX}} = 0.48$ as an example. The typical thickness of a MS flake is $5 \mu\text{m}$. It is evident that grain growth occurs predominantly perpendicular to the copper wheel—touching side of the flake where the melt solidifies first. The grain size is smaller on the copper wheel—touching side than on the copper wheel—averited side. A MS flake polished to approximately half of its thickness shows grain boundaries enriched in Sn (see Fig. 1b). According to XPD, all MS samples are type—I clathrate phases with a small amount of Sn as impurity phase. Fig. 1c shows for simplicity the XPD pattern for one MS sample of $x_{\text{EDX}} = 0.60$. During the SPS process a small amount of diamond phase Ge0.67Si0.33 forms, while the Sn impurity phase disappears (see Fig. 1c). The composition of the MS—SPS samples evaluated from EDX, their relative density and their lattice parameter are shown in Table I. The maximum amount of Sn in the type—I clathrate phase is approximately 0.60 at.%. which, unfortunately, is only slightly larger than the reported value in Ref. [11] (see also Table 1). The Cu content decreases with increasing $x_{\text{EDX}}$. This together with a possible appearance of vacancies influences the electrical transport, as further discussed below. All MS—SPS samples are well compacted, with relative densities $d$ between 95% and 98%.

Fig. 1d shows that the substitution of Ge by larger Sn atoms increases the lattice parameter $a$ in the hot pressed samples with a low substitution level $x_{\text{EDX}}$. However, in the MS—SPS samples with a higher substitution level $d$ decreases with increasing $x_{\text{EDX}}$. We assume that the latter is due to the decrease of $(\text{Cu}+\text{Ge})/$(Si), ratio, as Cu and Ge are larger than Si (see Table 1).

3.2. Transport properties

The charge carrier concentration $n_H = 1/RH$ was evaluated within a single—band approach, where $RH = \lim_{B\to 0} g_{H}B/\mu_B H$ corresponds to linear—response Hall coefficient [14]. For all samples $\mu_H$ is linear in $\mu_B H$ at all temperatures. The Hall coefficients show a negative sign, pointing to the dominance of electron—like conduction in all samples. The evaluated $K_H$ below 300 K is essentially a temperature independent, as typical for a simple metals. Taking into account the band gap energy of about 0.2 eV, as further discussed below, we assume that $K_H(T)$ is constant at all investigated temperature range as well. A metal—like behavior is observed as well from the temperature—dependent electrical resistivities $\rho$ of all $\text{Ba}_x\text{Cu}_y\text{Si}_z\text{Ge}_{35−x}\text{Sn}_x$ ($x_{\text{EDX}} = 0.48−0.60$) MS—SPS samples investigated here (Fig. 2b). Below room temperature $\rho(T)$ is described well by the Bloch—Grüneisen model containing a Mott—Jones $T^2$ term (solid lines in Fig. 2b). The $n_H$ values of the Sn substituted MS—SPS samples are larger ($n_H = 2.0−4.0 \times 10^{26} \text{ m}^{-3}$) than those of the hot pressed samples ($n_H = 1.0 \times 10^{26} \text{ m}^{-3}$) (see Fig. 2a). The increase of $n_H$ and decrease of $\rho$ with increasing $x_{\text{EDX}}$ might indicates a change of the electronic band structure of the samples. This can be understood within a phenomenological picture of the electronic band structure of TM containing clathrates [15]. The Fermi level lies within the conduction band. This explains the metal—like behavior of $\rho(T)$ and the negative sign of the Seebeck coefficient $S$, as further shown below. With higher $x_{\text{EDX}}$, the Fermi level is shifted more deep within the conduction band. Thus, the charge carrier concentration $n_H$ decreases and, consequently, the absolute values of $\rho(T)$ and $S(T)$ decrease. This change is possibly more related to the Cu and the vacancies content than the Sn content in the clathrate phase, as further discussed below.

In Fig. 2c we show the temperature dependence of the electrical
conducivities $\sigma$. At high temperatures $\sigma$ of $x_{\text{EDX}} = 0.57$ and $x_{\text{EDX}} = 0.60$ samples follows a temperature dependence of $T^{-3/2}$ most probably due to the presence of bipolar effects. Below ~650 K, $\sigma$ closely follows a temperature dependence of $T^{-1/2}$, implying an alloy scattering dominating carrier scattering mechanism, visible as well in the Hall mobility data above 40 K (Fig. 2d) [16,17].

The alloy scattering mechanism was observed as well in other TE materials [18–20]. The alloy scattering is most probably related to the intrinsic disorder in the clathrate type–I structure due to a presence of vacancies. Below ~40 K, the temperature dependencies of the Hall mobility, $m_H$, evaluated using the relation $m_H = \frac{R_H}{e \mu}$, are almost temperature independent, which is an indication of neutral–impurity scattering as dominating scattering mechanism (see Fig. 2d).

The temperature–dependent Seebeck coefficient $S(T)$ of $\text{Ba}_8\text{Cu}_5\text{Si}_6\text{Ge}_{35-x}\text{Sn}_x$ ($x_{\text{EDX}} = 0.48–0.60$) is linear in $T$ below about 600 K (Fig. 3a). The negative values are consistent with the negative Hall coefficients and confirm that electrons are the dominating charge carriers. A maximum $S_{\text{max}}$ and its temperature $T_{\text{max}}$ is observed in all $S(T)$ curves. $S_{\text{max}}$ and $T_{\text{max}}$ are constant for the hot pressed samples while $S_{\text{max}}$ decreases and $T_{\text{max}}$ increases for MS + SPS samples. The reason of this different behavior is due to different charge carrier concentration evaluated from the Hall coefficients measurements, $n_H$ (see Fig. 3b).

Generally, the charge carrier concentration in type–I clathrates can be estimated from a simple Zintl counting scheme. For the present clathrates this is written as $[\text{Ba}^{2+}]_8[\text{Cu}^{2+}]_5[\text{Si}^4]_6[\text{Ge}^{4+}]_35-x-y\text{Sn}^{0}]_x[\text{Si}^{0}]_y$. In theory, all hosts atoms which form the framework of studied clathrate system are expected to have a covalent character of their bonds within their four neighboring atoms and be in $sp^3$ hybridization. Therefore, the vacancies $\square$ are assumed to act as acceptors of four electrons ($4e^-/\square$). Four electrons per vacancy represent a rather high electron density which might be compensated by other substituted guest atoms resulting in a smaller electron density (charge) of the vacancy. It is evident that the chemical origin of guest atoms will influence the electron density of the vacancy in a different way.
Whether vacancy can accommodate four electrons or not is out of scope of this paper and it will not influence the comparison of the charge carrier concentration between the hot pressed and MS-SPS samples. Therefore, we consider the vacancy as electron acceptors of four electrons. From the Zintl counting scheme is clear that the substitution of Sn does not directly change the charge carrier concentration. However, if it leads to a change of the Cu or vacancy content, then it is indirectly leading to a change of the charge carrier concentration. Therefore, the reason for a constant $T_{\text{max}}$ and $S_{\text{max}}$ for the hot pressed samples is that the charge carrier concentration is rather constant within this sample series. Contrary to that, the conduction band in the MS-SPS samples is gradually filled with more charge carriers and the Fermi energy is shifted more deep within the conduction band. This is mainly due to an increase of Cu content with higher $x_{\text{EDX}}$. In order to excite more charge carriers into a conduction band for a constant band gap within a sample series (see Table 2), a higher temperature is required. Therefore $T_{\text{max}}$ gradually increases and $S_{\text{max}}$ gradually decreases with $n_{H}$ within MS-SPS sample series.

The lower charge carrier concentration in the Sn substituted hot pressed samples compared to the MS-SPS samples is due to the higher vacancy content in the crystal structure and due to the lower concentration of the Cu. Fig. 3c shows the vacancy concentration evaluated from the Hall coefficient measurements $y$ for both the hot pressed [11] and the MS-SPS samples as function of $n_{H}$. For example, the $y$ of the hot pressed and MS-SPS samples with the maximum Sn solid solubility is ~ 0.28 and 0.08, respectively. The discrepancy of the vacancy content between the hot pressed and MS-SPS samples might be related to the synthesis process: the longer sintering time of hot pressing favors the formation of vacancies. The discussion about absolute values of vacancies is not the main scope of this paper, nevertheless, the number of vacancies for the hot pressed samples is almost the same as determined using the Rietveld refinement of the XPD data (Ref. [11]) with a model derived from single crystal X-ray diffraction data of Ba$_8$Cu$_5$Si$_6$Ge$_{35}$ (Ref. [8]).

The Seebeck coefficient of the hot pressed Sn substituted samples is larger than that to the MS-SPS samples (see Fig. 3b). Taking into account the Zintl concept, it seems reasonable to assume that either the Cu content or the amount of vacancies would have to be...
increased in order to enhance the Seebeck coefficient values of MS-SPS samples. It is difficult to control the amount of vacancies, therefore the change of the Cu content in the samples would be favorable for the enhancement of the Seebeck coefficient.

3.3. Thermal properties

The temperature dependence of the thermal conductivity $k$ of all samples and their phononic parts $k_{ph}$ are shown in Fig. 3d. $k$ decreases with increasing temperature up to about 650 K. Above this temperature the bipolar contribution is observed, as in the case of the hot pressed samples (Ref. [11]). $k_{ph}$ was evaluated by subtracting the electronic part $k_{el}$ from the total thermal conductivity $k$. The $k_{el}$ was estimated using the Wiedemann–Franz law $k_{el} = L_0 T / \rho$ with $L_0 = 2.44 \times 10^{-8} \text{ V}^2 \text{K}^{-2}$. The decrease of $k_{ph}$ at low temperature can be understood as a sum of the Umklapp scattering of acoustic phonons ($k_{ph} \sim T^{-1}$) and alloy scattering ($k_{ph} \sim T^{-1/2}$) processes. A decrease of $k_{ph}$ with higher $x_{EDX}$ is most probably due to higher concentration of larger and heavier Sn substituent and vacancies content. $k_{ph}$ of MS-SPS samples at 750 K is twice smaller than the hot pressed samples [11].

The heat capacity of $x_{EDX} = 0.57$ MS-SPS sample is shown in Fig. 4a as an example. At high temperatures, the molar specific heat approaches Dulong–Petit’s law $C_p = 3N$, where $R$ is the universal gas constant and $N$ is the number of atoms per formula unit. To fit the phonon contribution $C_{ph}$ of $C_p$, the electronic contribution $C_{el}$ was estimated by fitting the data at low temperature to $C_p / T = \gamma + \beta T^2$ (Fig. 4, inset), where the Sommerfeld coefficient $\gamma$ represents the electronic and the $\beta$ term represents the phononic contribution. Fitting the data yields $\gamma = 9.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\Theta_0 = 302.6 \text{ K}$. Fig. 4b shows the specific data as $C_p / T^3$ vs $T$. The bell-like enhancement around 14 K can be accounted for by Ba guest vibrational modes. As seen from the good fit with a Debye contribution $C_D$ and two Einstein contributions $C_{E1}, C_{E2}$ as

Table 2

<table>
<thead>
<tr>
<th>$x_{EDX}$</th>
<th>$E_g$ (eV)</th>
<th>$m^*$ (m/amu)</th>
<th>$PF_{max}$ (10^4 W m^-1 K^-2)</th>
<th>$ZT_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.48</td>
<td>0.193</td>
<td>0.46</td>
<td>4.85</td>
<td>0.24</td>
</tr>
<tr>
<td>0.57</td>
<td>0.215</td>
<td>0.43</td>
<td>5.22</td>
<td>0.28</td>
</tr>
<tr>
<td>0.60</td>
<td>0.216</td>
<td>0.52</td>
<td>6.29</td>
<td>0.43</td>
</tr>
</tbody>
</table>
\[ C_p = \frac{12\pi^4 N_D k_B}{5} \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx + \sum_i p_i N_{E_i} R \left( \frac{\Theta_{E_i}}{T} \right)^2 \frac{e^{\Theta_{E_i}/T}}{(e^{\Theta_{E_i}/T} - 1)^2}, \]

where \( N_D \) and \( N_{E_i} \) are the numbers of Debye and Einstein oscillators per formula unit and \( x = \hbar \omega/k_B T \). \( \Theta_D \) and \( \Theta_{E_i} \) and \( p_i \) are the Debye temperature, Einstein temperatures and the number of degrees of freedom related to the \( i \)-th vibrational mode of the guest atoms, respectively [22]. Two Einstein temperatures were required to describe the anisotropic guest vibrations in two pentagonal dodecahedra and six tetrakaidecahedra cages, respectively. In the fitting procedure we fixed \( p_1 = p_2 = 3 \) and \( N_D = 54 - \sum N_{E_i} \). The best fit of the data for \( x_{\text{EDX}} = 0.57 \) MS+SPS sample was obtained with \( \Theta_D = 302.6 \) K, \( N_{E_1} = 2.2 \), \( N_{E_2} = 7.8 \), \( \Theta_{E_1} = 54.0 \) K and \( \Theta_{E_2} = 92.3 \) K. The sum of both Einstein modes \( \sum N_{E_i} \) for two separate Ba atoms, Ba1 located at the 2a site and Ba2 located at the 6d site, is 9.8, which is close to the theoretical amount of 8 Ba atoms per formula unit. These results suggest that mainly Ba atoms contribute to localized vibrations.

Fig. 4 shows the power factor \( S^2/\rho \) and the dimensionless figure of merit \( ZT \), calculated using the values of \( S \), \( \rho \) and \( k \). The \( ZT_{\text{max}} \) and \( \text{PF}_{\text{max}} \) are listed in Table 2. The highest \( ZT \) of 0.43 was reached at 773 K for \( x_{\text{EDX}} = 0.60 \).

4. Conclusions

We have investigated polycrystalline Ba8Cu5(Si,Ge,Sn)41 samples by measuring the electrical resistivity, Seebeck coefficient, Hall coefficient, heat capacity, and thermal conductivity. Our analysis shows that both the meltspun and spark plasma sintered (MS+SPS) and the hot pressed samples follow a Zintl rule if vacancies are assumed to be present. The higher charge carrier concentration and smaller Seebeck coefficient of the MS+SPS samples is due to a lower concentration of vacancies and a different concentration of Cu compared to the hot pressed samples. The MS+SPS samples exhibit charge transport dominated by alloy scattering at high temperatures, most probably due to the intrinsic disorder in the type-I clathrate structure, while neutral—impurity scattering dominates at low temperatures. The phononic thermal conductivity of the MS+SPS samples was lowered by a factor of two compared to the hot pressed samples. This result demonstrates the potential of the fast and economic melt—spinning technique.
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References


Fig. 5. Temperature dependence of (a) the power factor $\text{PF} = S^2/\rho$ and (b) the dimensionless figure of merit $ZT$ of Ba8Cu5Si6Ge35–Snx ($x_{\text{EDX}} = 0.48$–0.60). The lines are guides to the eye.


