HPHT Synthesis: Effects of the Synergy of Pressure Regulation and Atom Filling on the Microstructure and Thermoelectric Properties of Yb$_x$Ba$_{8-x}$Ga$_{16}$Ge$_{30}$

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ABSTRACT: Type-I clathrate compounds Yb$_x$Ba$_{8-x}$Ga$_{16}$Ge$_{30}$ have been synthesized by the high-pressure and high-temperature (HPHT) method rapidly. The effects of the synergy of atom filling and pressure regulation on the microstructure and thermal and electrical properties have been investigated. With the content of Yb atom increasing, the carrier concentration is improved, the electrical resistivity and the absolute Seebeck coefficient are decreased, while the thermal conductivity is reduced significantly. A series of extremely low lattice thermal conductivities are achieved, attributed to the enhancement of multiscale phonon scattering for the “rattling” of the filled guest atoms, the heterogeneous distribution of nano- and microstructures, grain boundaries, abundant lattice distortions, lattice deformations, and dislocations. As a result, a maximum $ZT$ of about 1.07 at 873 K has achieved for the Yb$_{0.5}$Ba$_{7.5}$Ga$_{16}$Ge$_{30}$ sample.

1. INTRODUCTION

Thermoelectric (TE) energy harvesting technology, which can transform waste heat into electricity directly based on TE materials, has drawn increasing attention.1−3 The energy conversion efficiency of TE materials can be represented by the dimensional figure-of-merit $ZT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $T$, and $\kappa$ are the Seebeck coefficient, the electrical conductivity, the absolute temperature, and the total thermal conductivity, respectively. $\kappa = \kappa_L + \kappa_e$ where $\kappa_L$ and $\kappa_e$ are the lattice thermal conductivity and the electronic thermal conductivity, respectively.4−6 It is clear that a material with a high $ZT$ value essentially needs a high $S$, a high $\sigma$, and a low $\kappa$ to enable more practical applications. The three parameters ($S$, $\sigma$, $\kappa$) are interdependent, and as a result, they are difficult to enhance individually. As we all know, it is vital to further develop high-performance TE materials targeting higher conversion efficiency. For acquiring a higher $ZT$ value, many strategies including nanostructure,7 the quantum confinement effect,8 intrinsic point defects,9 phonon engineering,10,11 band engineering,12 etc. have been developed to decouple these interrelationships.

Type-I clathrate TE materials, which possess a very stable and complex crystal structure and an intrinsically ultralow thermal conductivity, are typical “phonon glass electron crystal” (PGEC) materials.13−15 This TE material possesses a set of well-crystallized host framework structures, which not only pledge good electrical properties but also encapsulate multiple guest atoms. These guest atoms vibrate in a special way “rattling” in the host framework structure, which can affect the interaction of the heat-carrying phonons and reduce $\kappa_L$ effectively.16,17 Visibly, type-I clathrate compound, as one of the highly promising TE materials, has caused great concerns. The special construction and unique electrical-/phonon-transport properties ensure that the TE properties of Type-I clathrate materials can be upgraded substantially by an...
appropriate strategy. Regarding type-I clathrate materials, high figures-of-merit have been achieved in Ge-based clathrate compounds, such as a high maximum $ZT$ of 1.35 at 900 K for n-type single-crystal clathrates $Ba_{x}Ga_{16}Ge_{30}$ by the Czochralski method,\textsuperscript{18} 1.1 at 950 K for $Yb_{x}Ba_{7.5}Ga_{16}Ge_{30}$ compounds by the spark plasma sintering (SPS) method,\textsuperscript{19} and 0.91 at 900 K for $Ba_{7.7}Yb_{0.3}Ni_{0.1}Zn_{0.54}Ga_{13.8}Ge_{31.56}$ alloys by a high-pressure technique.\textsuperscript{20}

With the development of preparation technologies, they exhibit respective advantages in terms of optimizing TE performances, for example, the microwave hydrothermal method,\textsuperscript{21} melting methods, spark plasma sintering,\textsuperscript{22} etc. Many techniques have also been used to synthesize type-I clathrate compounds at present. However, compared with the HPHT method, most preparation technologies reveal their limitations. The HPHT method has a series of unique advantages, including tuning rapidly, shortening the synthesis time, simplifying procedures, large-scale production, one-step and intercepting high-pressure properties to ordinary pressure, etc.\textsuperscript{23–26} In this study, dual-atom-filled $Yb_{x}Ba_{8-x}Ga_{16}Ge_{30}$ compounds were successfully synthesized by the HPHT method, and anticipative good results were obtained. The TE performances have been enhanced by the synergy of Yb filling and pressure regulation. Above all, the lowest $\kappa$ of about 0.77 W m$^{-1}$ K$^{-1}$ was obtained at 873 K for $Yb_{1}Ba_{7}Ga_{16}Ge_{30}$ attributed to the interaction of the heat-carrying phonons with local vibration modes of the filled guest atoms and the strengthened scattering owing to the heterogeneous distribution of nano- and microstructures, grain boundaries, abundant lattice distortion, lattice deformations, and dislocations. Ultimately, the maximum $ZT$ of 1.07 was obtained at 873 K for the $Yb_{0.75}Ba_{7.25}Ga_{16}Ge_{30}$ sample owing to the reduction of $\kappa$ of 0.84 W m$^{-1}$ K$^{-1}$ and the relatively higher PF of 10.34 $\mu$W cm$^{-1}$ K$^{-2}$. The TE properties and microstructures are described in more detail below.

2. RESULTS AND DISCUSSION

Figure 1a shows the X-ray diffraction (XRD) patterns of $Yb_{x}Ba_{8-x}Ga_{16}Ge_{30}$ samples with $x = 0, 0.25, 0.5, 0.75$, and 1.0 synthesized by the HTHP method, in which all of the diffraction peaks in the samples ($x \leq 0.75$) correspond to type-I clathrate phases with the space group $Pm\overline{3}n$ (223). No second phases are observed in the samples ($x \leq 0.75$), indicating that the samples ($x \leq 0.75$) with a single-phase structure were successfully prepared. A small percentage of impurity phase Ge appears in the XRD spectrum of the $Yb_{0}Ba_{8}Ga_{16}Ge_{30}$ sample, which is denoted by a hollow inverted triangle. In other words, $x = 1$ is beyond the solid solubility limit of Yb in $Ba_{8}Ga_{16}Ge_{30}$ alloys. As we all know, the covalent radius of Yb ($\approx 1.74$ Å) is smaller than that of Ba ($\approx 1.98$ Å), so theoretically the lattice parameters ($a$) should reduce if Yb atoms substitute Ba sites. Figure 1b shows the shift of the (321) peak. The peak positions shift to higher angles with an increase in the filling Yb atom. The lattice parameters ($a$) of the samples synthesized using the HPHT method are shown in Figure 1c. From Figure 1c, it can be seen that the lattice parameters ($a$) linearly decrease with an increase in the Yb filling concentration. Obviously, both the shift of the peak and the change of the lattice parameters ($a$) are consistent with theoretical predictions. The lattice parameters ($a$) of the samples synthesized at high pressure are slightly smaller than those of the samples synthesized at ordinary pressure.\textsuperscript{27} This is due to the fact that high-pressure compression reduced interatomic distances, lattice constants, and interplanar distances.\textsuperscript{27} Meanwhile, this suggests that high-pressure effects are captured and returned to ordinary pressure after relieving the high-pressure, which also means that some advanced characteristics under high-pressure could be intercepted to ordinary pressure. In addition, high-pressure has the ability to tune the interatomic distance, which determines band structure and transport properties. Besides, compared with the traditional methods, the processing time of the HPHT method has been sharply reduced from a few days to 30 min. This implies that the HPHT method can be used to prepare type-I clathrate, and high figures-of-merit can be obtained with the right synthesis conditions using the HPHT method.

The cross-sectional surface microstructures of the $Yb_{Ba_{8-x}}Ga_{16}Ge_{30}$ samples are investigated in Figure 2. It is clear that there are no obvious cavities on the surface of all of the samples prepared by the HPHT method, indicating that these samples have relatively high densities. From Figure 2, we can find a large number of microstructures with the sizes of tens to hundreds of nanometers that heterogeneously distributed throughout the samples. The formation mechanism of the special microstructures is still mysterious, but it certainly
has some relationship with the gradient of pressures and temperature, due to reasons that require further investigation. The average grain size of these special microstructures is presented in Figure 2f. It is shown that the average grain size decreases with Yb filing, which indicates that Yb can prohibit the grain growth in the HPHT synthesis process. Although large micrograins of over 1 μm are present in the Yb0.5Ba7.5Ga16Ge30 sample, a large number of nanograins with grain sizes less than 100 nm also appear in the same sample. Thus, the average grain size is below 0.5 μm for the Yb0.5Ba7.5Ga16Ge30 sample. Therefore, it can be concluded that various nano- and microscale grains have been formed, which are helpful for reducing the thermal conductivity. The other samples are investigated in the same manner as this sample.

To better understand these microstructures, the SEM image and energy-dispersive X-ray spectroscopy (EDS) analysis of the selected region of Yb0.5Ba7.5Ga16Ge30 synthesized at 3 GPa are measured as revealed in Figure 3. The chemical compositions of two grains marked by A of Figure 3a are...
shown in Figure 3b. All elements (Yb, Ba, Ga, and Ge) are detected, and the actual compositions are listed in Table 1, which also indicates that the sample is successfully synthesized according to the nominal compositions. This demonstrates that the compositions of both nanograins are the same or close to the composition of the bulk material and both of them are Yb0.5Ba7.5Ga16Ge30 components. In addition, from Figure 3a, we can find that various grains with sizes of 72−1454 nm and some of the smaller nanograins (indicated by the white circle) are also present in this sample. Obviously, these microstructures can scatter the propagation of the middle-frequency phonons effectively and are beneficial for reducing the lattice thermal conductivity.

The EDS elemental mappings of the polished surface for Ba8Ga16Ge30 and Yb0.5Ba7.5Ga16Ge30 samples were measured as shown in Figure 4. Obviously, there are no element-rich areas, and all of the elements exhibit highly homogenous distributions within the measurement accuracy of EDS. The SEM observation on each sample notarizes that the chemical compositions of the samples are homogeneous. This confirms that the compositions of the nanograins are the same or close to the composition of the bulk material. The actual compositions, listed in Table 2, are determined from EDS measurement.

![Figure 3](https://example.com/fig3.png)

**Figure 3.** (a) SEM image of Yb0.5Ba7.5Ga16Ge30 synthesized at 3 GPa and (b) EDS analysis of the selected region A in (a).

![Table 1](https://example.com/table1.png)

**Table 1. Chemical Compositions of the Selected Region**

| selected region | Yb (%) | Ba (%) | Ga (%) | Ge (%) | actual composition       |
|-----------------|--------|--------|--------|--------|---------------------------|
| A               | 0.85   | 14.01  | 28.61  | 56.53  | Yb0.46Ba7.54Ga15.41Ge30.59 |
| A               | 0.81   | 14.05  | 28.58  | 56.58  | Yb0.44Ba7.56Ga15.39Ge30.61 |
| B               | 0.83   | 14.03  | 28.51  | 56.63  | Yb0.45Ba7.55Ge15.32Ge30.68 |

a Actual compositions were obtained by EDS analyses.

High-resolution transmission electron microscopy (HRTEM) micrographs were utilized to characterize the detailed microstructures of our representative sample prepared by the HPHT method, as illustrated in Figure 5. The HRTEM micrographs reveal that there are a large number of multiscale nanoparticles existing in the sample. The nanoparticles and orientations of the lattice fringe are indicated in Figure 5. The nanoparticles have various shapes and random lattice fringe orientations. Our samples have abundant lattice distortions, lattice deformations, and dislocations, as shown in Figure 5b−d. Investigating the reason for this is the result of the strain and constraint induced by high pressure. The nanoparticles, abundant lattice distortions, lattice deformations, and dislocations can effectively inhibit the propagation of the phonon and reduce the lattice thermal conductivity, as shown in the following descriptions.

![Figure 6](https://example.com/fig6.png)

**Figure 6a** shows the temperature-dependent electrical resistivities of YbxBa8−xGa16Ge30 compounds. With an increase in temperature, all of the electrical resistivities increase, which demonstrates that the YbxBa8−xGa16Ge30 compounds are degenerate semiconductors.28 It also can be seen from Figure 6a that the electrical resistivities generally decrease with the increase of Yb content (x ≤ 0.7). The relationship between the room-temperature carrier concentration, mobility, and Yb content that can help us understand the cause for the change in electrical resistivities is shown in Figure 6b. It can be noticed that the changes in carrier concentration are consistent with the changes in electrical resistivities except for the sample with x = 1.0. The electrical resistivity of Yb1Ba7Ga16Ge30 is higher than that of Yb0.7Ba7.25Ga16Ge30 due to the decrease of carrier mobility, which is affected by the second-phase Ge. The absolute value of carrier concentration is significantly enhanced with an increase in the Yb content, and this results from Yb substitution on the Ba site. The room-temperature carrier mobility decreases with increasing Yb substitution on account...
of the enhanced alloy scattering. On the whole, the increase in carrier concentration with increasing Yb content should be the main reason for the decrease of the electrical resistivities. Figure 7a shows the relationship between the Seebeck coefficient for Yb$_{x}$Ba$_{8-x}$Ga$_{16}$Ge$_{30}$ samples. In the entire measured temperature range, the values of the Seebeck coefficient are negative, which show n-type conductive behavior for all samples. With an increase in temperature, the absolute value of the Seebeck coefficient increases for the five samples. Meanwhile, the absolute value of the Seebeck coefficient decreases with an increase of the x content. With an increase in the carrier concentration, the absolute value of the Seebeck coefficient usually decreases. As shown in Figure 6b, the carrier concentration increases with an increase of the x content; thus, the absolute value of the Seebeck coefficient decreases with the enhanced carrier concentration, as shown in Figure 7a. The absolute value of the Seebeck coefficient reduces from 70 to $49 \mu V K^{-1}$ when x increases from 0 to 1 at room temperature. The maximum absolute values of Seebeck coefficients for the five specimens Yb$_{x}$Ba$_{8-x}$Ga$_{16}$Ge$_{30}$ (x = 0, 0.25, 0.5, 0.75, 1) are 194, 184, 178, 165, and $136 \mu V K^{-1}$, respectively. This change is consistent with that of the measured temperature range, the values of the Seebeck coefficient are negative, which show n-type conductive behavior for all samples. With an increase in temperature, the absolute value of the Seebeck coefficient increases for the five samples. Meanwhile, the absolute value of the Seebeck coefficient decreases with an increase of the x content. With an increase in the carrier concentration, the absolute value of the Seebeck coefficient usually decreases. As shown in Figure 6b, the carrier concentration increases with an increase of the x content; thus, the absolute value of the Seebeck coefficient decreases with the enhanced carrier concentration, as shown in Figure 7a. The absolute value of the Seebeck coefficient reduces from 70 to $49 \mu V K^{-1}$ when x increases from 0 to 1 at room temperature. The maximum absolute values of Seebeck coefficients for the five specimens Yb$_{x}$Ba$_{8-x}$Ga$_{16}$Ge$_{30}$ (x = 0, 0.25, 0.5, 0.75, 1) are 194, 184, 178, 165, and $136 \mu V K^{-1}$, respectively. This change is consistent with that of the
Electrical resistivity. They are a little higher than the reported results. The power factors (PF = $S^2/\rho$) at 300–873 K for Yb$_{Ba_{8-x}}$Ga$_{16}$Ge$_{30}$ compounds are presented in Figure 7b. With an increase in temperature, the PFs rise rapidly among the measured temperature range. We can see that the change of the PFs is not significant with the increase of the x content for the samples of x ≤ 0.75. The peak values of the PFs for samples Yb$_{Ba_{8-x}}$Ga$_{16}$Ge$_{30}$ (x = 0, 0.25, 0.5, 0.75, 1) are 10.98, 10.67, 10.34, 9.49, and 6.38 $\mu$W cm$^{-1}$ K$^{-2}$, respectively.

The total thermal conductivities for Yb$_{Ba_{8-x}}$Ga$_{16}$Ge$_{30}$ are plotted in Figure 8a. In the range of the testing temperature, the total thermal conductivity ($\kappa$) decreases with the increasing temperature for all samples. Obviously, the $\kappa$ of the dual filling samples are lower than that of the single filling one. The lowest $\kappa$ of 0.76 W m$^{-1}$ K$^{-1}$ has been obtained at 873 K for the Yb$_{Ba_{8}}$Ga$_{16}$Ge$_{30}$ sample. According to the Wiedenann–Franz law, $\kappa = L\rho$, where $L = 2.44 \times 10^{-8} \Omega$W K$^{-2}$ is the Lorenz number, we calculated the lattice thermal conductivity ($\kappa_L$) using the equation, $\kappa_L = \kappa - \kappa_e$, presented in Figure 8b. It can be found from Figure 8b that the $\kappa_L$ of all samples decreases significantly in the whole temperature range. Furthermore, the $\kappa_L$ decreases remarkably with the increase of the x content. There are two main reasons for the decreasing $\kappa_L$: On one hand, the scattering is the interaction of the heat-carrying phonons with local vibration modes of the filled guest atoms (Yb and Ba), can reduce the $\kappa_L$. The results also indicate that the reduction of $\kappa_L$ is partly caused by the filling of filling atoms. The scattering effect caused by single-atom filling on phonons is more remarkable than that by single-atom filling. On the other hand, the strengthened scattering owing to the complicated microstructures that show a heterogeneous distribution of nano- and microstructures (Figure 2), grain boundaries, abundant lattice distortions, lattice deformations, and dislocations (Figure 4). Therefore, $\kappa_L$ can be further reduced by the complicated microstructures. In this study, a lowest $\kappa_L$ of 0.07 W m$^{-1}$ K$^{-1}$ is achieved at 873 K for Yb$_{Ba_{8}}$Ga$_{16}$Ge$_{30}$. It also shows that $\kappa_L$ reduces gradually with an increase of the Yb content and deliberately engineered microstructures by the HPHT method.

The temperature dependence of ZT for Yb$_{Ba_{8-x}}$Ga$_{16}$Ge$_{30}$ samples, as shown in Figure 9. With an increase in temperature, the ZTs of all of the samples increase within the measured temperature range. The highest peak ZT (1.07) is achieved for Yb$_{Ba_{0.5}}$Ga$_{16}$Ge$_{30}$ at about 873 K, which is attributed to the relatively higher PF and significantly reduced thermal conductivity. Compared with previous studies, ZT increases by 30% at the same temperature. By comprehensively analyzing the excellent thermoelectric properties, desirable morphologies and appropriate synthesis time and temperature of the Yb$_{Ba_{8-x}}$Ga$_{16}$Ge$_{30}$ samples synthesized at high pressure, it can be concluded that HPHT combined with element doping or filling can optimize the TE properties of type-I clathrate TE materials.

3. Conclusions

Yb and Ba dual-filled n-type type-I clathrate Yb$_{Ba_{8-x}}$Ga$_{16}$Ge$_{30}$ materials have been rapidly synthesized by an excellent substitutive method, and good results are obtained as expected. The solubility limit of Yb in Ba$_8$Ga$_{16}$Ge$_{30}$ has been confirmed to be about 0.75 per unit formula at high pressure. The samples possess compact and desirable microstructures. With an increase in the Yb content, the carrier concentration is improved and the electrical resistivity is decreased. $\kappa_L$ is significantly reduced by multiscale phonon scattering, owing to the existence of rattling, a heterogeneous distribution of nano- and microstructures, grain boundaries, abundant lattice distortions, lattice deformations, and dislocations. Therefore, a lowest $\kappa_L$ of 0.07 W m$^{-1}$ K$^{-1}$ at 873 K is achieved for the Yb$_{Ba_{8-x}}$Ga$_{16}$Ge$_{30}$ sample. The significantly reduced $\kappa$ of 0.84 W m$^{-1}$ K$^{-1}$ and the relatively higher PF of 10.34 $\mu$W cm$^{-1}$ K$^{-2}$ result in the higher peak ZT of 1.07 at 873 K for Yb$_{Ba_{0.5}}$Ga$_{16}$Ge$_{30}$. As described above, the HPHT method has numerous advantages, which can provide us a new avenue to optimize the TE performances, and its popularization is worthwhile.
4. EXPERIMENTAL PROCEDURE

High-purity single elements barium (Ba: 99.5%), germanium (Ge: 99.999% metals basis), gallium (Ga: 99.999%), and ytterbium (Yb: 99% metal basis) were weighed according to the stoichiometric ratio of Yb:Ba$_8$:Ga$_{16}$Ge$_{30}$ and arc-melted into ingots. The ingots were ground to a fine powder by mortar and pestle and then loaded into a Retsch MM400 mixer mill with a rotational speed of 450 rpm for 1 h under Ar protection. The initial mixtures were shaped into a cylinder of about 3.5 mm thickness and 10.5 mm diameter by cold pressing agglomeration. The precursor samples were assembled into a sample chamber of 23 mm for HPHT synthesis. All experimental procedures were performed in cubic anvil high-pressure apparatus (SPD-6 × 1200). All samples were synthesized under a pressure of 3 GPa and at 1077 K for 30 min and then stopped and undergone high-pressure quenching quickly. In the end, releasing the pressure to the atmospheric pressure, the samples were polished, incised, and tested.

The crystal phases of the bulk samples were examined using an X-ray diffractometer (RigakuD/MAX-RA) with Cu Kα (λ = 1.5418Å) radiation in the 2θ range from 20 to 75°. Unit cell dimensions were determined from the peak location and the corresponding Miller indices using MDI Jade 5. Field-emission scanning electron microscopy (SEM, JEOL JSM-6700F) and energy-dispersive spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) were performed to observe the morphology, microstructure, and elemental composition of the samples. The Hall coefficient ($R_H$) (room temperature) was measured on a home-made system under a reversible magnetic field (0.6 T) and an electrical current (100 mA). The carrier concentration ($n$) was calculated by the relationship $n = 1/eR_H$, where $e$ is the electronic charge. The Hall mobility ($\mu_H$) was estimated using the formula $\mu_H = R_H/\rho$, where $\rho$ and $S$ were measured from 300 to 873 K using a ULVAC-RIKO ZEM-3 instrument. The thermal diffusivity $\lambda$ was measured using a Netzsch LFA-457 laser thermal conductivity instrument from 300 to 873 K. $\kappa$ was calculated via the formula $k = \lambda C_p D$, where $D$ is the sample density measured by the Archimedes method. $C_p$ was measured using Linseis STA PT-1750 equipment. ZTs were obtained based on the above-mentioned parameters.

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Notes

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