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Synthesis and high temperature thermoelectric transport properties of Si-based type-I clathrates*

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N-type Si-based type-I clathrates with different Ga content were synthesized by combining the solid-state reaction method, melting method and spark plasma sintering (SPS) method. The effects of Ga composition on high temperature thermoelectric transport properties were investigated. The results show that at room temperature, the carrier concentration decreases, while the carrier mobility increases slightly with increasing Ga content. The Seebeck coefficient increases with increasing Ga content. Among all the samples, $Ba_{7.93}Ga_{17.13}Si_{28.72}$exhibits higher Seebeck coefficient than the others and reaches -135 $\mu V \cdot K^{-1}$ at 1000 K. The sample prepared by this method exhibits very high electrical conductivity, and reaches 1.95×10^5 $S \cdot m^{-1}$ for $Ba_{8.01}Ga_{16.61}Si_{28.93}$ at room temperature. The thermal conductivity of all samples is almost temperature independent in the temperature range of 300–1000 K, indicating the behaviour of a typical metal. The maximum ZT value of 0.75 is obtained at 1000 K for the compound $Ba_{7.93}Ga_{17.13}Si_{28.72}$.

Keywords: type-I clathrate, thermoelectric materials, synthesis
PACC: 8120, 7215, 7430F

1. Introduction

During the last decade renewed interest has arisen in the search for improved thermoelectric materials for cooling and power generation applications. The performance of thermoelectric materials is usually evaluated by the dimensionless figure of merit ZT defined by $ZT=\alpha^2\sigma T/\kappa$, where σ, α, κ and T represent electrical conductivity, Seebeck coefficient, thermal conductivity and absolute temperature, respectively. Although significant improvements in the properties of thermoelectric materials have been achieved in the last 30 years, the maximum value of ZT is still near 1. The search for new thermoelectric materials with high ZT value has focused recently on novel compounds with a complex crystal structure such as filled skutterudites[1−5] and clathrates[6−9] mainly due to their remarkably low lattice thermal conductivity. Type-I clathrate (space group $pm-3n$) compounds are one of the promising thermoelectric materials because of their unique structure and properties related to their structure.[10,11] They contain two pentagonal dodecahedra and six hexakaidecahedra formed by B^{III} and B^{IV} atoms in the unit cell, and these polyhedra are linked by shared faces. The large cages inside the B^{III}–B^{IV} framework can incorporate alkali-earth atoms, which are located in the centre of the polyhedra and their large-amplitude vibration inside the cages reduces the lattice part of the thermal conductivity. On the other hand, these materials manage to maintain relatively good electrical conduction through the covalent sp^3 hybridized B^{III}–B^{IV} framework, which dominates the band structure and electronic transport properties of the compounds. Kuznetzov *et al*[12] have prepared polycrystalline $Ba_8Ga_{16}Si_{30}$, $Ba_8Ga_{16}Si_{30}$, $Ba_8Ga_{16}Ge_{30}$, $Ba_8Ga_{16}Sn_{30}$ and $Sr_8Ga_{16}Ge_{30}$ compounds in alumina crucibles coated on the inside with a graphite layer. The high temperature figure of merit value of clathrates was assessed based on the experimental Seebeck coefficient and resistivity data and taking into account the calculated thermal conductivities. The estimated maximum ZT value reaches 0.7 for $Ba_8Ga_{16}Ge_{30}$ and 0.87 for $Ba_8Ga_{16}Si_{30}$ at 700 K and 870 K, respectively. This reveals that the Si-based clathrate may have higher ZT value than the Ge-based clathrate at high temperature, but there are not many

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reports on the high temperature thermoelectric transport properties of Si-based type-I clathrates. In this work, Si-based type-I clathrates $Ba_8Ga_xGe_{46-x}$ filled with Ba with different Ga content (S_A: $x = 15.72$, S_B: $x = 16.61$, S_B: $x = 17.13$) were synthesized by combining the solid-state reaction method, melting method and spark plasma sintering (SPS) method. The effects of Ga composition on high temperature thermoelectric transport properties have been investigated.

2. Experimental

Because of the high chemical activity of barium, it is difficult to synthesize $Ba_8Ga_xSi_{46-x}$ compounds with melting methods directly. In this study, Si-clathrate compounds were synthesized using solid-state reaction methods and melting methods. In the first step, stoichiometric amounts of Ba (ingot, 99.9%) and Si (powder, 99.99%) were placed in a quartz tube coated on the inside with a graphite layer. Then the quartz tube was sealed under a pressure of 1.0×10^{-2} Pa, and heated slowly at a heating rate of 5 K/min to a temperature of 1100 K. They were maintained at this temperature for 9 hours, and then cooled down by furnace cooling. Second, stoichiometric amounts of Ga (ingot, 99.99%) and the product of the first step were placed in a quartz tube coated on the inside with a graphite layer. The quartz tube was sealed under a pressure of 1.0×10^{-2} Pa and then heated slowly at a rate of 5 K/min to of 1523 K,[12] maintained at this temperature for 5 hours, and then cooled down by furnace cooling. The bulk samples used to measure Seebeck coefficient, electrical conductivity and thermal conductivity were prepared by spark plasma sintering (SPS) and the sintering temperature and time were 1223 K and 10 minutes, respectively. The relative density of the obtained sintered bulk was about 97∼98%. The phase identification was characterized by x-ray diffraction (XRD, PANalytical X'Pert Pro x-ray diffraction). The composition was obtained by electron probe microanalysis (EPMA, JXA8800). The carrier mobility μ_H, carrier density N_n and Hall coefficient α at room temperature were measured using the van der Pauw method by the Accent, HL5500PC system. Electrical conductivity (κ) was calculated from the measured thermal diffusivity D, specific heat C_p, and density d using the relationship $\kappa = D \times C_p \times d$, where d is the density of the specimen. The thermal diffusivity (D) and specific heat (C_p) were measured by a laser flash method (Shinkuriko TC-7000). All the measurements were performed in the temperature range 300–1000 K.

3. Results and discussion

3.1. Structure of prepared specimens

Powder x-ray diffractions patterns of $Ba_8Ga_xSi_{46-x}$ compounds are shown in Fig.1 and parameters of the crystal plane are denoted. The samples prepared by this method all show a single phase, which is a typical structure of type-I clathrates with space group $pm\bar{3}n$. The lattice parameter of $Ba_{7.81}Ga_{15.72}Si_{29.83}$ is 10.52026 Å and cell volume is 1164.34 Å^3 well agree with the result of work done by the Kuznetzov group.[12] The XRD patterns shift to low diffraction angle with increasing Ga content, indicating the lattice parameter of the prepared samples increases with increasing Ga content due to the larger atomic radius of Ga compared with Si.

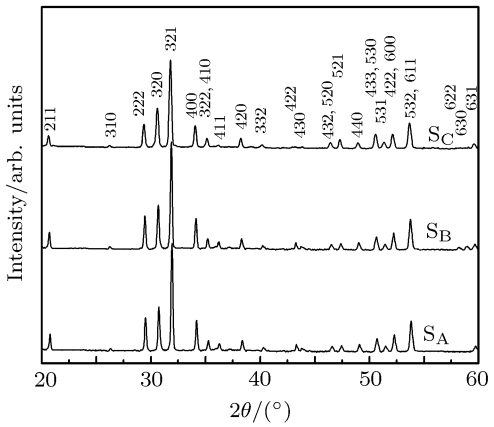


Fig.1. XRD patterns for $Ba_8Ga_xSi_{46-x}$ compounds (Where S_A, S_B, S_C is the sample for Ga content $x = 15.72$, $x = 16.61$, and $x = 17.13$ respectively obtained by EPMA).

3.2. Electrical transport properties

In Table 1, the Seebeck coefficient, electrical resistivity, carrier concentration, calculated effective carrier mass and composition obtained by EPMA for clathrate compounds, at room temperature are presented.

Table 1. Composition, rsistivity (ρ). Hall coeficient (R_H), carrier concentration (N_n), carrier mobility (μ_H), calculated effective carrier mass (m^*/m_0) for $Ba_8Ga_xGe_{46-x}$ clathrates at room temperature.

sample	composition	ρ/(mΩ·cm)	$R_H/(10^{-3}cm^3\cdot C^{-1})$	$N_n/(10^{21}cm^{-3})$	$\mu_H/(cm^2\cdot/V^{-1}\cdot s^{-1})$	m^*/m_0
S_A	$Ba_{7.81}Ga_{15.72}Si_{29.83}$	0.58	–5.5	6.31	1.67	5.4
S_B	$Ba_{8.01}Ga_{16.61}Si_{28.93}$	0.54	–1.94	3.22	3.55	3.6
S_C	$Ba_{7.93}Ga_{17.13}Si_{28.72}$	0.73	–9.8	1.13	7.32	1.9

All the compounds possess n-type conductivity and have a carrier concentration higher than 8.7×10^{20} in the literature.[12] The reason for the higher carrier concentration in the present work may be ascribed to vacancy absence in the framework. Okamoto *et al* [13] prepared Ge-based type-I clathrates with normal composition $Ba_8Ga_{16}Ge_{30}$ by arc melting, followed by annealing at 790°C in vacuum for 12 h, and then by furnace cooling. The structure refinement and energy dispersive x-ray spectroscopy (EDS) analysis indicates that there is a certain vacancy in the framework, and the actual total content of Ge and Ga is less than 46. In this work, the actual total content of Si and Ga is nearly equal to 46, indicating the vacancy absence in the framework. At room temperature the carrier mobility increases slightly with increasing Ga composition mainly due to weaker electron scattering caused by lower carrier concentration. The carrier mobility of all samples will decrease due to the stronger lattice vibration with the increase of temperature.

According to the charge compensation concept,[13–15] in $II_8III_{16}IV_{30}$ type-I clathrates, guest atoms donate electrons (as donors) to framework host atoms (as acceptors). Some (or all) of the electrons donated by guest atoms can be compensated by lone pairs formed in the cage structure through the elements of group III. In the present work, the lone pairs formed in the cage structure through the elements of group III increasing with the increase of Ga content, and then some of the electrons donated by Ba atoms compensate it; consequently electron concentration decreases with increasing Ga content.

The electrical conductivity of the samples as a function of temperature is shown in Fig.2. The samples prepared by this method exhibit relatively higher electrical conductivity due to the relatively higher carrier concentration. The electrical conductivities reach $1.56\times^5$ S·m^{-1}, 1.95×10^5 S·m^{-1} and 1.68×10^5 S·m^{-1} at room temperature for $Ba_{7.81}Ga_{15.72}Si_{29.83}$, $Ba_{8.01}Ga_{16.61}Si_{28.93}$ and $Ba_{7.93}Ga_{17.13}Si_{28.72}$, respectively. $Ba_{8.01}Ga_{16.61}Si_{28.93}$ compound possess the largest electrical conductivity due to moderate carrier concentration and carrier mobility. The electrical conductivity decreases monotonously with the increasing of temperature, showing a typical metallic behaviour.

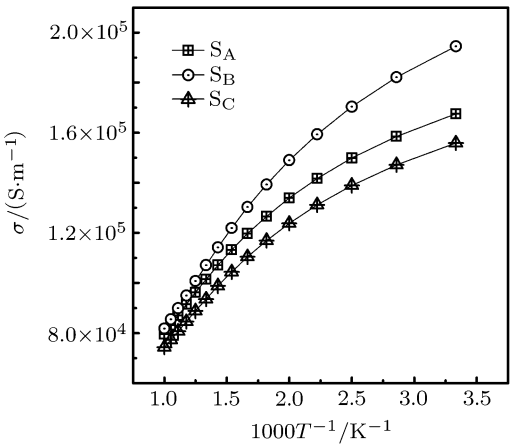


Fig.2. Temperature dependence of electrical conductivity for $Ba_8Ga_xSi_{46-x}$ clathrates.

Figure 3 shows the Seebeck coefficient of $Ba_8Ga_xSi_{46-x}$ clathrates as a function of temperature in the range 300–1000 K. The absolute value of the Seebeck coefficient gradually increases with increasing temperature, and does not reach its maximum value in the temperature range during the measurements. It is assumed that the extrinsic carrier concentration remains constant in the range 300–1000 K. The Seebeck coefficient of the samples increases with increasing of Ga content. Nolas *et al*[14] found that the effect of Ga/Ge ratio on the Seebeck coefficient α is sensitive for Ge-based clathrates with the voids filled with Sr, and the absolute value of α increases with increasing Ga/Ge ratio. In this study, the Ga/Ge ratio increases with the increase of Ga content and result in the increase of α, which agrees with the result for Ge-based clathrates.

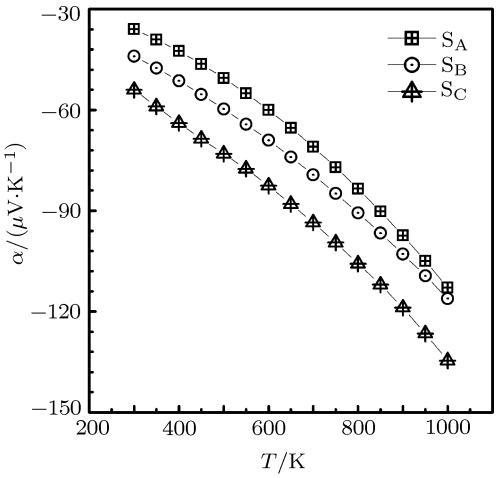


Fig.3. Seebeck coefficient as a function of temperature for $Ba_8Ga_xSi_{46-x}$ clathrates.

The carrier effective mass was estimated by expressing the Seebeck coefficient directly in terms of Fermi–Dirac integrals[16]

$$\alpha = \pm\frac{k_B}{e}\left[\eta - \frac{[r+(5/2)]\,F_{r+3/2}(\eta)}{[r+(3/2)]\,F_{r+1/2}(\eta)}\right], \qquad (1)$$

where k_B is Boltzmann's constant, e is the carrier charge, r is the exponent of the energy dependence of the carrier relaxation time, $\eta = E_F/k_BT$ is the reduced Fermi energy and $F(\eta)$ is the Fermi integral. The signs '+' and '−' correspond to valence band carriers and conduction band carriers, respectively. This estimate requires the following assumptions: a single carrier type in a parabolic band, the absence of multiband effects, and no phonon-drag effects. The carrier concentration is given by

$$n = N_0(T)(m^*/m_o)^{2/3}F_{1/2}(\eta), \qquad (2)$$

where m_0 is the free electron mass and m^* is the effective electron mass. Assuming mixed ionized impurity and phonon scatterings ($r = 1/2$), the estimated effective mass was calculated for the $Ba_8Ga_xGe_{46-x}$ specimens and is listed in Table 1. These m^* values decrease with increasing Ga content, due to the band structure affected by increasing Ga content. Except for $Ba_{7.93}Ga_{17.13}Si_{28.72}$ compound, the value of m^* is larger than that of the $Ba_8Ga_{16}Si_{30}$ compound prepared by melting method.[12]

The temperature dependence of power factor P ($P = \alpha^2\sigma$) for $Ba_8Ga_xSi_{46-x}$ is shown in Fig.4. At 1000 K, the highest temperature investigated, the power factor value of $Ba_{7.93}Ga_{17.13}Si_{28.72}$ is as large as 1.45×10^{-3} W·m^{-1}·K^{-2}.

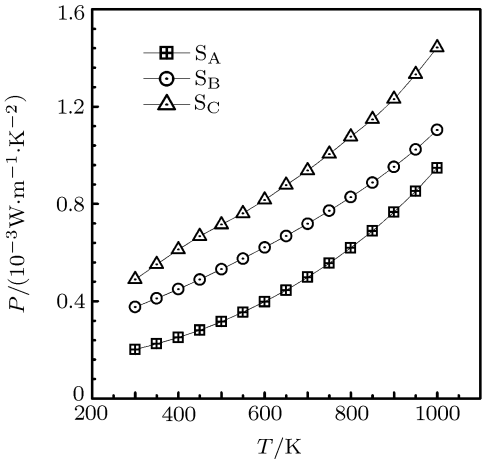


Fig.4. Temperature dependence of power factor for $Ba_8Ga_xSi_{46-x}$ clathrates.

3.3. Thermal conductivity transport properties

The thermal conductivity of all samples are almost temperature independent in the measured temperature range and they are about 1.90 W·m^{-1}·K^{-1}, 2.0 W·m^{-1}·K^{-1} and 1.85 W·m^{-1}·K^{-1} for the sample of S_A, S_B and S_C, respectively

Using the Wiedemann–Franz law[17] the carrier thermal conductivity κ_c is calculated as,

$$\kappa_c = L\sigma T, \qquad (3)$$

where L is the Lorenz number, σ is electrical conductivity, and T is absolute temperature. L can be calculated by Fermi level in the temperature range from 300 to 1000 K

$$L = \left(\frac{k_B}{e}\right)^2\left[\frac{[r+(7/2)]\,F_{r+(5/2)}(\eta)}{[r+(3/2)]\,F_{r+(1/2)}(\eta)} - \delta^2\right], \qquad (4)$$

where

$$\delta = \left[\frac{[r+(5/2)]\,F_{r+5/2}(\eta)}{[r+(3/2)]\,F_{r+1/2}(\eta)}\right]. \qquad (5)$$

The Fermi integral $F(\eta)$ is calculated by formula (1). Figure 5 shows the temperature dependence of carrier thermal conductivity for $Ba_8Ga_xGe_{46-x}$ compounds in the measured temperature range.

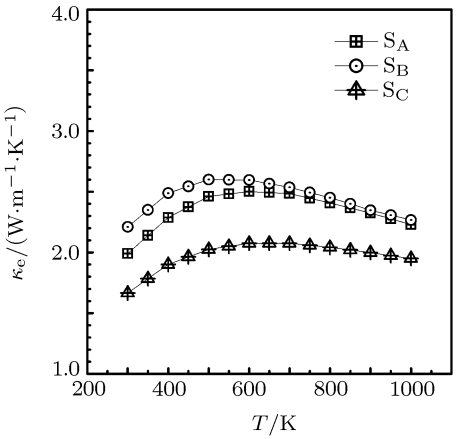


Fig.5. Temperature dependence of carrier thermal conductivity for $Ba_8Ga_xGe_{46-x}$ clathrates.

From Fig.5 it can be seen that the estimated carrier thermal conductivity nearly corresponds to the value of measured thermal conductivity. Although some errors may exist between the estimate values and actual values for the carrier thermal conductivity, this can imply that the lattice thermal is very small and the samples prepared here behave with the typical properties of a metal. The results[18] of electrical resistivity measurement show that the electrical resistivity of $Sr_8Ga_{11}Si_{35}$ type-I clathrates synthesized by floating-zone melting method have the characteristics of a metal, and the electrical conductivity is as high as 5.0×10^5 S·m^{-1} at a temperature of 300 K. This value is much higher than the value of the present samples at the same temperature. These results may reveal that the thermoelectric transport properties of Si-based type-I clathrates are very different from Ge-based clathrates[7,18] with the characteristics of a semiconductor, in which the lattice thermoelectric has a dominant role in the total thermal conductivity.

3.4. Figure of merit (ZT)

From the measured electrical conductivity (σ), Seebeck coefficient (α) and thermal conductivity (κ), ZT is calculated from ZT=$\alpha^2\sigma T/\kappa$. Figure 6 shows the temperature dependence of ZT for $Ba_8Ga_xGe_{46-x}$ compounds. The ZT of all samples increases with increasing temperature and does not reach its maximum value in the measured temperature range. ZT will increase on the assumption that measured temperature is further increasing. The maximum ZT value of 0.75 is obtained at 1000 K for the $Ba_{7.93}Ga_{17.13}Si_{28.72}$ compound.

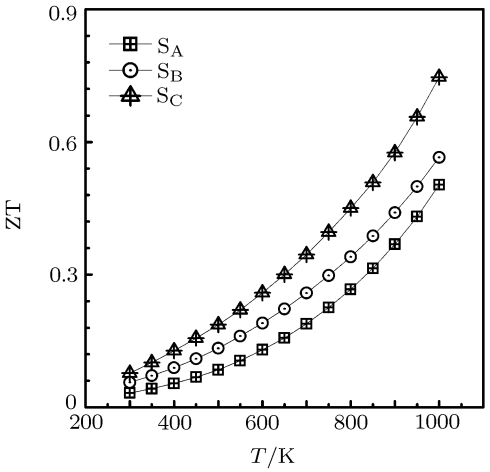


Fig.6. Temperature dependence of ZT for $Ba_8Ga_xSi_{46-x}$ clathrates.

4. Conclusions

In general, single phrase n-type $Ba_8Ga_xSi_{46-x}$ (x = 15.72, 16.61, 17.13) clathrates were synthesized by combining the solid-state reaction method, melting reaction method and SPS method. The results show that all the compounds possess n-type conductivity with a relatively high carrier concentration. At room temperature the carrier mobility and the Seebeck coefficient increase with increasing Ga composition. The samples prepared by this method exhibit very high electrical conductivity, which reaches 1.9×10^5 S·m^{-1} at room temperature for $Ba_{8.01}Ga_{16.61}Si_{28.93.}$ $Ba_{7.93}Ga_{17.13}Si_{28.72}$ exhibits a higher power factor in the measured temperature range and it reaches as much as 1.45×10^{-3} W·m^{-1}·K^{-2} at 1000 K. The thermal conductivity values of all the samples are almost temperature independent in the temperature range 300–1000 K and have the typical properties of a metal. The maximum ZT value of 0.75 is obtained at 1000 K for the $Ba_{7.93}Ga_{17.13}Si_{28.72}$ compound.

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