



## Evolution of thermoelectric properties of substituted Si-based clathrates prepared by HPHT



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### ABSTRACT

Polycrystalline bulk materials  $\text{Ba}_8\text{Cu}_x\text{Ge}_y\text{Si}_{46-x-y}$  ( $x = 0, 6; y = 0, 20$ ) were prepared by high-pressure and high-temperature (HPHT) method and characterized using X-ray diffraction and Rietveld refinement. Results of EDS analysis showed that the solubility limit of copper composition in this clathrate is about 5. Electrical properties measurements between 300 K and 720 K revealed the behavior of a degenerate semiconductor for all samples. As the framework elements increased, the Seebeck coefficient and electrical resistivity increased, but the thermal conductivity decreased greatly, which leads to significant enhancement on thermoelectric properties of the clathrates. The lattice defects of samples generated by high pressure efficiently reduced the lattice thermal conductivity.

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### 1. Introduction

Thermoelectric (TE) materials, which can be used for the conversion of heat to electricity, continue to be scientific interest since Slack brought up the concept of “phonon glass and electron crystal” (PGEC) [1–3]. PGEC materials would possess electrical properties normally associated with single crystal semiconductor but its thermal conductivity is similar to amorphous materials [4]. The performance of materials for thermoelectric properties is described by the figure of merit  $ZT$  defined as  $ZT = S^2T/\rho\kappa$ , where  $S$ ,  $\rho$ ,  $\kappa$ ,  $T$  are Seebeck coefficient, electrical resistivity, total thermal conductivity, and absolute temperature, respectively. The essential challenge wanting to design or discover better TE materials is low conversion efficiency, then improving the conversion efficiency becomes an important topic of the research [5].

Type-I clathrates, especially Si- and Ge-based, have been extensively examined as prospective TE materials because of unique structures and properties. Fig. 1 shows the type-I clathrate structure. The unit cell of type-I clathrate contains six tetrakaidecahedron and two dodecahedron which are formed by framework atoms and guest atoms encapsulated in those cages. The host atoms

form weak bonds with interstitial atoms, thus resulting in localized vibrational modes and scatter the phonons, which lower the thermal conductivity [6]. On the other hand, the covalently bonded framework promotes high electron mobility leading to relatively good electrical conductivity, which dominates the band structure as well as electronic transport properties of the compounds [7,8].

Efforts to optimize the thermoelectric performance of clathrates must improve the thermoelectric parameters, which are closely related to the details of the electronic structure. The electrical transport properties of clathrates are mainly controlled by the framework atoms and can be significantly changed by doping different atoms in the cages of the framework [9]. An increasing amount of systematic studies is currently devoted to the impact of the host structure on these compounds, which typically are substituted by a range of elements [10–14]. This way can modify the details of the electronic structure, which can increase the Seebeck coefficient, leading to the enhancement of thermoelectric performance. For another, the thermal conductivity of clathrates depends not only on the guests, but also on the framework atoms [15]. But, there is little experimental and theoretical knowledge in the literature about this.

In almost all of the researches on the clathrates, the starting materials used to be high purity elements of barium. But, the purity of barium metals is not easy to control owing to extremely high chemical reactivity. So, we use  $\text{BaSi}_2$  as one of the starting materials

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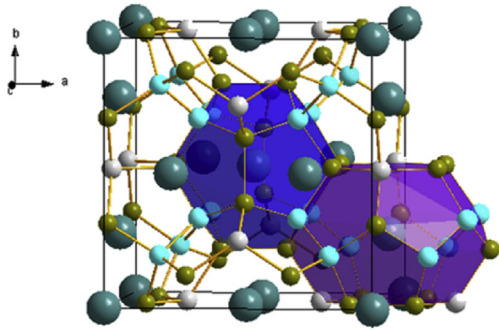


Fig. 1. The crystal structure of type-I clathrate contains 20- and 24-atom polyhedron.

in place of barium. On the other hand, the compounds are prepared by diverse techniques [9,16,17], which is partially offset because of complicated procedures and time consuming. Then, we have tried to synthesize type-I clathrates by a novel method of HPHT, which takes just an hour to synthesize clathrates. The method has been proved an effective approach to synthesize bulk materials, which can improve thermoelectric properties obviously and maintain the high pressure characteristics [18,19]. In this paper, we have successfully synthesized  $\text{Ba}_8\text{Cu}_x\text{Ge}_y\text{Si}_{46-x-y}$  using the HPHT method, and the effects of elemental substitution on thermoelectric properties will be discussed.

## 2. Experimental

### 2.1. Preparation of $\text{Ba}_8\text{Cu}_x\text{Ge}_y\text{Si}_{46-x-y}$ ( $x = 0, 6; y = 0, 20$ ) samples

Samples with nominal compositions  $\text{Ba}_8\text{Cu}_x\text{Ge}_y\text{Si}_{46-x-y}$  were prepared by HPHT method. Appropriate amounts of silicon (Si; 99.999% metals basis), germanium (Ge; 99.999% metals basis), copper (Cu; 99.999% metals basis) and  $\text{BaSi}_2$  obtained by arc melting method were weighed according to the stoichiometry of  $\text{Ba}_8\text{Cu}_x\text{Ge}_y\text{Si}_{46-x-y}$ . The compounds were uniformly mixed in an agate pestle and mortar in a glove box under nitrogen gas atmosphere. The mixtures were compressed into  $\Phi 10 \times 3.5$  mm cylinder and were encased with molybdenum foil inside an appropriate graphite crucible for HPHT synthesis. The pole shaped samples were prepared in China-type large volume cubic high-pressure apparatus (SPD-6  $\times$  1200) with a sample chamber of 23 mm on an edge at 3.5 GPa and 1110 K. The pressure was calibrated using standard substances to determine the change in resistance. The synthesis temperature was measured using a platinum–rhodium/platinum–rhodium6 (PtRh/PtRh6) thermocouple placed near the sample.

### 2.2. Characterization and structural refinement

The crystal structures of the samples were characterized by X-ray diffractions (XRD) (D/MAX-RA) using  $\text{Cu-K}\alpha$  radiation in the  $2\theta$  range from  $15^\circ$  to  $70^\circ$ . Microstructures and chemical compositions of phases were examined by scanning electron microscopy (FESEM, JEOLJSM-6700F) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2200FS). Structural refinement of the powder X-ray diffraction data was carried out using the GSAS software package.

### 2.3. Thermoelectric property measurements

Measurements of the electrical resistivity and Seebeck coefficient were performed on a ZEM-3 apparatus in temperature range

of 300 K–720 K. The errors in electrical resistivity and Seebeck coefficient measurements were estimated to be less than  $\pm 5\%$ , which did not affect the data analysis. The thermal diffusivity ( $D$ ) was measured using the laser flash technique (Netzsch LFA-427), and the specific heat ( $C_p$ ) was measured using DSC conversion with simultaneous thermal analysis (Linseis STA PT-1750) with sapphire revision. The thermal conductivity ( $\kappa$ ) was calculated by the relation  $\kappa = D \times C_p \times d$ , where  $d$  is the density of samples. The density ( $d$ ) of samples was tested using the Archimedes method.

## 3. Results and discussion

Fig. 2 shows the powder X-ray diffraction patterns of  $\text{Ba}_8\text{Cu}_x\text{Ge}_y\text{Si}_{46-x-y}$  prepared by HPHT. The sharp peaks reveal that the dominant phase is the type-I clathrate [cubic space group  $\text{Pm}\bar{3}\text{n}$  (No. 223)], with the trace amounts of secondary phase Si are observed in  $\text{Ba}_8\text{Cu}_6\text{Si}_{40}$ . To confirm that the samples prepared by HPHT are the type-I clathrate, the X-ray diffraction data are analyzed by the Rietveld structure refinement for  $\text{Ba}_8\text{Cu}_6\text{Si}_{40}$ , using the GSAS software package. Fig. 3 shows observed and the difference profile, and Table 1 gives the data collection and the refinement parameters for the Rietveld analysis of  $\text{Ba}_8\text{Cu}_6\text{Si}_{40}$ . From what is shown in Table 1 and Fig. 3, it can be confirmed that the results of the Rietveld analysis are reliable, and the compounds obtained in this work are type-I clathrates. In addition, the processing time prepared by HPHT method is reduced from several days to an hour. It indicates that the clathrates can be successfully synthesized by HPHT method. Lattice constant and measured densities for different proportion are given in Table 2. With the increasing of framework elements, the lattice constant monotonically increases, which can be qualitatively explained by the fact that the atomic radius of Ge (0.122 nm) or Cu (0.135 nm) in tetrahedral covalent bonds is larger than that of Si (0.117 nm) [20].

As an example shown in Fig. 4, SEM observation with mapping images obviously shows homogeneity in the distribution of the constituent elements in the clathrate phase. The chemical composition of clathrates texted by EDS analysis is listed in Table 3. From EDS analysis, it is inferred that the solubility limit of Cu is close to  $x = 5$ , which agrees with the reported value by Li [21]. If Ba atoms is set as 8, the total atoms of host framework for samples is slightly smaller than 46. Thus the EDS analysis on the chemical composition means the existence of deficiency [22].

Fig. 5(a) gives the HRTEM micrograph of  $\text{Ba}_8\text{Cu}_6\text{Ge}_y\text{Si}_{40-y}$  prepared by HPHT. What is noteworthy is that the lattice orientation is in disorderly growth pattern, which can be easily found inside our

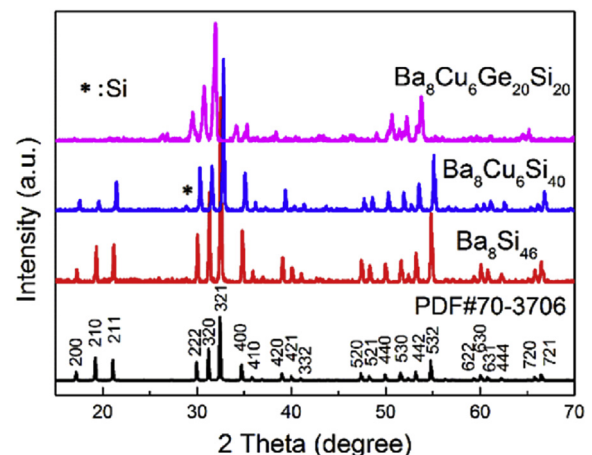


Fig. 2. XRD patterns of  $\text{Ba}_8\text{Cu}_x\text{Ge}_y\text{Si}_{46-x-y}$  prepared by HPHT.

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