

# Thermoelectric Properties of $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$ Clathrate Compounds

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The effect of Pd substitution on the electronic and thermoelectric properties for polycrystalline  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  ( $x=3-5$ ) clathrate compounds has been investigated. The Pd atoms can be incorporated into the crystallographic 6c site of the crystal lattice. Both *p*- and *n*-type samples with varying carrier concentration can be successfully prepared by changing Pd composition. The Seebeck coefficient for *n*-type  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  is larger than that for *n*-type  $\text{Ba}_8\text{Ga}_x\text{Ge}_{46-x}$  at the same carrier concentration. The analysis of transport properties suggests that the large density of states effective mass (about  $4m_0$ , where  $m_0$  is the free electron mass) leads to the enhanced Seebeck coefficient.

Key words: thermoelectric properties, Clathrate, palladium, Seebeck coefficient, Hall mobility

## 1. INTRODUCTION

Semiconducting type-I clathrate compounds with a general formula  $\text{M}_8\text{X}_{46}$  ( $\text{M}=\text{Sr}, \text{Ba}; \text{X}=\text{Si}, \text{Ge}, \text{Sn}$ ) have been studied extensively as promising candidates for thermoelectric applications because they combine glasslike thermal conductivity and good electronic transport properties. [1-6] The unit cell of type-I clathrates contains two pentagonal dodecahedra and eight hexakaidecahedra formed by X atoms, which are fully disordered on the three distinct framework sites. The large cages inside the framework can incorporate alkali-earth atoms and their anharmonic vibration inside the cages reduces the lattice thermal conductivity through an interaction of the filling atoms with a wide spectrum of low frequency phonons. On the other hand, these materials maintain relatively good electronic conduction through the covalent  $sp^3$  hybridized framework, which dominates the band structure and electronic transport properties of the compounds.

It has been reported that Si or Ge atoms at the crystallographical 6c sites can be replaced by transition metals. [7, 8] Kawaguchi *et al.* [9] reported that  $\text{Ba}_8\text{Mn}_2\text{Ge}_{44}$  clathrate shows ferromagnetic properties due to the interaction of the localized *d* electrons on Mn atoms with the conduction electrons. We have recently reported that in  $\text{Ba}_8\text{Pt}_x\text{Ga}_y\text{Ge}_{46-x-y}$  ( $y=16-4x$ ) system the Pt atoms are preferentially incorporated into the 6c site and the Seebeck coefficient is greatly enhanced with increasing Pt composition while the Hall mobility is hardly affected. [10] This result suggests that there is potential for improving the thermoelectric properties of clathrate materials by transition metal substitution. It is important to investigate systematically the effects of transition metal on the electronic properties of clathrates to elucidate the cause of enhancement of Seebeck coefficient. In this paper, we report on the synthesis of polycrystalline  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds with varying Pd compositions and their thermoelectric properties in an effort to begin the systematic survey.

## 2. EXPERIMENTAL PROCEDURE

Polycrystalline  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples with nominal Pd

compositions  $x=3-5$  were prepared by arc melting stoichiometric quantities of high-purity constituent elements in an argon atmosphere. The obtained ingots were then ground to fine powders ( $<90 \mu\text{m}$ ) and sintered inside graphite dies at  $750-740^\circ\text{C}$  and 30 MPa for 60 min in an argon atmosphere by a spark plasma sintering technique. Sample density was more than 98 % of the theoretical density. Powder x-ray diffraction measurements were performed to check the crystal structure.

The electrical conductivity  $\sigma$  and the Seebeck coefficient  $S$  were measured in the temperature range of 300–900 K. Hall measurements were performed at room temperature by applying an external magnetic field of 1 T using the van der Pauw method. The Hall mobility  $\mu$  was determined from the electrical conductivity  $\sigma$  and the Hall coefficient  $R_H$  using  $\mu=\sigma R_H$ .

## 3. RESULTS AND DISCUSSION

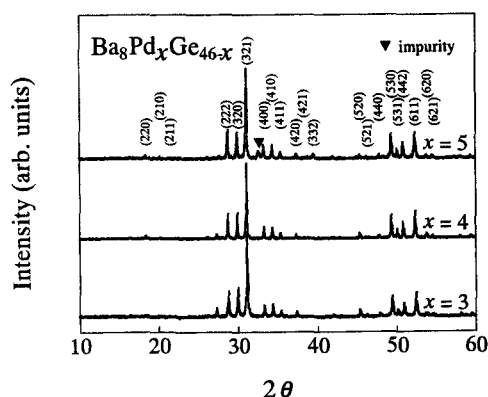


Fig. 1 X-ray diffraction patterns for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples with  $x=3, 4,$  and  $5$ .

Fig. 1 shows x-ray diffraction patterns for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds with different Pd compositions  $x=3, 4,$  and  $5$ . From x-ray diffraction measurements it

was found that almost all samples were single phase materials with the clathrate structure. However, x-ray diffraction peaks from an impurity phase were observed for samples with high Pd compositions ( $x=4.5$  and  $5$ ). The lattice constant increases with increasing Pd composition, but tends to be saturated at high Pd compositions ( $x>4$ ). One of the important features in the x-ray diffraction analysis is that the intensity ratio among the three low-angle diffraction peaks indexed by (222), (320), and (321) planes sensitively varies with the occupation of the crystallographic 6c sites, as reported for  $\text{Ba}_8\text{Mn}_2\text{Ge}_{44}$  clathrate compound. [9] It is clearly found that the relative intensity of the (320) peak decreases as the Pd composition increases. This can be interpreted in terms of the increase of Pd occupation of the 6c site in  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds.

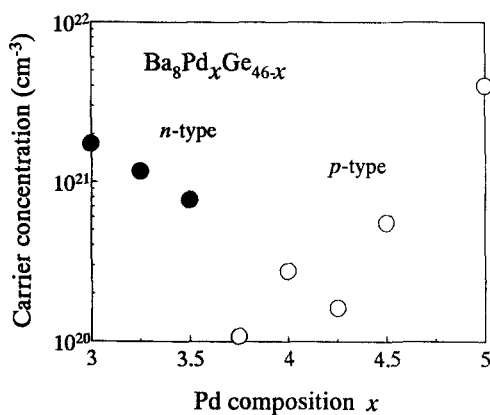


Fig. 2 Hall carrier concentration as a function of Pd composition  $x$  for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples. Open and solid plots represent  $p$ -type and  $n$ -type, respectively.

Fig. 2 shows the Hall carrier concentration at room temperature as a function of Pd composition  $x$  for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds. The Hall coefficient at room temperature was found to be negative for  $3 \leq x \leq 3.5$  and positive for  $3.75 \leq x \leq 5$ . This result is represented by solid and open plots in Fig. 2. As described below, it is noted that the sample with  $x=3.75$  shows negative Seebeck coefficient. The carrier concentration decreases with increasing Pd composition up to  $x=3.5$ , then increases with increasing  $x$ . It is found that both  $p$ - and  $n$ -type  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds with different doping levels can be successfully prepared by varying Pd-to-Ge ratio. It can be considered that Pd acts as tetravalent acceptors that compensate the electrons donated from divalent Ba ions. The electronic band calculations on transition metal clathrates made by Akai *et al.* [11] show that the transition metals (Cu, Ag, Au) act as acceptors supplying with four holes in the clathrates. The change of the carrier concentration with Pd composition can be explained qualitatively by this model. The deficiency of Ba from the stoichiometry and the influence of impurity will occur deviation from the model.

The Seebeck coefficient  $S$  at room temperature for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds are plotted in Fig. 3 as a function of carrier concentration. The data for  $\text{Ba}_8\text{Ga}_y\text{Ge}_{46-y}$  samples are also shown by dashed lines for

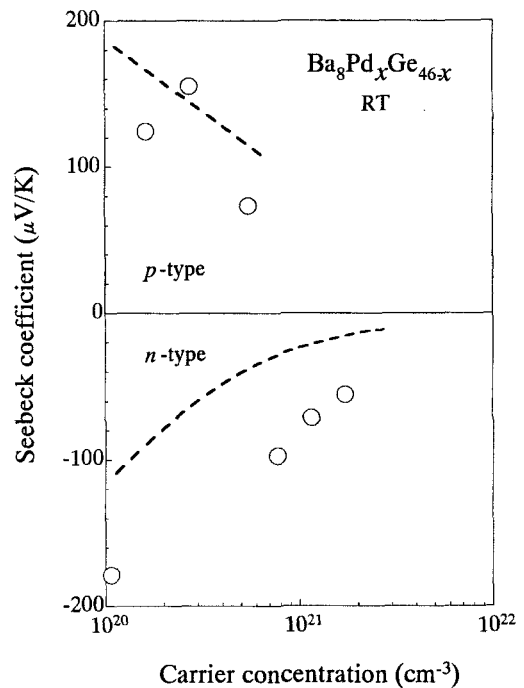


Fig. 3 Seebeck coefficient  $S$  at room temperature as a function of carrier concentration for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples.

comparison. The Seebeck coefficient values for  $n$ -type  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples are more than two times larger than those for  $n$ -type  $\text{Ba}_8\text{Ga}_y\text{Ge}_{46-y}$  samples at similar carrier concentrations. On the other hand, the Seebeck coefficient values for  $p$ -type  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples are roughly equivalent to those for  $p$ -type  $\text{Ba}_8\text{Ga}_y\text{Ge}_{46-y}$  samples. The Seebeck coefficient is related to the details of the electronic structure near the Fermi level. According to Boltzmann transport theory, the variation in the density of states near the Fermi level is important to the magnitude of the Seebeck coefficient. Proximity of a steeply sloping band edge to the Fermi level will be favorable to a large value of the Seebeck coefficient. We estimated the density of states effective mass  $m^*$  using a single parabolic band model with acoustic phonon scattering, as described elsewhere. [12] The density of states effective mass for  $p$ - and  $n$ -type  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds was found to be about  $3m_0$ – $4m_0$ , where  $m_0$  is the free electron mass. This value is about three times larger than that for  $n$ -type  $\text{Ba}_8\text{Ga}_y\text{Ge}_{46-y}$  and comparable to that for  $p$ -type one. According to the band structure calculation on  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ , [13] the lowest conduction bands arise from bonding between Ba and the antibonding framework orbitals involving atoms in the 6-ring. Thus, the preferential occupation of the 6c site in the 6-ring by Pd may have a great influence on the conduction band structure.

Figs. 4 (a) and 4 (b) show the Hall mobility at room temperature as a function of carrier concentration for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds. In Figs. 4 the data for  $\text{Ba}_8\text{Ga}_y\text{Ge}_{46-y}$  samples are also shown by dashed lines for comparison. The Hall mobility values for  $n$ -type  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples are smaller than those for  $n$ -type  $\text{Ba}_8\text{Ga}_y\text{Ge}_{46-y}$  at similar carrier concentrations. This is

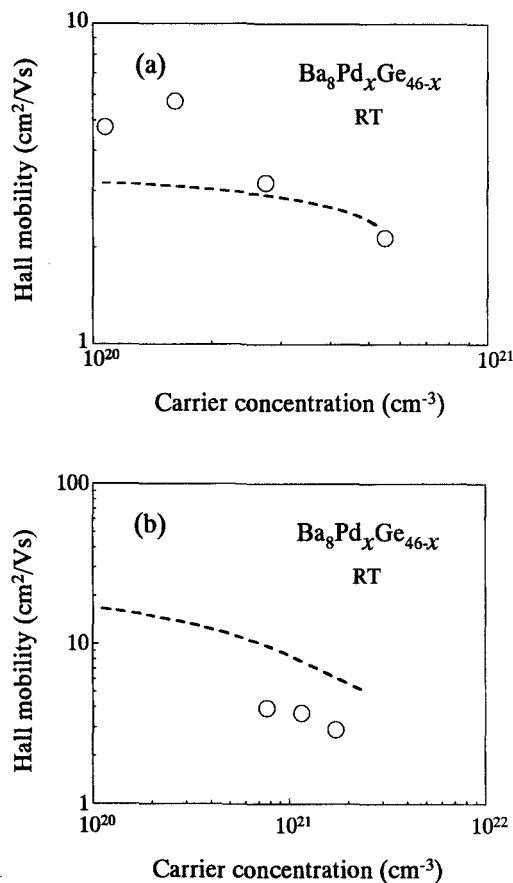


Fig. 4 Hall mobility at room temperature as a function of carrier concentration for (a) *p*-type and (b) *n*-type  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples.

presumably due to the large carrier effective mass for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds. The Hall mobility values for *p*-type  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples are relatively large as compared to those for *p*-type  $\text{Ba}_8\text{Ga}_y\text{Ge}_{46-y}$  samples. The carrier mobility values are smaller than those for crystalline Ge with the diamond-type crystal structure at room temperature at the same carrier concentration. The Ba ions are likely to cause Coulomb scattering of the carriers.

Fig. 5 shows the Seebeck coefficient as a function of temperature for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples with different Pd compositions  $x$ . The sign of the Seebeck coefficient agrees with that of the Hall coefficient except for  $x=3.75$ . The difference in the sign between the Hall coefficient and the Seebeck coefficient for  $x=3.75$  may be attributed to the effect of two-band conduction due to significant contributions both from electrons and holes. It is interesting to see that the Seebeck coefficient for *p*-type samples and *n*-type sample with  $x=3.75$  shows the maximum near room temperature. For *n*-type samples with  $x=3-3.5$ , the Seebeck coefficient gradually increases with increasing temperature, and exhibits a maximum at high temperatures, then starts to decrease due to intrinsic conduction. It is found that  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds have large Seebeck coefficient at relatively low temperature range.

Fig. 6 shows the electrical conductivity as a function

of inverse temperature for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  compounds with different Pd compositions  $x$ . For *n*-type samples with  $x=3-3.5$ , at low temperatures, the electrical conductivity is typical for heavily doped semiconductors and decreases almost linearly with increasing temperature. At high temperatures, the electrical conductivity increases with increasing temperature due to the intrinsic conduction. We estimated the activation energy  $E_a$  about 0.12 eV from the analysis of the high-temperature properties using a relation  $\sigma \propto \exp(E_a/k_B T)$ .

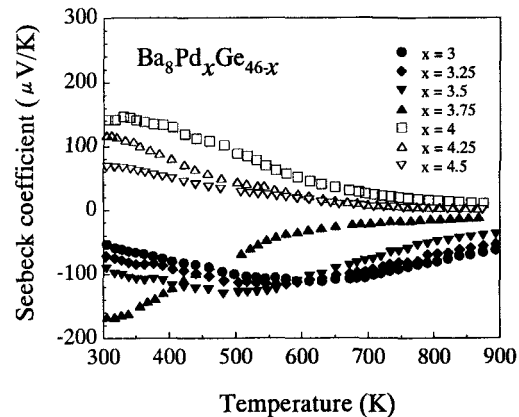


Fig. 5 Seebeck coefficient as a function of temperature for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples.

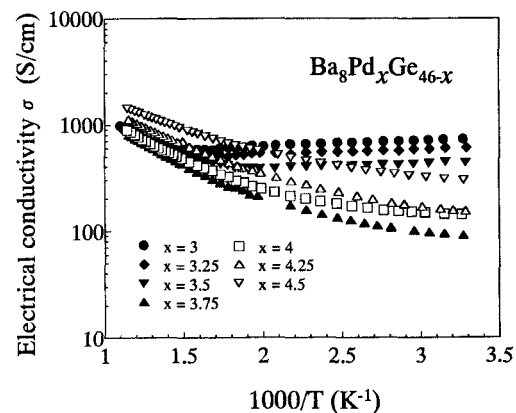


Fig. 6 Electrical conductivity as a function of inverse temperature for  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  samples. Open and solid plots represent *p*-type and *n*-type, respectively.

#### 4. CONCLUSION

We have investigated the electronic and thermoelectric properties of polycrystalline  $\text{Ba}_8\text{Pd}_x\text{Ge}_{46-x}$  clathrate compounds with varying Pd compositions. The results are summarized as follows:

- (1) The Ge atoms at the 6c site in the clathrate structure can be replaced by Pd atoms.
- (2) Both *p*- and *n*-type compounds with different doping levels can be successfully prepared by varying Pd-to-Ge ratio.
- (3) The Seebeck coefficient for *n*-type compounds

is about two times larger than that for  $n$ -type  $Ba_8Ga_yGe_{46-y}$  compounds at similar carrier concentrations.

- (4) The enhanced Seebeck coefficient can be attributed to the large density of states effective mass ( $\sim 4m_0$ ) as compared to that for  $Ba_8Ga_yGe_{46-y}$  compounds.

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