学位論文全文の要約

論 文 題 目 Thermoelectric properties of type-VIII clathrate $Ba_8Ga_{16}Sn_{30-x}Ge_x$ and $Ba_8Ga_{16-x}In_xSn_{30}$ single crystals grown by self-flux and Bridgman methods.

（自己フラックス法及び垂直ブリッジマン法による VIII 型クラスレート $Ba_8Ga_{16}Sn_{30-x}Ge_x$ と $Ba_8Ga_{16-x}In_xSn_{30}$ の単結晶育成と熱電物性研究）

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Type-VIII clathrate $Ba_8Ga_{16}Sn_{30}$ (BGS) is a promising thermoelectric (TE) material in the temperature range 200- 300℃ . Fine tuning of the ratio of Ga/Sn in the single crystals enhanced the TE properties. The maximum values of the dimensionless figure of merit *ZT* were reported to be 0.88 and 0.90 at 450 K for the *p*-type and *n*-type, respectively. On other hand, *ZT* values of substituted BGS samples are reported to strongly depend on the doped elements such as Al, Zn, Sb and Cu, substitution by other elements may enhance *ZT* values. For the construction of a TE module, both *n*- and *p*-type samples larger than 10 mm in diameter are necessary. Bearing these in mind, we have improved the methods of crystal growth of type-VIII BGS with high *ZT* value by two ways; one is the substitution in the flux growth and the other is the vertical Bridgman growth.

This thesis includes four parts. In the first part, the phase diagram was investigated by DTA on raw materials with different compositions as well as BGS single crystals with additional Ga at different ratios. We have found that the raw elements react to form into the type-VIII BGS when elements are heated to 465 ºC. A liquidus line above the peritectic point of BGS at 495 ºC was identified from an exothermic peak at 611 - 654

ºC in the cooling process. This finding was used to revise the Sn-Ba(Ga/Sn)$_4$ pseudo-binary phase diagram and it is instructive in growing *p*-type BGS single crystals.

In the second and third parts, we have chosen the Ge and In to substitute cage atoms Sn and Ga, respectively, which are expected to enhance *ZT* values of BGS. We have prepared single crystals of type-VIII $Ba_8Ga_{16}Sn_{30-x}Ge_x$ and $Ba_8Ga_{15.9-x}In_xSn_{30.1}$ by Ga and Sn flux, respectively. The TE properties of that are measured and discussed.

For Ge substituted samples, the crystals have been grown by the Ga-flux method. The real compositions are described as $Ba_8Ga_{15.9}Sn_{30.1-x}Ge_x$ ($0 \leq x \leq 4.73$). The diameter of single crystals increased from 3 mm for $x = 0$ to 8 mm for $x = 0.55$ but did not increase more for higher x. It appears that the presence of a small amount of Ge is effective for the growth of *p*-type crystals by reducing the vacancies in the cage. The structural refinement of powder x-ray diffraction data confirmed that the Ge atoms prefer to occupy the 2a and 24g sites among the four sites of the cage. By tuning the delicate balance between the Seebeck coefficient α and electrical resistivity ρ, the maximum *ZT* of 0.87 was achieved for $x = 0.07$ at 540 K.

For In substituted samples, single crystals with chemical composition of $Ba_8Ga_{15.9-x}In_xSn_{30.1}$ ($0 \leq x \leq 0.6$) were obtained by the Sn-flux method. All samples show *n*-type behavior in both α and Hall coefficient. With increasing x up to 0.20, the value of ρ and $|\alpha|$ decrease by 50% and 30%, respectively. The carrier density of the samples are nearly invariant with x, while the carrier mobility increases from 27.8 cm^2/Vs for $x = 0$ to 59.6 cm^2/Vs for $x = 0.20$. The value of lattice thermal conductivity κ_{latt} at 300 K significantly decreased from 0.58 W/Km to 0.41 W/Km with the increase in x up to 0.20. This is attributed to the enlargement of rattling motion of the guest atoms due to the increase of the cage space. The maximum *ZT* of 1.05 is obtained at 540 K for $x = 0.20$.

In the fourth part, the vertical Bridgman method is employed to obtain large single crystal of BGS based on the preceding experiments by the flux method. We have tried to

grow *n*- and *p*-type BGS crystals from initial from initial compositions of Ba8Ga16Sn40 and Ba8Ga16Sn29.5Ge0.5, respectively. As a result, single crystals of both *n*-type and *p*-type larger than 10 mm in diameter were obtained. The values of α and ρ weakly change along the vertical direction of the as grown crystals, whereas the thermoelectric powder factor shows little variation. The maximum *ZT* values are 0.84 at 460 K and 0.60 at 520 K for *n*-type and *p*-type crystal, respectively. Our experiments have indicated that the Bridgman method is applicable to grow still larger crystals of type-VIII BGS with both type carriers. Such crystals with optimized carrier densities will serve as the materials for manufacturing TE modules, which will operate effectively in the temperature range 200-300℃ .