JOURNAL OF MATERIALS SCIENCE **37** (2002) 4691 – 4696

# Enhancement of the yield of high-quality ingots in the zone-melting growth of p-type bismuth telluride alloys

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The influences of zone melting growth speed on the thermoelectric properties of p-type bismuth telluride alloys were investigated. When the growth speed was fast, thermoelectric properties were uniform along ingots, as the composition of the molten zone did not change significantly. On the other hand, when growth speed was slow, thermoelectric properties varied along ingots due to the change of the solidified composition determined by the composition of a molten zone. The maximum figure of merit appeared in the middle of an ingot grown at slow growth speed. In the present study, the molten zone leveling method was developed as an attempt to extend the region with high figure of merit. The basic idea of the method was to preserve a uniform composition of liquid at the solid-liquid interface during growth of an ingot so as to obtain a uniform composition of precipitated solids. Ingots composed of two sections with different compositions were used to control the accumulation of Te within the molten zone. As a result, high figure of merit could be obtained over more than 90% of ingot when zone melting growth speed was slow.

## 1. Introduction

$Bi_2Te_3$-$Sb_2Te_3$ solid solutions have been widely used as p-type thermoelectric materials near room temperature. Usually, processes for producing this material include a zone melting growth method, a powder sintering method using milling, a hot pressing method and the like. Among these methods, the zone melting growth method can produce a thermoelectric material having excellent thermoelectric properties, and thus is used as a major process for producing a p-type $Bi_2Te_3$-$Sb_2Te_3$ based thermoelectric material. The basal plane of this material is aligned parallel to the drawing direction during growth when the growth speed is not too fast. The maximum performance is achieved when thermoelectric properties of the growth direction are used.

In general, the figure of merit ($Z$) indicating the performance of the thermoelectric material is represented by the following expression:

$$Z = \frac{\alpha^2\sigma}{\kappa} \tag{1}$$

where $\alpha$ is the Seebeck coefficient, $\sigma$ is electric conductivity and $\kappa$ is thermal conductivity. The thermoelectric properties of the $Bi_2Te_3$-$Sb_2Te_3$ alloys are mainly influenced by carrier concentration of a solidified solid phase when composition of the alloy is fixed. The carrier concentration of the alloy is determined by the amount of anti-structure defect by which the carriers are created. It is well known that the deficiency of Te in the equilibrium composition of 22.5%$Bi_2Te_3$-77.5%$Sb_2Te_3$ solid solution is caused by the antistructure defects which are formed through the replacement of Te sites by Bi(Sb) atoms [1]. Since the amount of antistructure defect is proportional to a degree of deviation of the solid phase composition from the stoichiometric compound composition, the solidified solid phase composition has a decisive influence on the thermoelectric properties of the alloy. It is commonly known that the maximum figure of merit is obtained at the composition near 25%$Bi_2Te_3$-75%$Sb_2Te_3$ where the lattice thermal conductivity is minimum. Taking into account that the alloy solidified near the stoichiometric composition contains carriers with higher concentration than a proper amount, excess Te is added to the stoichiometric composition prior to the crystal growth in order to optimize the solid phase composition. When solid solutions with excess Te are grown slowly by the zone melting growth method, thermoelectric properties vary along ingots. Anuhkin *et al.* [2] and Ha *et al.* [3] explained that this variation is caused by the variation of the Te composition within the molten zone during the zone melting growth. As the $Sb_2Te_3$ rich $Bi_2Te_3$-$Sb_2Te_3$

solid solution has retro grade solubility of Te, alloys precipitated from unfavorable liquid composition exhibit poor thermoelectric properties. Therefore only parts of ingots can be used for modules of high performance. In the present study an attempt was made to expand the portion of an ingot with high figure of merit by controlling the composition of the molten zone.

## 2. Experimental

High purity (99.99%) Bi, Te, and Sb granules (~5 mm) were washed with 10% nitric acid, acetone, and distilled water to remove surface oxide layers. Appropriate amounts of Bi, Te and Sb were weighed to make 150 g of $Bi_2Te_3$-$Sb_2Te_3$ solid solutions and charged into a quartz tube with excess Te less than 5 wt%. the inside wall of the quartz tube was carbon-coated by acetone cracking. The quartz tube was evacuated to $10^{-5}$ torr and sealed. Bi, Te and Sb in the quartz tube were melted at 800°C for 2 hours using a rocking furnace to ensure composition homogeneity, and quenched to room temperature. Ingots of $22.5Bi_2Te_3$-$77.5Sb_2Te_3$ solid solutions were then grown by the zone melting growth method. The length of grown ingots was about 150 mm. Temperature of the zone melting furnace was 850°C and growth speed ranged between 0.1 and 2 mm/min. The length of the zone melting furnace was 50 mm and it was vertically drawn by a stepper-motor which was controlled by a computer. The grown ingots have the (111) cleavage planes aligned parallel to the growth direction and specimens of $5 \times 5 \times 12$ ($mm^3$) were cut along the growth direction. The electrical resistivity was measured by the four-probe method. The Seebeck coefficient ($\alpha$) was measured by the heat-pulse method [4] and the thermal conductivity ($\kappa$) was determined by the Harman method [5]. Metallography was carried out using an optical microscope and the presence of free Te was checked by the XRD analysis.

## 3. Result and discussion

### 3.1. Effects of growth speed

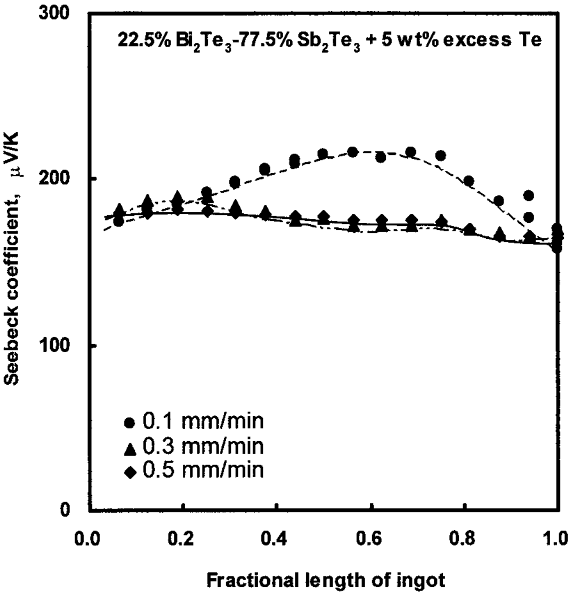

*Figure 1* The variation of the Seebeck coefficient along ingots at different growth speed.

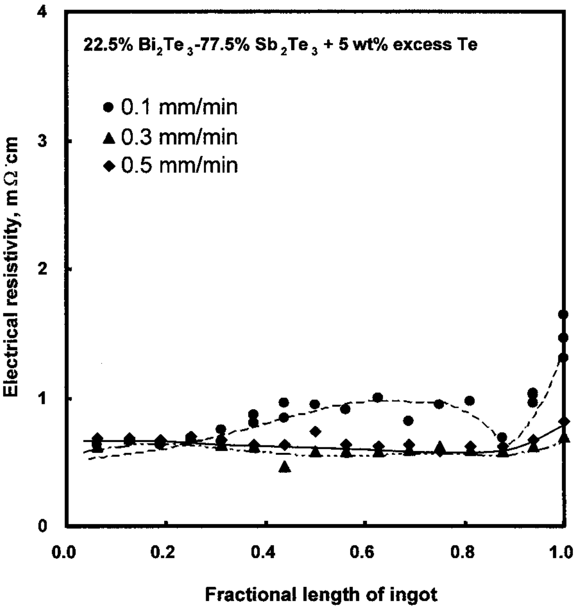

*Figure 2* The variation of the electrical resistivity along ingots at different growth speed.

Ingots of 22.5%$Bi_2Te_3$-77.5%$Sb_2Te_3$ solid solutions with 5 wt% excess Te were grown by the zone melting growth method. Fig. 1 shows that the Seebeck coefficient of an ingot grown by 0.5 mm/min was uniform along the growth direction while that of an ingot grown by 0.1 mm/min initially increases and then decreases after showing the maximum at the middle of the ingot. Fig. 2 shows the electrical resistivities for the same ingots used in the measurement of the Seebeck coefficient. The behavior of the electrical resistivity is similar to that of the Seebeck coefficient. This implies that this material is extrinsic at room temperature and that the carrier concentration decreases and then increases along the growth direction when growth speed is slow (0.1 mm/min) while it does not vary when growth speed is fast (0.5 mm/min). In $Bi_2Te_3$-$Sb_2Te_3$ alloy system, carriers are generated by anti-struture defects [1]. These defects make the precipitated solid composition deviate slightly from the stoichiometric compound composition. Thus the variation of the carrier concentration, in other words, the variation of the Seebeck coefficient and the electrical resistivity in the slowly grown ingot can be explained by the variation of the precipitated solid composition as long as the growth mode is planar. As the partition coefficient ($\kappa$) of Te is less than 1 [6], Te will be rejected and then accumulated in the molten zone when growth front is planar. When the zone melting growth proceeds as much as a distance $x$, the average concentration of the excess Te in the molten zone will follow the Equation 2

$$C = C_o(1 + x/L) \tag{2}$$

where, $C$ is the concentration of excess tellurium in the molten zone and $L$ is the length of the molten zone. $C_o$ is the amount of the excess Te in an ingot before growth. This formula is valid when the solubility of the solute is very small like the present system. Distribution of the excess Te within the molten zone depends on the liquid convection and diffusion. In the present system the steady state does not occur because the bulk composition is always higher than the composition of the precipitated solid phase (see Fig. 3). Te will be continuously accumulated until the eutectic composition is reached. Fig. 3 shows a schematic micro phase diagram for 22.5%$Bi_2Te_3$-77.5%$Sb_2Te_3$-Te system. The equilibrium solid phase boundary of the Te rich side of 22.5%$Bi_2Te_3$-77.5%$Sb_2Te_3$ solid solution is slightly deviated from the stoichiometric composition to the direction of the Te deficient side and it has a retrograde solubility with temperature as indicated in the area 1 in Fig. 3. As the steady state does not occur, the solid solubility of Te in the precipitated 22.5%$Bi_2Te_3$-77.5%$Sb_2Te_3$ solid solution will increase and then decreases following the phase boundary. In other words, at an initial stage of solidification, the concentration of Te in the liquid phase is low, and so the concentration of Te in the precipitated solid phase is also low. As the solidification goes on, the concentration of Te in the liquid phase continues to be increased as indicated by the arrow at the liquid phase boundary in Fig. 3. The Te composition in the precipitated solid phase composition is correspondingly increased following the arrow at the solid phase boundary in Fig. 3. In this way, the solid phase having the maximum Seebeck coefficient is precipitated in the middle of growth. The concentration of Te in the liquid phase, however, is continuously increased even thereafter, and thus the concentration of Te in the solidified begins to be decreased due to the retrograde solubility of Te. Fig. 4 shows cleaved sections of ingots grown at different growth speed. The ingot grown at 0.1 mm/min was single crystal or bi-crystal, which implies that the growth mode at this growth speed

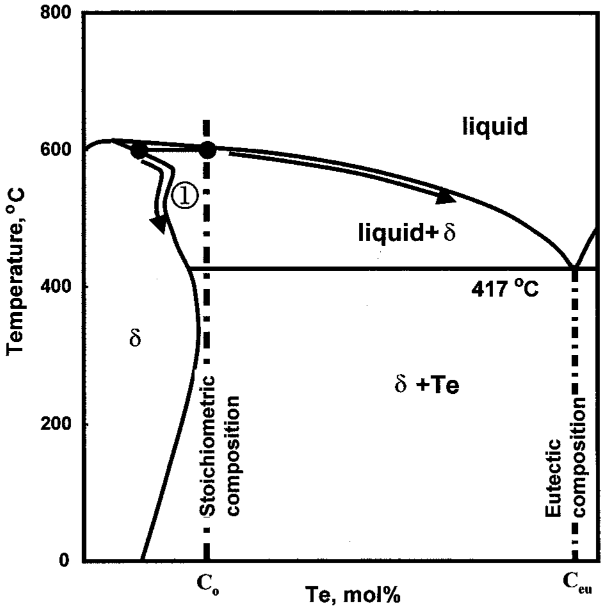

*Figure 3* A schematic pseudo binary phase diagram for 22.5%$Bi_2Te_3$-77.5%$Sb_2Te_3$-Te system; arrows indicate growth paths.

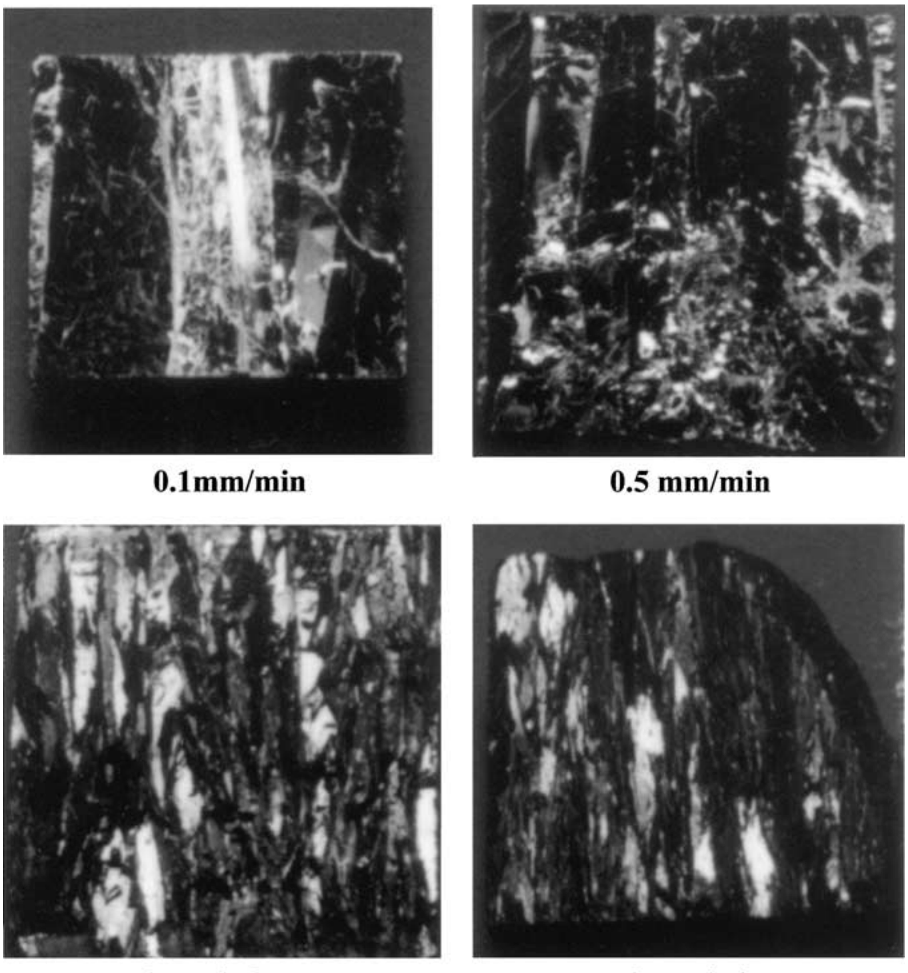

*Figure 4* Longitudinal cross sections of ingots grown at different growth speed.

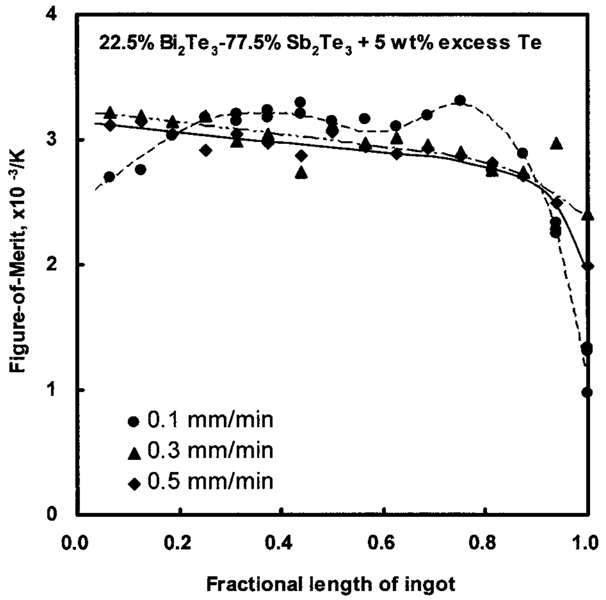

*Figure 5* The variation of the figure of merit along ingots grown at different growth speed.

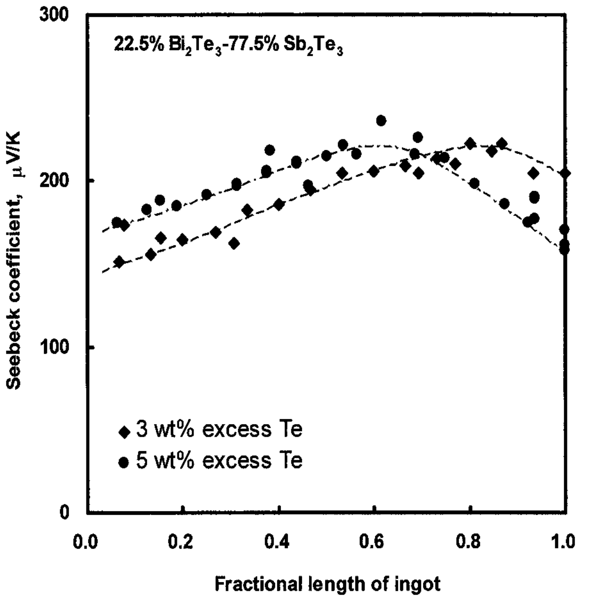

*Figure 6* The variation of the Seebeck coefficient along ingots grown at 0.1 mm/min with different amount of excess Te.

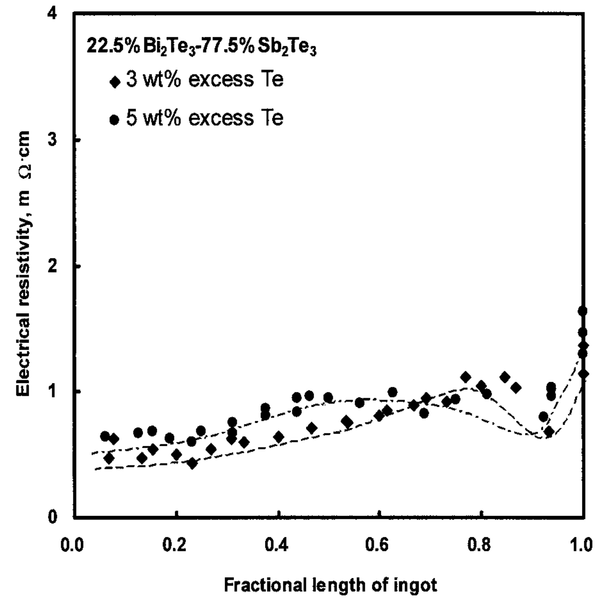

*Figure 7* The variation of the electrical resistivity along ingots grown at 0.1 mm/min with different amount of excess Te.

was nearly planar. Thus variations of the Seebeck coefficient and the electrical resistivity in Fig. 1, Fig. 2 seem reasonable. On the other hand, ingots grown at faster speed than 0.5 mm/min was poly crystal and their growth direction became more irregular with increasing growth speed (See Fig. 4). The even thermoelectric properties of the ingot grown at 0.5 mm/min can be explained as follows. When the growth mode changes from planar to dendritic, rejected solute (Te) atoms at the growth front cannot be pushed away to the front direction. Most of them are trapped within inter-dendritic region. Consequently, composition in the molten zone and corresponding composition of the precipitated solid are not altered during growth. Fig. 5 shows the variation of the figure of merit along ingots. The figure of merit of an ingot grown at 0.1 mm/min shows a peak at the middle of ingot. The maximum value appeared at the region where the Seebeck coefficient was around 220 $\mu$V/K. The figure of merit of an ingot grown at 0.5 mm/min did not change much along ingot and it was normally less than $3.0 \times 10^{-3}$ K$^{-1}$.

## 3.2. Effects of the amount of excess Te

Fig. 6 shows the variation of the Seebeck coefficient along ingots grown at 0.1 mm/min with different amount of excess Te. The peak where the Seebeck coefficient becomes the maximum appears early with increasing the amount of the excess Te. The peak height is same regardless of the amount of excess Te. This result can be easily explained by the accumulation rate of the rejected solute (Te). Te will be accumulated fast with increasing amount of excess Te. The phase boundary, however, is not dependent on the amount of the excess Te. Therefore, the peak height remains unchanged. As shown in Fig. 7 the electrical resistivity also shows the same behavior. The optical microscopy and XRD analysis did not show the presence of the segregated free Te between cleavage planes on an ingot grown at 0.1 mm/min although they were found on an ingot grown at 0.5 mm/min. Thus it is expected that the variation of the electrical resistivity of the sample grown at 0.1 mm/min is largely determined by the carrier concentration which depends on the equilibrium composition of the precipitated solid.

## 3.3. The molten zone leveling method

From the above result, it was found that high figure of merit can be obtained by the zone melting method with a slow growth rate. Unfortunately, this high figure of merit is obtained only within a particular region. The ratio of this region is shortened with increasing the length of a ingot and this region appears at different place depending on the amount of the excess Te. When the required figure of merit is not so high, yield may be enhanced by growing ingots at high-speed of 5 mm/min or more. However, in order to produce a thermoelectric

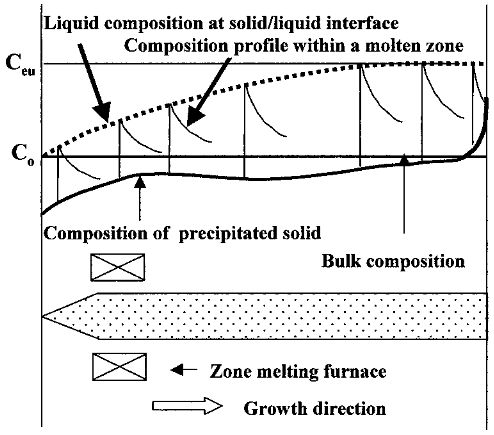

*Figure 8* A schematic illustration for the variation of the liquid composition at solid-liquid interface and the precipitated solid composition during conventional zone melting growth.

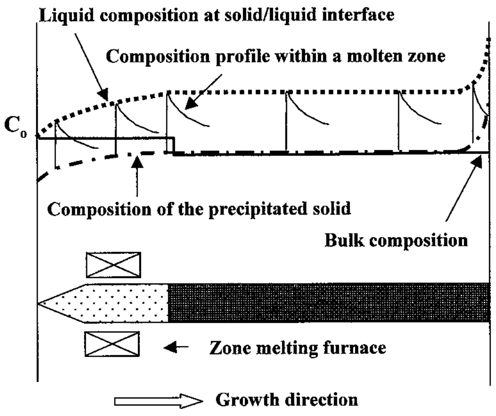

*Figure 9* A schematic illustration for the variation of the liquid composition at solid-liquid interface and the precipitated solid composition during zone melting growth using the molten leveling method.

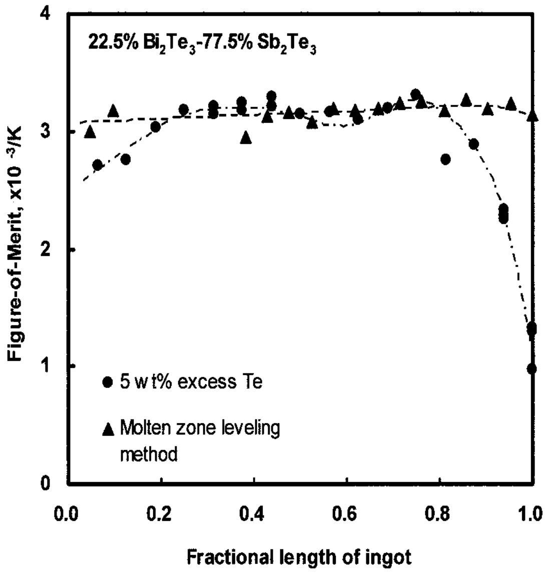

*Figure 10* Comparision of figure of merits for ingots grown by conventional method and the molten zone leveling method.

module with excellent thermoelectric properties, the low-speed growth of the ingot must be applied even though their yield is not good. In the present study we tried to extend the yield of ingot for high speed growth. The main idea was to level the composition of the molten zone during growth in order to produce ingots of uniform composition. At normal growth condition, the Te content of liquid within molten zone increases continuously as shown in Fig. 8. The composition within the molten zone, however, can be leveled if we use two sections of ingots with different compositions as shown in Fig. 9. The ingot 1 of the first part contains normal amount of excess Te and the successively connected ingot 2 has different amount of excess Te. The composition of the ingot 2 is the composition of the precipitated solid whose figure of merit becomes maximum during growth of the ingot 1. One of easy ways to obtain this composition is as follows. First, the ingot 1 having normal excess Te (3–5 wt%) is grown at low growth speed in a preliminary test to produce a thermoelectric material having same thermoelectric properties as shown in Fig. 1. A section exhibiting the highest figure of merit is taken out of the grown ingot. The composition of this section is analyzed and determined as the composition of the second ingot 2. Fig. 9 illustrates compositions of the precipitated solid and of the liquid at the solid-liquid interface during growth of two sections of ingot. It also depicts the variation of the compositions profiles at the solid-liquid interfaces. During the growth of the first section of ingot, the solute Te will be accumulated and the composition of the liquid at the solid-liquid interface reaches the composition at which the solid with maximum figure of merit is precipitated. After that region, an ingot with the composition identical with that of the last part of the precipitated solid is connected. In that case no more Te will be pushed into the molten zone and the Te within the molten zone will not be consumed to precipitate a solid. In other words, artificial steady state is made. Therefore the precipitated solid from the second section of the ingot will have constant composition along the ingot. The first section can be made short with increasing the amount of the excess Te. In the present experiment, an ingot with 5 wt% excess tellurium was used as a first section and an ingot with 0.2 wt% deficient Te was used as the second section on the basis of the result obtained from the above-mentioned preliminary test. In Fig. 10 the variation of the figure of merit of the ingot grown by the molten zone leveling method is compared with that grown by the ordinary growth method. As shown in the figure, the figure of merit keeps high value (higher than $3.2 \times 10^{-3}$ $K^{-1}$) even at the end of the ingot. Even though a long ingot (about 300 mm) was used for the second section, the figure of merit was substantially uniform and high. Therefore it was concluded that enhancement of the yield of high quality ingots was successful by the molten zone leveling method in the zone melting growth of p-type bismuth telluride alloys.

## 4. Conclusions

From the above results the following can be concluded. The variation of the thermoelectric properties during the zone melting growth of the 22.5%$Bi_2Te_3$-77.5%$Sb_2Te_3$ solid solution was mainly caused by the variation of the composition of the precipitated solid. When growth speed was fast, uniform thermoelectric properties were obtained because of small compositional segregation along the precipitated ingot. When growth speed was slower then 0.1 mm/min, thermoelectric properties varied along an ingot and the maximum figure of merit appeared in the middle of an ingot. However, the yield of material with high figure of merit was limited. In this paper the molten zone leveling method was suggested to extend the portion of high quality ingot whose figure of merit is higher then $3.2 \times 10^{-3}\ \mathrm{K}^{-1}$ and enhancement of the yield of high quality ingots with higher than 90% could be achieved.

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*Received 28 March 2001*
*and accepted 16 July 2002*