

A NEW MULTIPHASE THERMOELECTRIC MATERIAL FOR POWER GENERATION

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Abstract

A new multiphase class of thermoelectric alloys formed by combining  $\text{AgSbTe}_2$  with pseudobinary compounds selected from the family  $(\text{Bi,Sb})_2(\text{Te,Se})_3$  were studied in the temperature range from room temperature up to  $300^\circ\text{C}$ . The superior thermoelectric properties of these alloys at temperatures above  $150^\circ\text{C}$  were attributed an increase in the carrier mobility and a reduction in the lattice and ambipolar thermal conductivity. High thermoelectric energy conversion efficiency can be achieved for power generators operating at about  $250^\circ\text{C}$ .

Introduction

Among the best known currently used polycrystalline thermoelectric materials are  $(\text{Bi,Sb})_2(\text{Se,Te})_3$ ,  $\text{PbTe}$  and  $\text{Si-Ge}$ <sup>1</sup>. Each excels over a different temperature range. The  $\text{Bi}_2\text{Te}_3$  based materials possess their highest thermoelectric figure-of-merit at ambient temperatures. The figure-of-merit of  $\text{PbTe}$  polycrystalline materials excel in the  $300^\circ\text{C}$  to  $500^\circ\text{C}$  range. The  $\text{Si-Ge}$  alloys are best suited for high temperature application in the temperature range from  $600^\circ\text{C}$  to  $1000^\circ\text{C}$ . None of these materials is well suited for applications in the  $100^\circ\text{C}$  to  $300^\circ\text{C}$  range. This is indeed unfortunate, because it is in this temperature range that a wide variety of low quality process and waste heat is found<sup>2</sup>. Such sources include: geothermal, catalytically burnt fuel, and waste heat from internal combustion gasoline or diesel engines.

In this paper, we discuss the properties of a novel class of multiphase thermoelectric materials which address this need<sup>3</sup>. These are formed by alloying pseudobinary compounds belonging to the family  $(\text{Bi,Sb})_2(\text{Te,Se})_3$  with up to a few percent of  $\text{AgSbTe}_2$ . Both n and p-type alloys have been formed. Both materials we term TABS for convenience.

The quest for thermoelectric material with ever higher figure of merit has lead to the use of multicomponent alloys which possess compositional disorder to screen short wavelength phonons. Long wavelength phonons can be blocked by polycrystallinity since the surface of grains are intrinsically very disordered. While polycrystallinity is thus supportive of high thermoelectric figure of merit, its utility is countered by the fact that grain boundaries are observed to be sources of electrical resistivity, destructive to good performance.

Understanding and manipulating the local order in regions of disorder such as like grain boundaries is important in establishing high intergrain electrical

conductivity. One way of accomplishing this is by applying the principles of chemical modification<sup>4,5</sup> to "modify" the grain boundaries so as to increase electrical conductivity without an increase in phonon conductivity. This can be termed "macroscopic chemical modification".

The structure of the TABS alloys is crystallites with modifying grain boundary regions, containing various Ag and Te phases. It is observed that the temperature at which the thermoelectric figure-of-merit, Z, reaches a maximum can be tailored over the  $100\text{-}300^\circ\text{C}$  temperature range by changing the content of grain boundary modifying phase. The intergrain boundary phases which are present thus may play a role in maintaining electrical mobility while controlling thermal conductivity.

Experimental

The usual procedure followed in preparing p-TABS alloys was to separately synthesize pseudobinary bismuth antimony telluride (BAT, notation:  $\text{Bi}_{.4-z}\text{Sb}_{.4-z}\text{Te}_{.6}$ ) and silver antimony telluride (here written  $\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.5}$ ). The compounds were synthesized by weighing out the proper amounts of the respective constituent elements, sealing these in a quartz tube at  $10^{-5}$  Torr, and melting them several hours at a temperature above the highest melting temperature of the elements. The contents were thoroughly mixed several times during the melt to insure the complete reaction and homogeneity. Thereafter, the melts were rapidly quenched.

After these compounds were synthesized, each was crushed and the appropriate amounts of each (the majority component is BAT) were weighted out and combined in a quartz tube which was sealed in vacuum. The tube had a inner diameter of at least 4mm. The alloys were formed via modified vertical Bridgman method by dropping the quartz tube through a vertical temperature gradient. The gradient spans the range between the inside temperature of the furnace,  $650^\circ\text{C}$  and room temperature. The tube was dropped at a rate of 30 mm/hr for p-type materials, under a constant temperature gradient of  $30^\circ\text{C}/\text{cm}$  to form the polycrystalline ingot. The notation which we adopt for the alloys is  $(\text{Bi}_{.4-z}\text{Sb}_{.4-z}\text{Te}_{.6})_{100-x}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.5})_x$ . The materials reported span  $x = 0.2$  to  $x = 2.0$ ,  $0.1 \leq z \leq 0.2$ .

The procedure to form the n-type alloys is analogous to that used for p-type alloys. Instead of BAT, the starting majority component is bismuth telluride selenide. The notation used for n-TABS is  $(\text{Bi}_{.4}\text{Se}_{.6-y}\text{Te}_y)_{100-x}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.5})_x$ ,  $0.06 \leq y \leq 0.18$ ,  $x \leq 1$ . The dropping rate was 10mm/hr.

The alloy composition and elemental distribution was determined by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX). Employing a 10 keV accelerating voltage resulted in x-ray spatial resolution of 0.5 $\mu$ m. Spectrum acquiring times of up to 1000 seconds were used.

The thermoelectric figure-of-merit, Z, was measured using the Harman technique<sup>6</sup>. The electrical conductivity,  $\sigma$ , was calculated from AC measurements of resistance. The Seebeck coefficient, S, as a function of the temperature, was determined from measurements of the voltage produced by a temperature gradient across the sample. The sample was placed between two copper blocks maintained at a temperature difference of about 15-20<sup>o</sup>C. The thermal conductivity, K, is calculated from the relation:

$$Z = \frac{S^2 \sigma}{K} \quad (1)$$

given that Z, S and  $\sigma$  have been measured.

### Results and Discussion

#### p-Type alloys

Figures 1 through 4 show the temperature dependence of the electrical conductivity,  $\sigma$ , the Seebeck coefficient, S, the figure of merit, Z, and the thermal conductivity, K respectively for a series of alloys possessing x=0.5 to 2.0. The curves for the various p-type alloys are labeled with the percent incorporation of the AgSbTe<sub>2</sub> compound.

In their thermoelectric properties, these alloys most closely resemble the (Bi-Sb)<sub>2</sub>Te<sub>3</sub> group. This is not surprising since that is their major constitute. The effect of AgSbTe<sub>2</sub> addition is to increase conductivity rather dramatically. When x=2.0,  $\sigma$  (25<sup>o</sup>C) = 4750 ( $\Omega$ cm)<sup>-1</sup> (Figure 1). Based on theoretical fitting, using a two band model<sup>7</sup>, it is deduced that the increase in  $\sigma$  is due in part to an increase in carriers and in part to an increase in mobility.

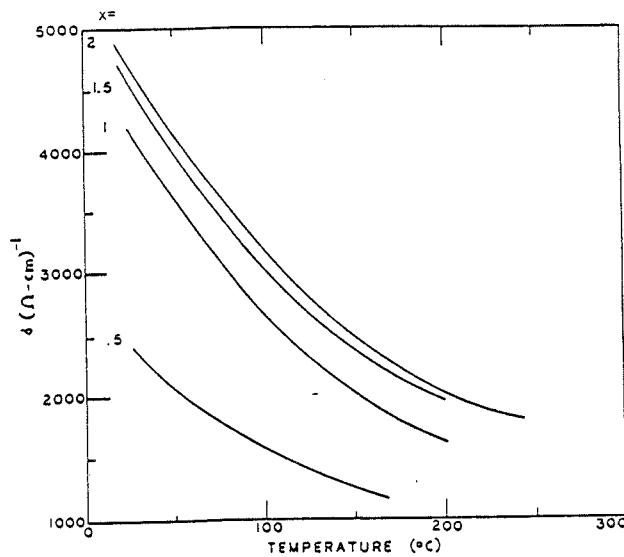


Figure 1. The electrical conductivity of p-type multiphase alloys of composition (Bi<sub>1</sub>Sb<sub>3</sub>Te<sub>6</sub>)<sub>100-x</sub>(Ag<sub>25</sub>Sb<sub>25</sub>Te<sub>50</sub>)<sub>x</sub>, with various amounts of added Ag<sub>25</sub>Sb<sub>25</sub>Te<sub>5</sub>.

The room temperature Seebeck coefficient, on the other hand, decreases as x increases. Once one percent

incorporation (x=1) is reached, however, the Seebeck coefficient does not vary substantially. In all these alloys, S increases to a maximum with increasing temperature. The key point is that temperature at which the maximum is reached shifts to higher temperature as x increases. The decrease in S at elevated temperatures is related to ambipolar diffusion. The onset of intrinsic behavior is delayed in highly conductive alloys such as these. This also delays the onset of ambipolar thermal conductivity. Thus, the maximum in figure of merit also shifts to higher temperature with increasing x (Figure 3); however, the thermal conductivities remain

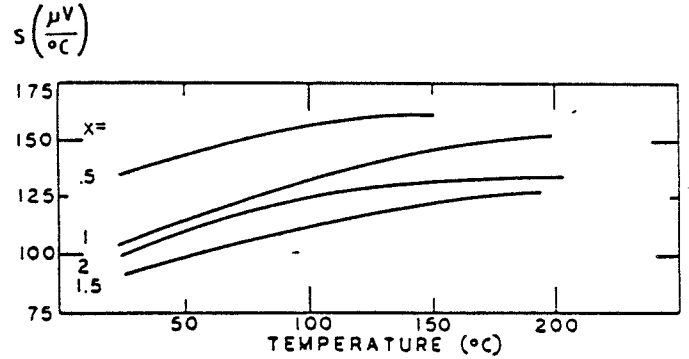


Figure 2. The Seebeck Coefficient of the p-type multiphase alloys of compositions (Bi<sub>1</sub>Sb<sub>3</sub>Te<sub>6</sub>)<sub>100-x</sub>(Ag<sub>25</sub>Sb<sub>25</sub>Te<sub>50</sub>)<sub>x</sub>, with various amounts of added Ag<sub>25</sub>Sb<sub>25</sub>Te<sub>5</sub>.

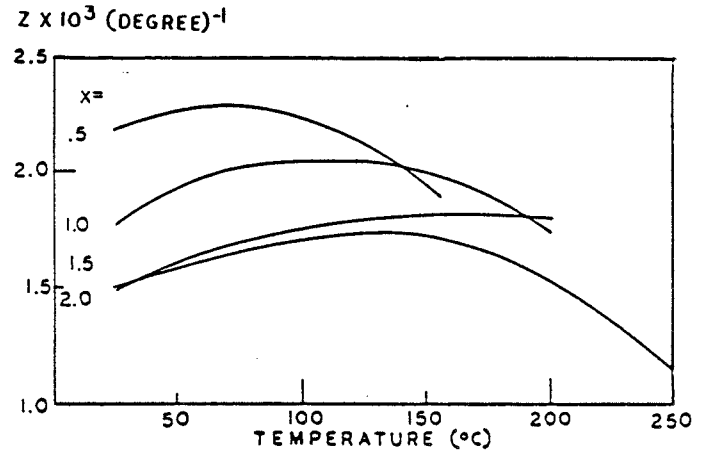


Figure 3. The temperature dependence of the figure-of-merit of the p-type multiphase alloys of compositions (Bi<sub>1</sub>Sb<sub>3</sub>Te<sub>6</sub>)<sub>100-x</sub>(Ag<sub>25</sub>Sb<sub>25</sub>Te<sub>50</sub>)<sub>x</sub>, with various amounts of added Ag<sub>25</sub>Sb<sub>25</sub>Te<sub>5</sub>.

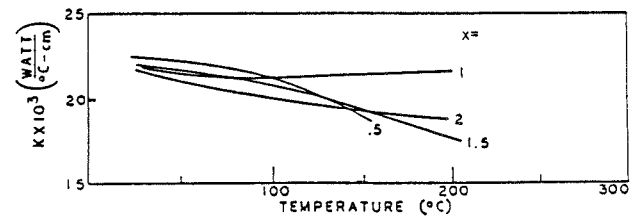


Figure 4. The thermal conductivity of p-type multiphase alloys of composition (Bi<sub>1</sub>Sb<sub>3</sub>Te<sub>6</sub>)<sub>100-x</sub>(Ag<sub>25</sub>Sb<sub>25</sub>Te<sub>50</sub>)<sub>x</sub>, with various amounts of added Ag<sub>25</sub>Sb<sub>25</sub>Te<sub>5</sub>.

substantially the same and relatively constant for each alloy (see Fig. 4). The maximum Seebeck coefficient appears to decrease somewhat with the increased incorporation of the  $\text{AgSbTe}_2$  (Figure 2). From this data, it can be seen that the alloys can be tailored by the appropriate amount of incorporation of  $\text{AgSbTe}_2$  for optimized thermoelectric performance within the targeted temperature range from  $100^\circ\text{C}$  up to  $250^\circ\text{C}$ .

$S^2 \delta \times 10^6 \text{ (WATT / cm / } ^\circ\text{C}^2)$

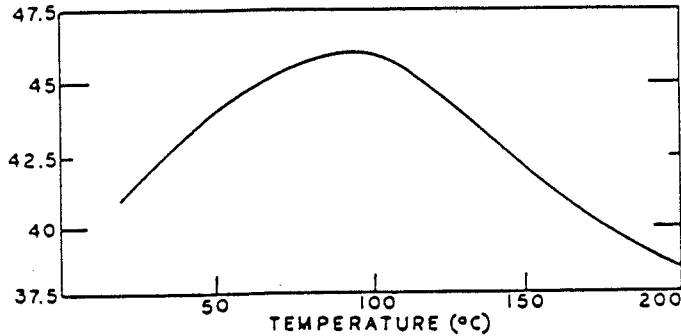


Figure 5. The electrical product  $S^2 \delta$  of p-type multiphase alloy of composition  $(\text{Bi}_{.1}\text{Sb}_{.3}\text{Te}_{.6})_{99}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50})_1$ .

Figure 5 shows the electrical product  $S^2 \delta$  for the  $(\text{Bi}_{.1}\text{Sb}_{.3}\text{Te}_{.6})_{99}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50})_1$  alloy over the temperature range of about  $25^\circ\text{C}$  to  $200^\circ\text{C}$ . The  $S^2 \delta$  product exhibits maximum of  $46 \times 10^{-6} \text{ (Watt/cm/}^\circ\text{C}^2)$  at about  $100^\circ\text{C}$ .

$Z \times 10^3 \text{ (DEGREE)}^{-1}$

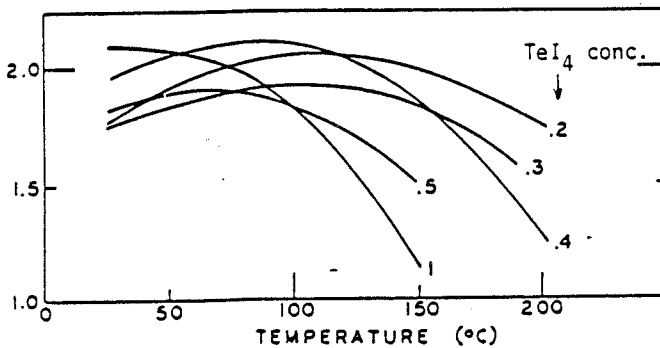


Figure 6. The figure-of-merit,  $Z$ , of the p-type multiphase alloy of composition  $(\text{Bi}_{.1}\text{Sb}_{.3}\text{Te}_{.6})_{99}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50})_1$  with different concentrations of  $\text{TeI}_4$  dopants.

Figure 6 shows the figure-of-merit for the  $(\text{Bi}_{.1}\text{Sb}_{.3}\text{Te}_{.6})_{99}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50})_1$  alloy over the temperature range from room temperature up to  $200^\circ\text{C}$  for concentrations of  $\text{TeI}_4$  dopants from 0.2 to 1 weight percent. Thus, doping aids the tailoring of the thermoelectric properties of the alloys for different desired temperature ranges. The alloy containing about 0.2 percent  $\text{TeI}_4$  exhibits the best overall figure-of-merit for  $x=1$  over the entire temperature range displayed.

## n-Type Alloys

We have prepared various n-type multiphase alloys of various compositions  $(\text{Bi}_{.40}\text{Te}_{.42-.54}\text{Se}_{.06-.18})_{99}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50})_1$  doped with various  $\text{TeI}_4$  concentrations varying from 0 to 0.2 weight percent. We have found the same electrical conductivity increase with the incorporating of 1 percent of  $\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50}$  (Figure 7) and that doping the alloy with 0.1 weight percent of  $\text{TeI}_4$  is also helpful. These exhibit a high figure-of-merit over the temperature range above  $100^\circ\text{C}$  up to about  $300^\circ\text{C}$  (Figure 8).

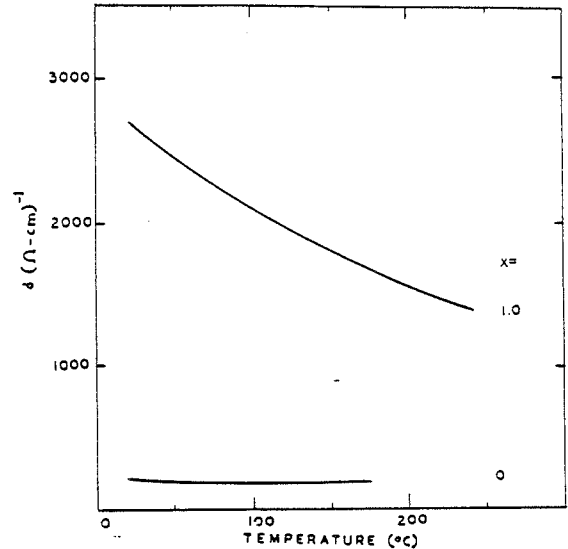


Figure 7. The electrical conductivity of n-type multiphase alloy of composition  $(\text{Bi}_{.4}\text{Te}_{.42}\text{Se}_{.18})_{100-x}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50})_x$ , with various amounts of added  $\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.5}$ .

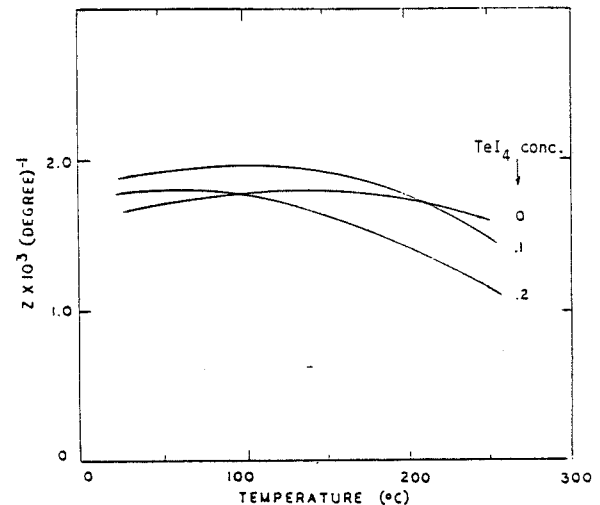
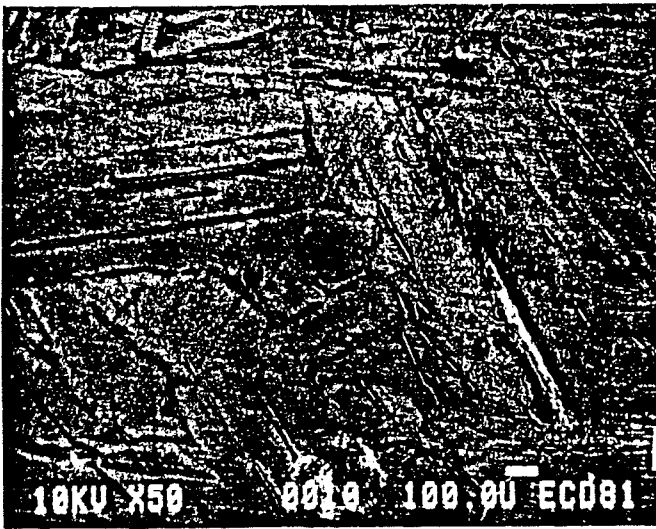


Figure 8. The figure-of-merit of n-type multiphase alloy of composition  $(\text{Bi}_{.4}\text{Te}_{.42}\text{Se}_{.18})_{99}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50})_1$ , with various  $\text{TeI}_4$  doping concentrations.

## Structure and Doping

Figure 9 shows the SEM micrographs of the etched cross section (Figure 9a) and the fractured grain

boundary plane along the growth direction of the grown p-type ingot (Figure 9b). The EDX analysis reveals that the composition of the matrix crystallinities corresponds essentially to the composition of  $(\text{Bi}_{.1}\text{Sb}_{.3}\text{Te}_{.6})$ . The crystallinities are randomly oriented, have random sizes and are of random shapes. Areas of the fractured grain boundary plane consist of Ag-Te with no Sb or Bi. The silver to tellurium ratio in the grain boundary regions varies with the noticeable amounts up to 2:1. Several areas in the grain boundaries also were found to consist completely of tellurium. These grain boundary phases may contribute to the higher conductivity and mobilities of these alloys aiding conductivity between grains.

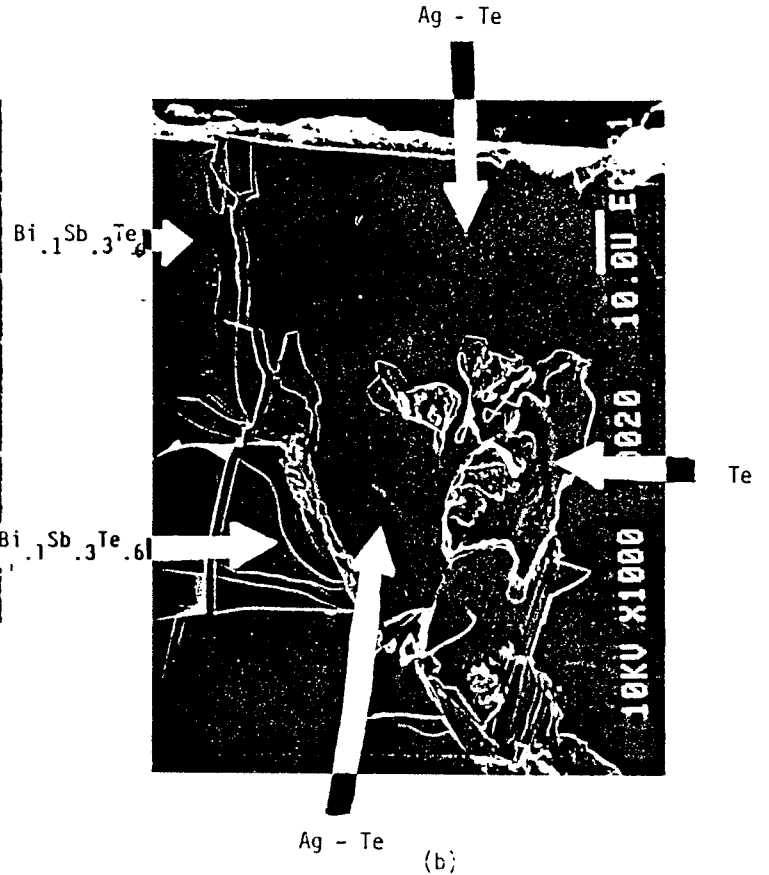


(a)

### Stability

We have studied the stability of the multiphase TABS materials by isothermal annealing the alloys at  $250^{\circ}\text{C}$ . Figure 10 shows the figure-of-merit of a  $(\text{Bi}_{.1}\text{Sb}_{.3}\text{Te}_{.6})_{.99}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50})_1$  alloy as a function of temperature after the thermal treatment at different times up to 376 hours. The material is stable after 100 hours heat treated and exhibits higher Z at temperature below  $200^{\circ}\text{C}$  and a slightly lower Z above  $200^{\circ}\text{C}$ .

### Comparisons



(b)

Figure 9. The SEM micrographs of the etched cross section (a) and the fractured grain boundary plane along the growth direction (b) of the p-type multiphase alloy of composition  $(\text{Bi}_{.1}\text{Te}_{.3}\text{Se}_{.6})_{.99}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50})_1$ .

Silver is a known dopant for tellurides<sup>8</sup>. We were able to rule out doping as the explanation for the current phenomena by adding silver alone to  $\text{Bi}_{.1}\text{Sb}_{.3}\text{Te}_{.6}$ . The observed effect is markedly different. Conductivity increases but not as much as with the addition of  $(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.5})$  and both the figure-of-merit and the Seebeck coefficient drop substantially. The use of relatively large amounts of a modifying substance to produce an electrical effect distinct from doping is reminiscent of the chemical modification of amorphous semiconductors<sup>9</sup>. These disordered polycrystalline materials may provide a macroscopic analogue to the chemical modification of amorphous materials.

In the temperature range from about  $100\text{--}300^{\circ}\text{C}$ , the TABS multiphase alloys exhibit a higher dimensionless figure-of-merit, ZT, (see Figure 11) than do conventional materials. The product ZT is the appropriate way to compare performance of thermoelectric materials over a large temperature range since thermoelectric conversion efficiency for optimized devices depends on it<sup>1</sup>.

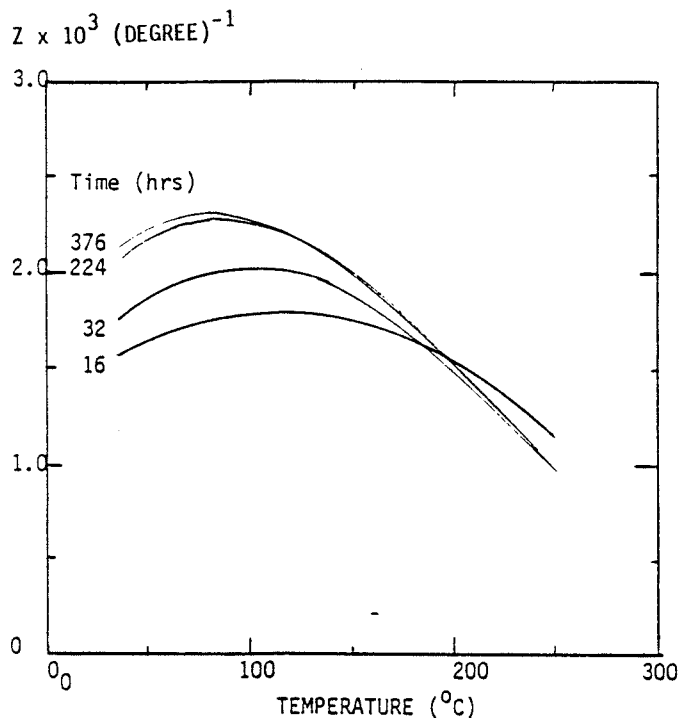


Figure 10. The figure-of-merit,  $Z$ , of p-type multiphase  $(\text{Bi}_{.1}\text{Sb}_{.3}\text{Te}_{.6})_{.99}(\text{Ag}_{.25}\text{Sb}_{.25}\text{Te}_{.50})_{.1}$  alloy as a function of temperature after the isothermal annealing at  $250^{\circ}\text{C}$  for various times.

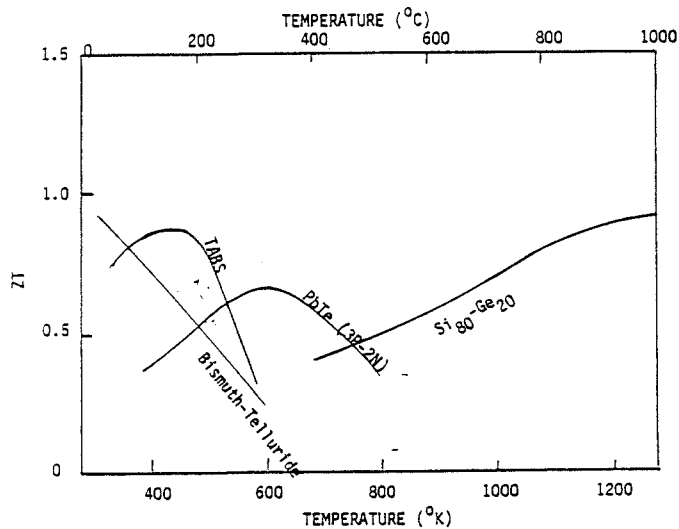


Figure 11. The dimensionless figure-of-merit,  $ZT$  as a function of temperature of the p-type multiphase materials in comparison with other thermoelectric materials.

### Conclusions

We have presented a new multiphase class of thermoelectric materials, called TABS. These possess superior thermoelectric properties in the temperature range from  $100$  to  $300^{\circ}\text{C}$ .

### References

1. F.D. Rosi, Solid-State Electronics 11 (1968) 833.
2. D.K. Benson and T.S. Jayadev "Thermoelectric Energy Conversion - Economical Electric Power from Low Grade Heat", 3rd Intl. Conf. on Thermoelectric Energy Conversion, March, 1980, Arlington, Texas.
3. T.S. Jayadev, O.V. Nguyen, U.S. Patent #4,447,277.
4. S.R. Ovshinsky, Proc. of the 7th Intl. Conf. on Amorphous and Liquid Semiconductors, June 27-July 1, 1977, Edinburgh, Scotland, pp. 519-523.
5. S.R. Ovshinsky, J. of Non-Cryst. Solids, 42 (1980) 335.
6. T.C. Harman, J. Appl. Phys., 29 (1958) 1373.
7. Sonya Frota Pessoa, to be published.
8. C.H. Champness, Chapter 8 in Tellurium, ed. W. Charles Cooper. (Van Nostrand - Reinhold, Company, New York, 1971).
9. R. Flasck, M. Izu, K. Sapru, T. Anderson, S. R. Ovshinsky and H. Fritzsche, Proc. of the 7th Intl. Conf. on Amorphous and Liquid Semiconductors, June 27-July 1, 1977, Edinburgh, Scotland, pp. 524-28.