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Article · January 2000

DOI: 10.1063/1.1290971

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Citation: AIP Conf. Proc. **504**, 1494 (2000); doi: 10.1063/1.1290971
View online: http://dx.doi.org/10.1063/1.1290971
View Table of Contents: http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=504&Issue=1
Published by the American Institute of Physics.

Thermoelectric Properties of $Bi_{2(1-x)}In_{2x}Te_3$ Ternary Samples

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Abstract. Low temperature thermoelectric properties of $Bi_{2(1-x)}In_{2x}Te_3$ ternary samples have been measured in the 50-300 K temperature range. At room temperature, the thermal conductivity decreases with increasing In_2Te_3 content, reaches a minimum at x=0.2 and then slightly increases with increasing In_2Te_3concentration. For x=0.1 and x=0.2 samples, the thermal conductivity varies approximately as 1/T, which may indicate that the defect scattering with phonon is predominant to thermal conduction. Seebeck coefficient and electrical resistivity have been measured and the thermoelectric figure merit calculated. The maximum value obtained is *ZT*=0.5 around 300 K, a value comparable to those of state-of-the-art thermoelectric semiconductors. From x-ray diffraction measurements, it is found that these samples are composites with In_2Te_3 particles in Bi_2Te_3. In this case, the phonons would be scattered by the inclusion particles, depending on their size which is critical for achieving an increase in *ZT* compare to Bi_2Te_3. An increase in *ZT* could be achieved for an optimal particle size of In_2Te_3.

INTRODUCTION

Thermoelectric devices are attractive to waste heat recovery and small refrigeration applications. However, more efficient materials (*i.e.* materials with high thermoelectric figure of merit) are required to expand to commercial users. A low thermal conductivity is one of the conditions to achieve a high thermoelectric figure of merit, $Z=\alpha^2/\rho(\kappa_c+\kappa_l)$, where α is the Seebeck coefficient, ρ is the electrical resistivity and κ_c, κ_l are carrier and lattice contributions to the thermal conductivity, respectively (Goldsmid, 1982). For a good thermoelectric semiconductor, a high Seebeck coefficient, low electrical resistivity and low thermal conductivity are naturally required. Here the electrical resistivity, Seebeck coefficient and carrier contribution to the thermal conductivity are closely related to the each other. A decrease in the electrical resistivity simultaneously leads to the decrease in the Seebeck coefficient and the increase in the carrier contribution to the thermal conductivity. This shows a difficulty for improving *Z* by controlling these electronic parameters in conventional semiconductors. On the other hand, a lattice contribution to thermal conductivity is only related to the lattice properties such as phonon energy and phonon dispersion spectrum (Slack, 1979). A phonon behavior can be controllable without changing the electrical properties. Therefore reducing thermal conductivity may be a way to achieve higher *Z*.

To reduce the thermal conductivity of thermoelectric materials, several ways have been performed and tested. One of the efficient methods may be the introduction of small particles as phonon scattering centers. For example, the reduction of thermal conductivity of $CoSb_3$ by adding PbS was reported (Anno *et al.*, 1998). These results explain that small particles become efficient phonon scattering centers. It has been known that the introduction of point

CP504, *Space Technology and Applications International Forum–2000*, edited by M. S. El-Genk

defects is also an effective way to reduce the thermal conductivity (Stary *et al.*, 1995). Therefore we considered that the introduction of small particles with defect structures into the thermoelectric materials can strongly reduce the thermal conductivity.

Bi_2Te_3 and its related alloys have attractive thermoelectric properties and possess relatively high thermoelectric figures of merit around room temperature. For Bi_2Te_3 r, an investigation of the lattice thermal conductivity in the PbTe-Bi_2Te_3 system was performed and a decrease of lattice thermal conductivity was observed (Christakudi *et al.*, 1992). On the other hand, In_2Te_3 is a semiconducting compound with a large number of vacancies in the In lattice sites (Zaslavski and Sergeeva, 1961). Therefore it is likely that the In_2Te_3 may become phonon scattering centers due to defects when Bi_2Te_3-In_2Te_3 ternary composites could be formed. Furthermore, quite recently, the enhancement of thermoelectric power factor in composite materials was reported (Bergman and Fel, 1999). They pointed out that the power factor of composites can be greater than those of both the pure components, with the greatest enhancement always achieve in a parallel slabs microstructure with definite volume fractions for the two components. From the phase diagram of the Bi_2Te_3-In_2Te_3 system, the existence of a eutectic region for small In_2Te_3 concentrations (Belotskii *et al.*, 1970) can be observed. Thus it is expected to form a composite structure in $Bi_{2(1-x)}In_{2x}Te_3$ system. In this paper we report the low temperature thermoelectric properties of $Bi_{2(1-x)}In_{2x}Te_3$ ternary composites. The structure was investigated by the XRD measurements. From the electrical resistivity, Seebeck coefficient and thermal conductivity data, thermoelectric figures of merit have been calculated.

EXPERIMENTAL DETAILS

Polycrystalline $Bi_{2(1-x)}In_{2x}Te_3$ alloys were synthesized by a reaction of Bi_2Te_3 and In_2Te_3 alloys. Bi_2Te_3 and In_2Te_3 binary alloys were prepared from melting of high purity Bi (99.999%) or In (99.9999%) and Te (99.9999%) powders. Stoichiometric mixtures were sealed in evacuated quartz ampoules (2 x 10^{-5} Torr) and heated at 1100 K for 4 h for Bi_2Te_3 and 1200 K for 4h for In_2Te_3, respectively. The ampoules were then slowly cooled through the solidus temperatures to room temperature. The samples were then crushed into powders. Desired amounts of Bi_2Te_3 and In_2Te_3 powders were then weighted, loaded and sealed in evacuated quartz tubes (2 x 10^{-5} Torr). These mixtures were heated at 1300 K for 1 h and rapidly cooled by quenching them into ice bath. X-ray diffraction (XRD) and electron probe micro-analysis (EPMA) were used to analyze the structure and composition of the $Bi_{2(1-x)}In_{2x}Te_3$ samples.

Disk-shaped samples were cut into the size of 8 mm in diameter and 0.5 mm in thickness. Electrical conductivity and Seebeck coefficient were measured in the temperature range 50-300 K by a van der Pauw and a temperature gradient methods, respectively. The Seebeck coefficient was measured with a temperature difference of 10 K. The Au film of 50 nm thickness was deposited on the samples to obtain an ohmic contact. The ohmic nature was confirmed by the linearity of current-voltage. Thermal conductivity was measured in the temperature range 80-300 K by a laser flash method using a ruby laser with 6 J/pulse power and λ=694.3 nm wavelength.

RESULTS AND DISCUSSION

Figures 1 (a) and (b) show the XRD results for two $Bi_{2(1-x)}In_{2x}Te_3$ samples with x=0.1 and x=0.2. The peaks corresponding to Bi_2Te_3 and In_2Te_3 compounds are clearly observed and the intensity of peaks for In_2Te_3 becomes relatively strong when the In_2Te_3 concentration increases. From the phase diagram, the $Bi_{2(1-x)}In_{2x}Te_3$ system presents a eutectic in small In_2Te_3 concentration regions. Therefore the $Bi_{2(1-x)}In_{2x}Te_3$ samples with x<0.2 seem to consist of the Bi_2Te_3-In_2Te_3 composite structure.

Figure 2 shows the room temperature thermal conductivity of $Bi_{2(1-x)}In_{2x}Te_3$ ternary composites. The room temperature thermal conductivity decreases, and reaches minimum at x=0.2, then slightly increases with increasing the concentration of In_2Te_3. We can see the strong reduction of thermal conductivity in small In_2Te_3 concentrations. This reduction of thermal conductivity may be due to phonon scattering with eutectic regions of In_2Te_3 in Bi_2Te_3 matrix.

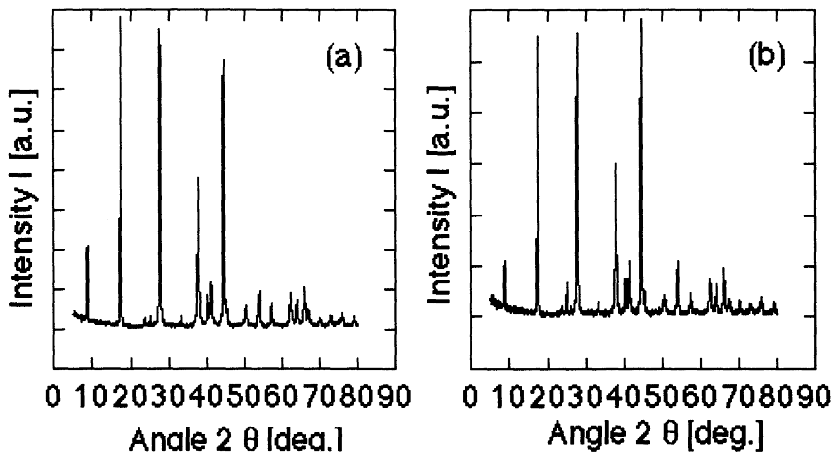

FIGURE 1. X-ray diffraction patterns for $Bi_{2(1-x)}In_{2x}Te_3$ samples with (a) x=0.1 and (b) x=0.2.

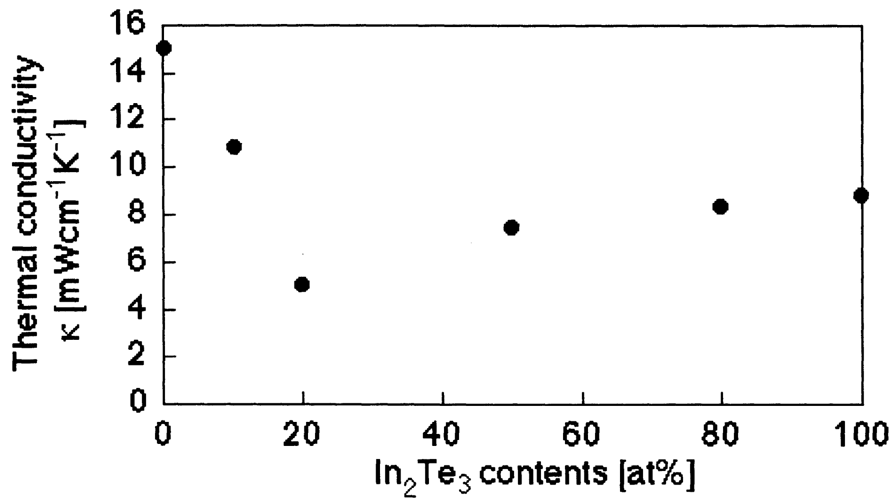

FIGURE 2. Room temperature thermal conductivity of $Bi_{2(1-x)}In_{2x}Te_3$ samples.

Figure 3 shows the temperature dependence of thermal conductivity for two $Bi_{2(1-x)}In_{2x}Te_3$. The thermal conductivity depends on the relation proportional to inverse temperature T^{-1}. This shows that defect scattering with phonons is dominant in the heat conduction process (Dey and Chaudhuri, 1975). This suggests that the eutectic region of In_2Te_3 in Bi_2Te_3 play the similar role as that of defects due to the defective structure of In_2Te_3.

Figures 4 and 5 show the temperature dependence of the electrical resistivity and Seebeck coefficient for the $Bi_{2(1-x)}In_{2x}Te_3$. In the x≤0.2 region, the electrical resistivity slightly increases with increasing In_2Te_3 concentration. Seebeck coefficient decreases with increasing In_2Te_3 concentration. We consider that the decrease in Seebeck coefficient is due to a small increase in the carrier concentration. Thus the small increase in electrical resistivity may be related to the carrier scattering with the In_2Te_3 particles.

From the measurement results of electrical resistivity, Seebeck coefficient and thermal conductivity, thermoelectric figures of merit *ZT* were calculated. Figure 6 shows the temperature dependence of the figure of merit *ZT* for the x=0.1 and x=0.2 samples. A maximum of about *ZT*=0.5 at 300 K is achieved for x =0.1 sample. For x=0.2 sample,

the maximum of ZT is achieved at higher temperature than 300 K. We believe that the composites may lead to materials with higher ZT.

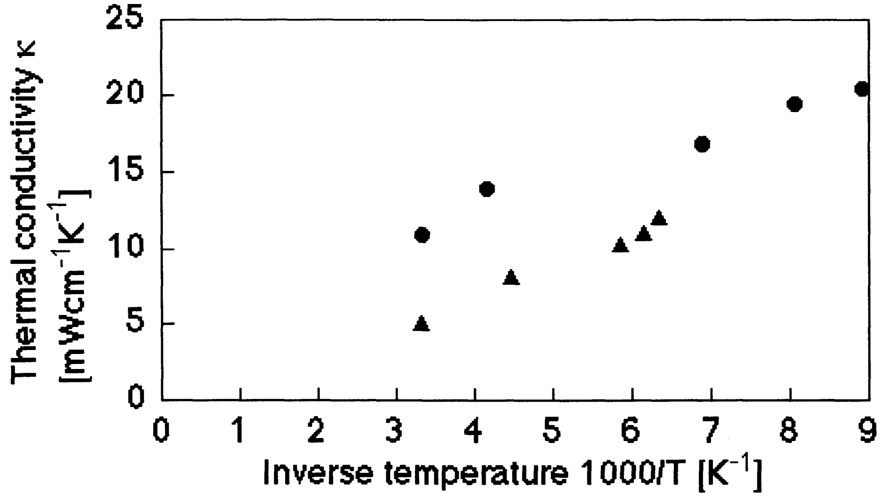

FIGURE 3. Temperature dependence of thermal conductivity for two $Bi_{2(1-x)}In_{2x}Te_3$ samples with ●: x=0.1 and ▲: x=0.2.

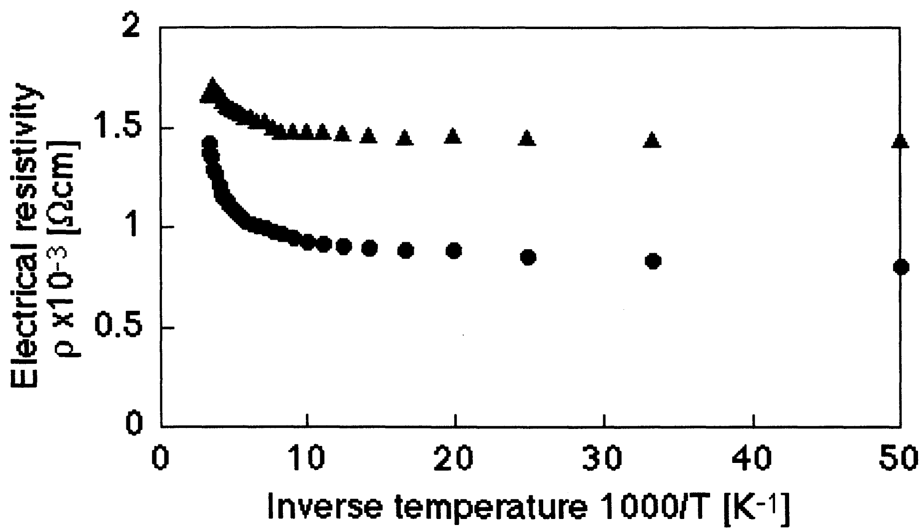

FIGURE 4. Temperature dependence of electrical resistivity for $Bi_{2(1-x)}In_{2x}Te_3$ samples with ●: x=0.1 and ▲: x=0.2.

CONCLUSION

Structure and low temperature thermoelectric properties of $Bi_{2(1-x)}In_{2x}Te_3$ ternary samples were investigated. From the XRD measurement and thermal conductivity behavior, it was demonstrated that the $Bi_{2(1-x)}In_{2x}Te_3$ samples with $x \leq 0.2$ are of composite type. From the Seebeck coefficient and electrical resistivity measurements, the thermoelectric figure of merit for x=0.2 sample would reach a ZT=1.0 at slightly above 300 K. This value is comparable to those of state-of-the-art thermoelectric semiconductors. This suggests that the composite materials involving defect structure may lead to materials with higher ZT..

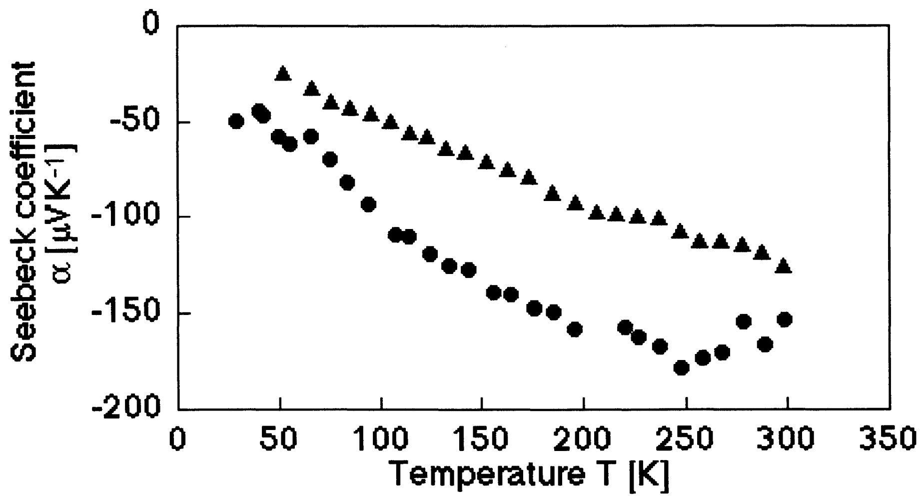

FIGURE 5. Temperature dependence of Seebeck coefficient for $Bi_{2(1-x)}In_{2x}Te_3$ samples with ●: x=0.1 and ▲: x=0.2.

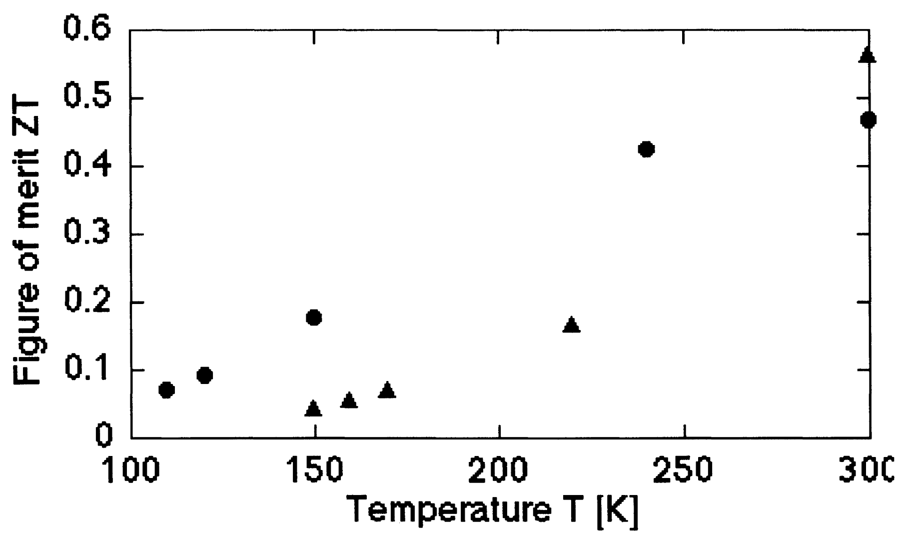

FIGURE 6. Temperature dependence of dimensionless figures of merit for $Bi_{2(1-x)}In_{2x}Te_3$ with ●: x=0.1 and ▲: x=0.2.

ACKNOWLEDGMENTS

The authors express their thanks to Dr. T. Okutani of the HNIRI and Prof. K. Mukasa and Dr. E. Hatta of Hokkaido University for their useful discussions. The authors also thank Mr. M. Sasamori and Miss. S. Nagahara for their experimental assistance. One of the authors (M.F.) is also grateful to the Science and Technology Association of Japan for a fellowship research grant at HNIRI.

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