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TEMPERATURE DEPENDENCE OF THE THERMOPHYSICAL PROPERTIES OF $Bi_{1.5}Sb_{0.5}Te_3$

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Abstract

The thermophysical properties (thermal diffusivity a, specific heat C_p and thermal conductivity λ) of $Bi_{1.5}Sb_{0.5}Te_3$ were measured in the temperature range 300–700 K. The results showed that the contribution of the charge carriers to the thermal conduction is negligibly small in comparison with the contribution of phonons at high temperatures. On the other hand, the heat conduction due to the simultaneous thermal diffusion of electrons and holes is important as well as the lattice thermal conduction. The explanation of the results was supported by using electrical conductivity measurements and X-ray diffraction.

Keywords: $Bi_{1.5}Sb_{0.5}Te_3$, thermophysical properties

Introduction

In recent years special attention has been directed to the study of some of the physical properties of the Bi–Sb–Te system because of its useful technical applications in thermoelectric devices [1–9]. Unfortunately, the literature does not provide consistent information about the thermal properties of $Bi_{1.5}Sb_{0.5}Te_3$.

At high temperatures, the phonon scattering mechanism should be made of a normal three-phonon, Umklapp process and a phonon scattering process by point defects. As the phonon scattering by the boundary is dominant at very low temperatures, it can be ignored completely at temperatures higher than room temperature. On the other hand, the heat transport resulting from the thermal diffusion of free charge carriers and from simultaneous thermal diffusion of electrons and holes are noticeable. Generally, the electronic component of the thermal conductivity of a semiconductor is smaller than the lattice component, but in the case of an intrinsic semiconductor, the simultaneous thermal diffusion of electrons and holes becomes very important in the explanation of the thermal conduction mechanism.

In the present work, the temperature dependence of the thermophysical properties (thermal diffusivity a, specific heat C_p and thermal conductivity λ)

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of $Bi_{1.5}Sb_{0.5}Te_3$ was measured in the temperature range 300–700 K. The behaviour of the three parameters was characterized and discussed.

Experimental

Bulk specimens of $Bi_{1.5}Sb_{0.5}Te_3$ were prepared by the usual melt-quench technique. The constituents Bi, Sb and Te (of 99.999% purity) were weighed and sealed in an evacuated silica tube, which was then heated at ~1073 K for 12 h. During the melting process, the tube was frequently agitated in order to intermix the constituents to ensure homogenization of the melt. The melt was then quenched in water maintained at ~273 K. X-ray diffraction analysis (XRD) revealed that this method results in a polycrystalline product. Cutting, polishing and washing techniques were used for the preparation of samples in disc form with flat surfaces.

The non-steady state or plane thermal wave method was used for simultaneous measurements of thermal diffusivity, specific heat and thermal conductivity. The experimental set-up, methods of analysis and calculations were basically as described in details elsewhere [10–17]. The measurements were performed under a pressure less than 10^{-5} Torr.

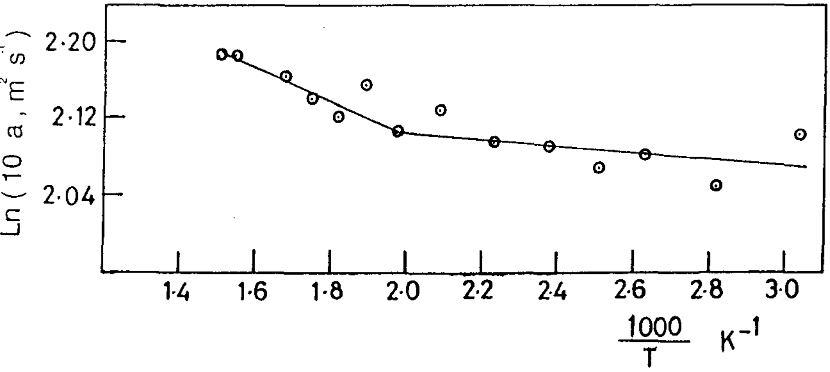

Fig. 1 Temperature dependence of the thermal diffusivity, *a*

Results and discussion

The temperature dependences of the thermophysical properties (a, C_p and λ) are shown in Figs 1–3, respectively. The experimental results show that the behaviour of the thermal parameters can be characterized by two principal features:

1. In the temperature range 300–549 K, the thermal parameters slowly increase with increasing temperature.

2. Above 549 K, the thermal parameters rapidly increase with increasing temperature.

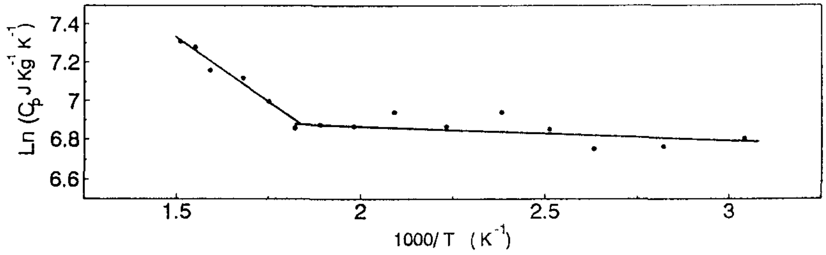

Fig. 2 Temperature dependence of the specific heat, C_p

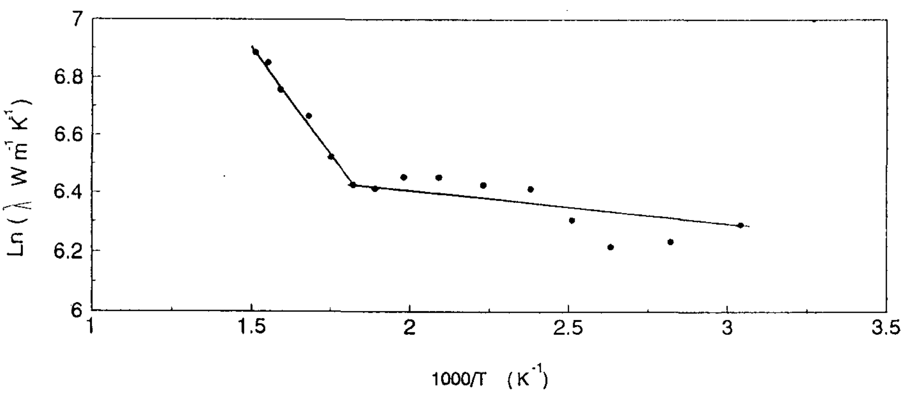

Fig. 3 Temperature dependence of the thermal conductivity, λ

The above features show that the heat transfer in $Bi_{1.5}Sb_{0.5}Te_3$ is mainly due to the lattice component (300–549 K) and the electronic component becomes effective at high temperatures (above 549 K).

The X-ray diffractogram shown in Fig. 4 confirms that the structure contains some crystalline phases which can be identified as $Bi_{1.5}Sb_{0.5}Te_3$, Bi_2Te_3 and Sb_2Te_3. In addition, the intensity due to $Bi_{1.5}Sb_{0.5}Te_3$ crystals is higher than that of the other crystalline phases. Figure 4 shows that there is no change in the crystalline phases before and after thermal measurements. This means that no chemical change occurs in the composition $Bi_{1.5}Sb_{0.5}Te_3$ after the thermal measurements. These results coincide with those recorded in the literature [6, 7]. Therefore, the change in the thermal properties should be due to the base composition $Bi_{1.5}Sb_{0.5}Te_3$.

Over each of the mentioned temperature ranges the $\ln(L)$ *vs.* $(1/T)$ plots (L refers to any of the thermal parameters) are linear, according to the following Arrhenius-like equation [17]:

$$L = L_o \exp(-E_L/kT)$$

where L_o represents the pre-exponential factor or the temperature independent value of L, k is the Boltzmann constant and E_L is the activation energy for a particular mechanism which contributes to a certain thermal parameter. The activation energies E_L and the pre-exponential factors L_o were calculated and listed in Tables 1 and 2, respectively. The most characteristic features of the results shown in Figs 1–3 and Table 1 reveal the activation enhancement of the thermal parameters with rising temperature. These can be attributed to the contribution of more than one mechanism to the thermal transport during the temperature rise.

Table 1

Activ. energy	a	C_p	λ
E_1 / eV	0.00276	0.00431	0.00862
E_2 / eV	0.02870	0.12830	0.13342

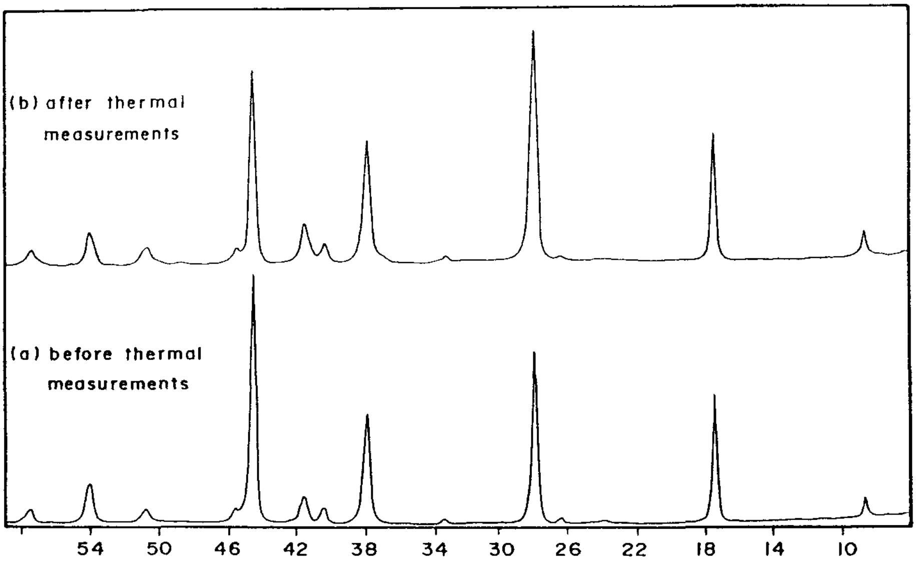

Fig. 4 X-ray diffractograms for the specimen

The activation energy of the thermal conductivity, λ approximately equals the sum of those of the thermal diffusivity and the heat capacity. This is due to the fact that $\lambda = a\ C_p\ d$, where d is the bulk density of the material. It is also seen that the activation energy of the thermal conductivity is greater than that of the optical gap [7] and that deduced from the electrical conductivity [6]. This is due the difference between the participating mechanisms in both the electrical and thermal transport. Moreover, the contribution of the charge carriers to the thermal transport is very weak. This might prove that the thermal transport processes mainly involve the participation of phonons. The thermal conductivity, λ (Fig. 3) increases as the temperature increases. This result is in agreement with that of Volklein *et al.* [8].

Table 2

$a_o/m^2\cdot s^{-1}$	$Cp_o/J\cdot kg^{-1}\cdot K^{-1}$	$\lambda_o/W\cdot m^{-1}\cdot K^{-1}$
7.925×10^{-4}	8.916	0.509

The total thermal conductivity, λ of semiconductors is, in general, represented as follows [1]:

$$\lambda=\lambda_e+\lambda_{ab}+\lambda_l$$

where λ_e is the electronic component of the thermal conductivity, λ_{ab} is the thermal conductivity by the simultaneous diffusion of electrons and holes and λ_l is the lattice thermal conductivity.

The electronic thermal conductivity λ_e is related to the electrical conductivity σ as follows [18]:

$$\lambda_e=L\,\sigma\,T$$

where L is the Lorentz number considered to be equal to $1.4893\times10^{-8}W\cdot\Omega\cdot K^{-2}$ for semiconductors [18] and T is the absolute temperature. The electronic thermal conductivity of the compound is evaluated by measuring the electrical conductivity as a function of the temperature as shown in Fig. 5. As it is seen, the calculated values of λ_e are about three orders of magnitude smaller compared with the measured

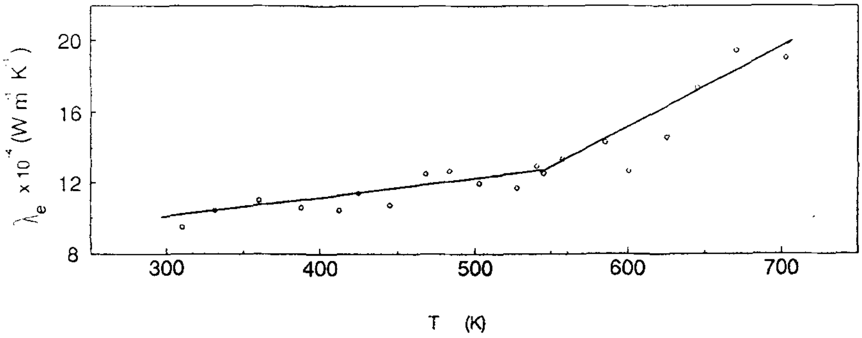

Fig. 5 Electronic thermal conductivity as a function of the temperature

value of the thermal conductivity λ. Thus, the electronic contribution to the thermal conductivity is a very small component of the total thermal conductivity.

If both electrons and holes take part in the thermal conduction of a semiconductor at the same time, there is an additional electronic thermal conduction besides the electronic thermal conduction determined by the Wiedemann-Franz law [19]. When a temperature gradient is applied on a specimen, electrons and holes or equal number are created more at the hot end than at the cold end of the specimen by the thermal excitation of electrons from the valence band to the conduction band. Then these electrons and holes diffuse along the temperature gradient and recombine at the cold end of the specimen to attain local thermal equilibrium. The thermal conductivity in the high temperature range cannot be understood without the thermal conduction by the ambipolar thermal diffusion [1]. At high temperatures, the thermal conductivity resulting from the ambipolar thermal diffusion may be compared with the lattice thermal conductivity. The lattice thermal conductivity is dominant in any temperature range.

Conclusions

It is concluded that the behaviour of the thermal properties (a, C_p and λ) of $Bi_{1.5}Sb_{0.5}Te_3$ as a function of the temperature can be characterized by two temperature ranges. In the temperature range 300–549 K, the increase in the thermal parameters is attributed pre-dominantly to the phonon scattering mechanisms. In the following temperature range 549–662 K, in addition to phonon scattering, electrons and ambipolar thermal diffusion are responsible for the increase in the thermal parameters. Generally, the temperature dependence of the thermal properties of this compound can be described by an Arrhenius-like equation.

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Zusammenfassung — Im Temperaturintervall 300–700 K wurden die thermophysikalischen Eigenschaften (Temperaturleitvermögen *a*, spezifische Wärme C_p, und die Wärmeleitfähigkeit λ) von $Bi_{1.5}Sb_{0.5}Te_3$ vermessen. Die Ergebnisse zeigen, daß der Beitrag der Ladungsträger zur thermischen Leitung im Vergleich zum Beitrag von Phononen bei höheren Temperaturen vernachlässigbar gering ist. Andererseits ist die Wärmeleitung infolge der simultanen thermischen Diffusion von Elektronen und Löchern genauso wichtig wie die Gitter-Wärmeleitung. Die Deutung der Ergebnisse wurde durch Anwendung von Messungen der elektrischen Leitfähigkeit und durch Röntgendiffraktion bestätigt.