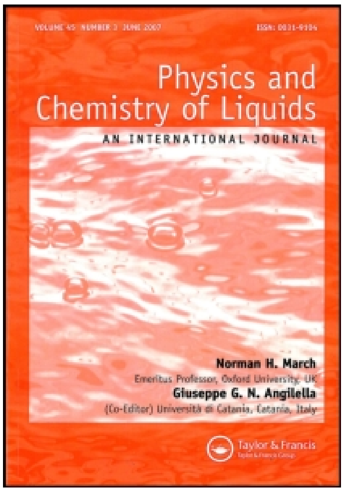

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Electrical Conductivity, Thermoelectric Power, and Thermal Conductivity of $Bi_{29}Tl_{35}Se_{36}$ Chalcogenide Glass Semiconductors in Solid and Liquid States

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ELECTRICAL CONDUCTIVITY, THERMOELECTRIC POWER, AND THERMAL CONDUCTIVITY OF $Bi_{29}Tl_{35}Se_{36}$ CHALCOGENIDE GLASS SEMICONDUCTORS IN SOLID AND LIQUID STATES

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The properties of chalcogenide glass semiconductors of $Bi_{29}Tl_{35}Se_{36}$ is investigated by the electrical conductivity, thermoelectric power and thermal conductivity as a function of temperature from room temperature to near 500°C. The experimental data of the electrical conductivity and thermoelectric power are analyzed in terms of a model developed from the density of states and electrical transport in solid amorphous semiconductors[1]. The activation energy calculated from electrical conductivity data is found to be 0.11 eV for the solid and 0.66 eV for the liquid. Moreover, the coefficient of the linear decrease of energy gap with temperature was found to be $\gamma = 10.37 \times 10^{-4}$eV/K°.

Measurements of the thermal conductivity of our sample were carried out from the room temperature to near 500° C. These measurements of thermal conductivity were carried out using the concentric cylinder method. The temperature dependence of the thermal conductivity was explained by postulating different mechanism[2] for (λ) in semiconductors. Values of room temperature electronic and bipolar thermal conductivity [$\lambda_e(30)$ and $\lambda_{bp}(30)$] for the investigated sample were calculated, moreover these values estimated at 0° C. The thermal conductivity due to atomic motion (λ_a) also is calculated.

Also the thermoelectric Q-factor (Z) is calculated for our sample in solid and liquid states.

Keywords: Electrical and thermal conductivity; chalcogenide glass

1. INTRODUCTION

Chalcogenide glasses have been attracting much attention in the fields of electronics as well as infrared optics, since they exhibit several peculiar phenomena applicable for devices such as electrical switches and or memories, image storage and photo resist. The trend of using amorphous semiconductor materials rather than carefully prepared crystalline semiconductors in electronic devices was appealing, but the development of amorphous electronic devices needs further investigation of such materials. One of the interesting semiconducting glasses in the $Bi_{29}Tl_{35}Se_{36}$ chalcogenide glass sample due to its use as an active material in memory switching devices [3]. Tohge et al. [4,5], were the first point out the rule of Bi in the appearance of *n*-type conduction in chalcogenide glasses.

The aim of the present contribution is to investigate the electrical conductivity, thermoelectric power and thermal conductivity of $Bi_{29}Tl_{35}Se_{36}$ in solid and liquid states to try to join them with through thermoelectric Q-Factor Z. The melting point of $Bi_{29}Tl_{35}Se_{36}$ is about 280° C.

2. EXPERIMENTAL

The $Bi_{29}Tl_{35}Se_{36}$ samples were prepared from highly pure elements (Bi, Tl and Se) of 99.999% purity. The proper amounts of each element were weighed out and put into quartz tubes which were then evacuated and sealed, and placed inside a rotating furnace which was used to obtain homogeneous materials. The temperature of the furnace tube was raised gradually by 1000° C and held for 24 h. After heating, the tube was quenched in water.

Measurements of the electrical conductivity and thermoelectric power were carried out in the measuring cell [6] which was made from ceramic material and was fitted with graphite electrodes, heaters and thermocouples for accurate measurements of temperature up to 0.2° C.

The working space between the electrodes was made highly homogeneous and spacing between the electrodes was 1 mm. A highly stabilized power supply, a sensitive galvanometer capable of measuring currents as low as 10^{-9} A.

Measurements of thermal conductivity were carried out using the concentric cylinder method [7,8,9] where 0.5 gm of the material in the liquid state was poured into the cylindrical gap between two concentric graphite cylinders kept in nitrogen atmosphere. The systems was fitted with a heater and sensitive thermocouples for accurate measurements of temperature within ±0.2°C and thermal conductivity was calculated using the formula:-

$$K = \frac{Q \ln (d_2/d_1)}{2\pi L(T_1 - T_2)}$$

where d_1 and d_2 are the diameters of the inner and outer cylinders, T_1 and T_2 are the temperatures on both sides of the sample, L is the length of the cylinders and Q is the quantity of heat generated. The quantity of heat flowing per second through the sample is given by:

$$Q = m\left(\frac{\Delta T}{\Delta t}\right)C$$

where m is the mass of external cylinder, $(\Delta T/\Delta t)$ is the temperature gradient and C is the specific heat of graphite. Measurements were carried out in a wide range of temperatures below and above the melting point.

3. RESULTS AND DISCUSSION

Figures (1) and (2) show the temperature dependence of the electrical conductivity and thermoelectric power in the solid and liquid states. In solid state the electrical conductivity increases with temperature, then increases near melting point. In the liquid state the electrical conductivity increases exponentially with temperature, the activation energy in the solid state is $E_{a1\,\mathrm{solid}} = 0.11\mathrm{eV}$ and in the liquid state is $E_{a2\,\mathrm{liquid}} = 0.66$ eV. The thermoelectric power is positive in solid state which indicates that $Bi_{29}Tl_{35}Se_{36}$ is a p-type semiconductor. After melting the thermoelectric power decreases with temperature and near 303° C it changes sign and become negative. After the melting point a sudden decrease in thermoelectric power is observed, which may be attributed to changes in the short range order on melting, and the subsequent decrease in carrier mobility. Moreover, the electrical conductivity increases with temperature.

The negative behavior of the thermoelectric power in the liquid state at higher temperature can be understood in terms of a transition

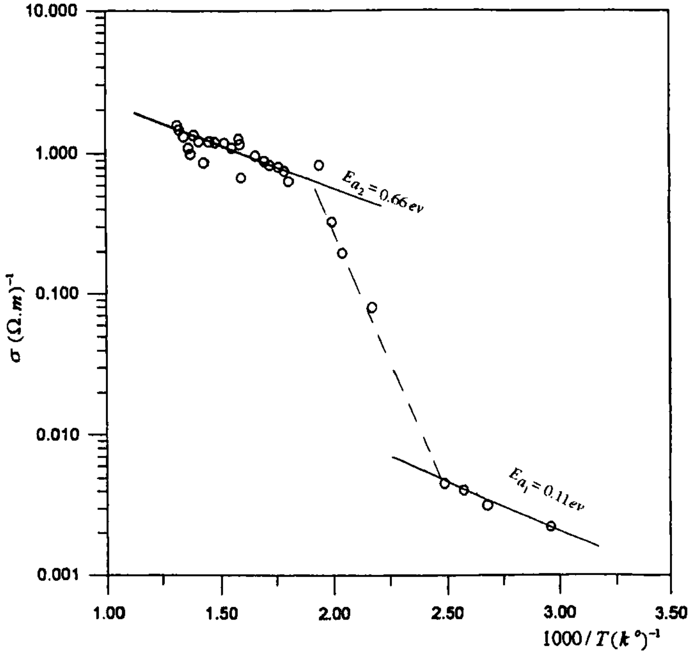

FIGURE 1 Temperature dependence of the electrical conductivity of $Bi_{29}Tl_{35}Se_{36}$ in the solid and liquid states.

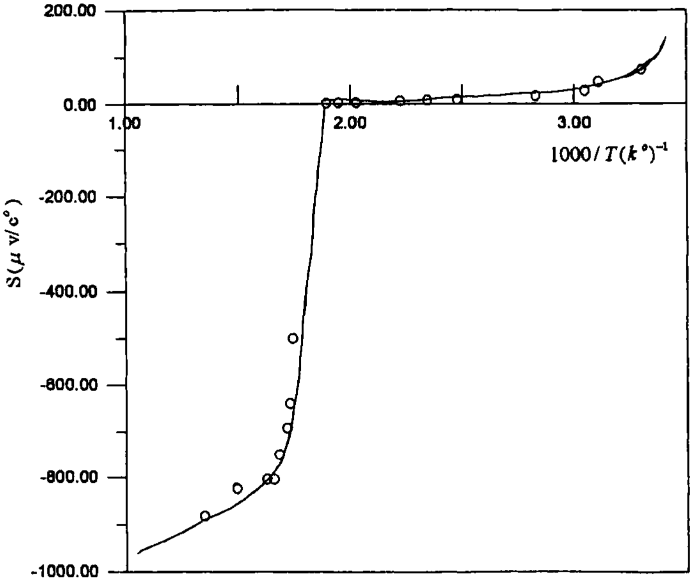

FIGURE 2 Temperature dependence of thermoelectric power of $Bi_{29}Tl_{35}Se_{36}$ in the solid and liquid states.

between transport in two different bands. The region between the peaks-in magnitude of the thermoelectric power is explained by ambipolar transport [10], which suggests that there is cancelation between the positive and negative contributions to the thermoelectric power due to hole and electron transport [10].

Various workers [11,12] have attributed the negative values of the thermoelectric power to a large predominance of electrons in electrical transport. The present data can be adequately interpreted according to the model developed by Mott[1] for amorphous semiconductors. This model is derived from that proposed by Cohen [13] *et al.*, and by Davis and Mott [14] for a solid amorphous semiconductor. According to this model, the electronic structure of energy bands is not significantly different from that in the corresponding crystal. The main difference is that the electronic states at the band edges are "tailed" into the forbidden gap and become localized. Therefore, the conduction mechanism changes radically from crystalline to amorphous structure. To explain the positive sign of the thermoelectric power, it is supposed that the range of localized states in the conduction band is wider than in the valence band.

Two conduction processes may occur:

(a) Conduction due to holes excited into extended states at E_V.
(b) Conduction due to holes excited in localized states near the band edge with an activated mobility.

If it is assumed that the range of localized states and activation energy for hole mobility is small compared with the energy gap, then the electrical conductivity in both cases may be expressed as:

$$\sigma = \sigma_0 \exp\left(-\frac{E_f - E_v}{KT}\right) \tag{1}$$

The values of the constant σ_0 varies strongly with the conduction process $(E_f - E_v)$ depends on temperature and is given by:

$$E_f - E_v = E - \gamma T \tag{2}$$

Thus:

$$\sigma = \sigma_0 \exp(\gamma/K)\exp(-E/KT) \tag{3}$$

The temperature coefficient γ may be calculated directly from the thermoelectric power which is expressed as:

$$S = \frac{K}{e}\left[\frac{E(0)}{KT}\frac{\gamma}{K} + A\right] \quad (4)$$

where the constant A is related to scattering mechanisms. If A is known, γ can be determine directly from the intercept on the $1/T = 0$ axis of a plot of S versus $1/T$. By combining expressions (1) and (4), we obtain the relation between σ and S:-

$$\sigma = \sigma_0 \exp(-e\frac{S}{k} + A) \quad (5)$$

From which the constant σ_o can be calculated. In $Bi_{29}Tl_{35}Se_{36}$ the straight line between ln σ and S (Fig. 3) extrapolated to $1/T = 0$ yields:

$$\gamma/K = [(S_o/86) + A)].$$

For $A \geq 0$, is $\gamma/K \geq$ So/86. According to Cutler and Mott (15), the constant A is of order unity for disordered structures. However, recent investigation of the thermoelectric power of amorphous chalcogenides [16] suggests that A may be larger than unity for highly disordered materials. In our discussion we assume $A = 1$. Then the coefficient γ is found 10.37×10^{-4}eV/°K.

This high value of γ-indicates that the temperature dependence of the gap for liquid $Bi_{29}Tl_{35}Se_{36}$ is the same order as that found for liquid Te-Se alloys [17]. It seams likely that the difference between the distance from one atom to nearest and next-nearest neighbours decrease, Mott [1].

Figure (3) shows the dependence of ln σ as a function of S. The variations of ln σ are linear with S according to relation (5) in the temperature range where the expressions (1) and (4) can be satisfied. With the assumption $A = 1$, the value of the intercept on the $S = 0$ axis yield $\sigma_o = 1.5 \times 10^{-2}\Omega^{-1}m^{-1}$ for $Bi_{29}Tl_{35}Se_{36}$ with value of σ_o, the conduction is probably due to holes excited in extended states.

The large linear decrease of the gap may give rise to the transition from semiconducting to metallic behaviour expected at high temperature. At the gap contracts with increasing temperature, the tails of conduction and valence bands become more pronounced. At sufficiently high temperature these tails overlap, leading to a filling in of the gap and the disappearance of localization. Consequently, the electrical conductivity shows a weak temperature dependence, and the thermoelectric power should approach zero slowly.

The temperature dependence of the thermal conductivity of $Bi_{29}Tl_{35}Se_{36}$ is shown in Figure [4]. In solid state the thermal conductivity increases linearly with temperature near to the melting point, where up the melting point of $Bi_{29}Tl_{35}Se_{36}$ is accompanied by

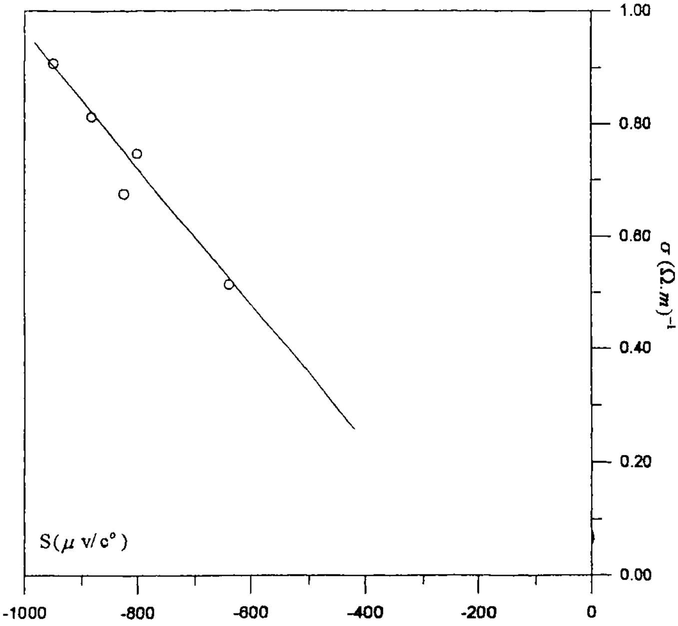

FIGURE 3 Electrical conductivity versus thermo-electric power for $Bi_{29}Tl_{35}Se_{36}$ in liquid state.

TABLE I

$T = 0°C$	$\sigma_o^*(\Omega.m)^{-1}$	$\lambda_e(0)$	$\lambda_{ph}(0)$
$273°K$	$0.33(\Omega.m)^{-1}$	$0.805 \times 10^{-8} W/m.°K$	$4.59 \times 10^{-8} W/m.°K$
$T = 30°$ C	$\sigma(30)(\Omega.m)^{-1}$	$\lambda_e(30)$	$\lambda_{pb(30)}$
$303°K$	$0.15 \times 10^{-2}(\Omega.m)^{-1}$	$0.37 \times 10^{-10} W/m.°K$	$1.9 \times 10^{-10} W/m.°K$

*$\sigma(o)$ and $\sigma(3o)$ are obtained from the intercept on the $1/T = 0$ in Figure (1).

increase exponentially with temperature. In the liquid state (λ) continues to increase with temperature, however, the rate of increase if faster than in the solid state. The increase in thermal conductivity with temperature in the amorphous state may be attributed to the increase of the heat capacity and phonon component of the thermal conductivity with temperature, according to the relation [18]:

$$\lambda_{\text{lattice}} = \frac{1}{3} CVL \tag{6}$$

where (C) is the heat capacity per unit volume, (L) is the phonon mean free path, and (V) is the velocity of the motion of the material.

In the liquid state, inspite of the weaking of the bonds between the molecules, the thermal conductivity continues to increase with temperature with a faster rate which indicates that additional mechanism contributes to the thermal conductivity of a liquid semiconductor can be analyzed in terms of four contribution [10]:

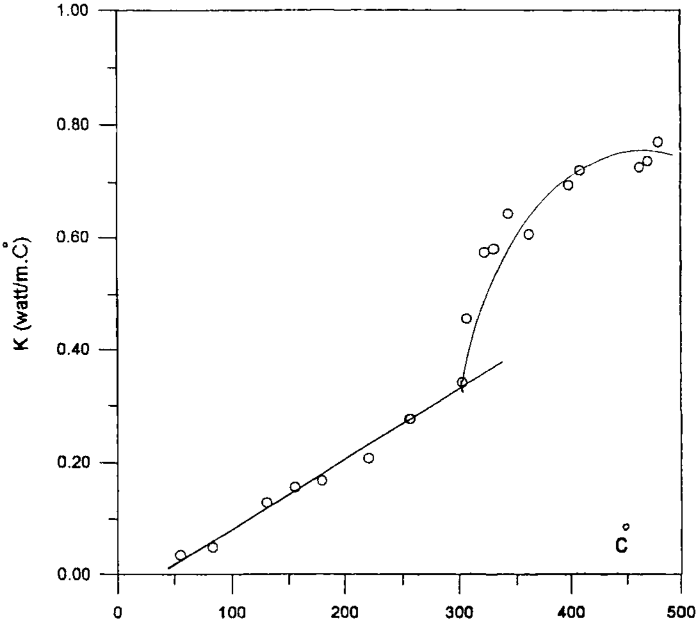

FIGURE 4 Temperature dependence of thermal conductivity of $Bi_{29}Tl_{35}Se_{36}$ in the solid and liquid states.

$$\lambda = \lambda_a + \lambda_e + \lambda_{bp} + \lambda_{ph} \tag{7}$$

where (λ_a) is the contribution of atomic motion, (λ_e) is the electron contribution, (λ_{bp}) is the bipolar contribution, and λ_{ph} is the photon component of the thermal conductivity.

The electronic contribution to thermal conductivity calculated using the Wiedemann-Franz law:

$$\lambda_e = L_o\ \sigma T \tag{8}$$

where (σ) is the electrical conductivity, and (L_o) is the Lorentz number which is given by [19]:

$$L_o = \pi/3\,(K/e)^2 = 2.44 \times 10^{-8}\, W\Omega/^\circ K^2 \tag{9}$$

Values of room temperature electronic and bipolar thermal conductivity $\lambda_e(30)$ and $\lambda_{bp}(30)$ for the investigated sample were calculated according to the following equation (10)[20] and equation (8), using values of $\sigma(30)$, given in table I:

$$\lambda_{bp} = \frac{3}{4\pi^2}\lambda_e\left[\frac{E_a}{KT}+4\right]^2 \tag{10}$$

where E_a is the activation energy in the solid state $(E_{a_{\text{solid}}} = 0.11\text{eV})$, K is the Boltzmann constant and T is the absolute temperature.

Although the contribution of λ_{pb} is greater than that of λ_e [at zero °C and at room temperature 30° C], both them may be neglected as compared with the measured thermal conductivity. The quantity (λ_a) sets a lower limit to (λ). Since most of the thermal motion of a liquid is vibrational in character then the value of (λ_a) is given (10) by:

$$\lambda_a = \frac{9k\nu}{\pi a} \tag{11}$$

where ν is the vibration frequency $\cong 3 \times 10^{12} s^{-1}$, (a) is the atomic radius, and K is the Boltzmann constant. From Eq. (11) (λ_a) is about 0.35 W/m. °K, in the same order of Cutler[10].

But the photon contribution to thermal conduction is given by [10]:

$$\lambda_{ph} = 16/3\ n^2\ BT^2/\alpha \tag{12}$$

TABLE II

The Phase	*T°C*	*Thermoelectric Q-Factor (Z) (deg^{-1}).*
In solid State	83 187	1.49×10^{-11}deg^{-1} 3.54×10^{-11}deg^{-1}
In Liquid State	471 481	13.7×10^{-7}deg^{-1} 16.99×10^{-7}deg^{-1}

where (n) is the refractive index, (B) is the Stefan-Boltzmann constant and (α) is the optical absorption coefficient. Powell's theoretical calculations show that the ratio between the thermal conductivity of material at melting point in the crystalline $\lambda_{(s)}$ and liquid state $\lambda_{(L)}$ is given by L

$$\frac{\lambda_s}{\lambda_L} = e^{3/2 \frac{r}{KT_m}} \tag{13}$$

where (T_m) is the melting point and (r) is the atomic heat of melting of material.

It is of considerable interest to determine the potential value of liquid semiconductors in devices for thermoelectric power conversion. Knowing the thermal conductivity coefficient (λ), the electrical conductivity (σ), and the thermoelectric power (S) one can determine the figure of merit for thermoelectric conversion (Z) using the expression [22]:

$$Z = S^2\sigma/\lambda \tag{14}$$

where $(\lambda), (S), (\sigma)$ and (Z) mention above. Then, the values of $(\lambda), (\sigma)$ and the thermal-emf were used to evaluate the thermoelectric Q-factor (Z) for our sample $Bi_{29}Tl_{35}Se_{36}$ in both solid and liquid states at the same temperature which uses during the calculations each of $(\lambda), (S)$ and (σ).

The theoretical calculation results of (Z) given in Table II.

4. CONCLUSION

The electrical conduction in liquid $Bi_{29}Tl_{35}Se_{36}$ could be analyzed by the model developed by Mott. The electrical conduction mechanism is due to holes excited into extended states near the band edge and the energy gap is 1.34 eV. The factor which gives the temperature dependence of the energy gap is found to be 10.37×10^{-4} eV/°K, which shows a large decrease of the gap with temperature.

Thermal conductivity increases gradually with temperature up to the melting point. The electronic (λ_e) and bipolar $\lambda_{(pb)}$ contributions to thermal conductivity at room temperature are found to be 0.37×10^{-10} W/m.K° and 1.9×10^{-10} W/m.K° respectively. Also the thermal conductivity due to atomic motion (λ_a) is found to be 0.35 W/m.°K. A calculation of the Q-factor (Z) from data on thermal conductivity (λ), the electrical conductivity (σ) and thermo-emf (S) in the solid and liquid state shows that the value of Z fluctuates within the limits $(1.49 - 3.54) \times 10^{-11}\mathrm{deg}^{-1}$ in solid and $(13.7 - 16.99) \times 10^{-7}\mathrm{deg}^{-1}$ in liquid.

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