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THERMAL CONDUCTIVITY OF GE_{25} BI_{40} TE_{35} AND GE_{25} BI_{40} SB_{35} SEMICONDUCTING CHALCOGENIDE GLASSES IN SOLID AND LIQUID STATES.

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ABSTRACT:

An investigation is made on the thermal conductivity for the ternary semiconducting chalcogenide glasses Ge_{25} Bi_{40} Te_{35} and Ge_{25} Bi_{40} Sb_{35} in solid and liquid states in a wide range of temperatures from room temperature (~30°C) to near 600°C. Measurements of thermal conductivity λ were carried out using the concentric cylinder method which is based on the flow of heat through a cylindrical wall. The temperature dependence of λ was explained by postulating different mechanisms for the thermal conductivity in Semiconductors. The contribution of electronic, phonon, and bipolar mechanisms to the heat transfer is evaluated. The thermoelectric Q -Factor (Z) is estimated for both samples in the solid and liquid states.

INTRODUCTION:

Studies on semiconducting glasses Ge-Bi-Te and Ge-Bi-Sb systems have received attention because of their remarkable threshold and memory switching properties (Sakai et al 1974). Some attempts have been proposed to explain threshold switching and memory effects in these glasses. The structural, thermal, and electrical properties of these material are very important for better understanding of their transport mechanism (Gadzhiev et al 1977). Very little work has been reported on the thermal properties of these glass compositions.

The aim of present contribution is to study the thermal conductivity of Ge_{25} Bi_{40} Te_{35} and Ge_{25} Bi_{40} Sb_{35} in a wide rage of temperatures in the solid and liquid states.

EXPERIMENTAL DETAILS

The samples were prepared by melting the proper amounts of highly pure component elements (99.999%). The materials were sealed in evacuated tubes at 10^{-5} torr and heated at 1200 °C for 24 h with frequent rocking to ensure homogenization of the melt. Then the tubes were quenched in iced-water to obtain the samples in an amorphous state.

Measurements of thermal conductivity were carried out using the concentric cylinder method (Sharaf et al 1991) where 0.5gm of the material was put into the cylindrical gap between two concentric graphite cylinders kept in

nitrogen atmosphere (Abdelmohsen et al 1989). The system was fitted with a heater and sensitive thermocouples for accurate measurements of temperature and the thermal conductivity was calculated using the formula (Abou El-Ela et al 1979):

$$\lambda = \frac{Q \ln (d_2/d_1)}{2\pi L (T_1 - T_2)} \quad (1)$$

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 (Sharaf et al 1991):

$$Q = m \left(\frac{\Delta T}{\Delta t}\right) S \quad (2)$$

Where m is the mass of the external cylinder ($\simeq$ 830 gm), $\left(\frac{\Delta T}{\Delta t}\right)$ is the temperature gradient and S is the specific heat of graphite ($\simeq$ 0.22 cal/g.deg). Measurements were carried out in a wide range of temperatures below and above the melting point.

The melting point of Ge_{25} Bi_{40} Te_{35} and Ge_{25} Bi_{40} Sb_{35} are at 320°C and 360 °C respectively.

RESULTS AND DISCUSSION

Figures (1) and (2) show the temperature dependence for the measured thermal conductivity for Ge_{25} Bi_{40} Te_{35} and Ge_{25} Bi_{40} Sb_{35} in the solid and liquid states. The results were obtained by an absolute method under steady - state thermal conditions (Sharaf 1997).

For Ge_{25} Bi_{40} Te_{35} and Ge_{25} Bi_{40} Sb_{35} there is an increase in thermal conductivity with temperature in the solid state, which is in agreement with (Kittel, 1976), it may be attributed to the increase of heat capacity with temperature. This can be explained with the relation (Kittel, 1976):

$$\lambda_{lattice} = \left(\frac{1}{3}\right) CVL \quad (3)$$

Where C is the heat capacity per unit volume, V is the phonon velocity, and L is the mean free path of phonons. In the amorphous solids the wavelength of phonons carrying thermal energy is equal to the energy of the average distance between the molecules, (Adler et al 1985) and is nearly temperature independent. But the thermal conductivity dependence of temperature in the solid state is due to

the linear increase of the heat capacity and phonon mean free path (Alder et al 1985).

The increase of thermal conductivity before melting (Part a b) with respect to both Ge_{25} Bi_{40} Te_{35} and Ge_{25} Bi_{40} Sb_{35} may be attributed to a process of transition from the amorphous to a highly elastic state which consequently increases the mobility of the molecules and increases the distances between the molecules which is followed by the stimulation of rotational oscillations of molecules. (Powell 1958).

The decrease of thermal conductivity (Part bc) during softening and melting with respect to Ge_{25} Bi_{40} Te_{35} and decrease of the thermal conductivity (Part bc) for Ge_{25} Bi_{40} Te_{35} after the melting point can be attributed to the decrease of density on softening and melting and subsequent increase of the distance between the molecules (Glazov et al 1969). This leads to a weakening of the bonds between the molecules and an increase in the disordered arrangement. The decrease of thermal conductivity can be attributed to the decrease of the heat capacity and the mean free path of the phonons (Glazov et al 1969).

Cutler had shown that the λ of a semiconductor can be analyzed in terms of four contributions, phonons (λ_{ph}), bipolar (λ_{bp}), electronic (λ_e) and the contribution of the atomic motion (λ_a) thermal conductivities (Cutler 1977):

$$\lambda = \lambda_e + \lambda_{ph} + \lambda_{bp} + \lambda_a \qquad (4)$$

By knowing the values of the room temperature electrical conductivity (σ_R) together with the activation energy (E_g), the bipolar λ_{pb} and the electronic λ_e thermal conductivities can be estimated. The bipolar thermal conductivity was calculated from the following formula (Bellabarab et al 1981 and Sharaf 1997):

$$\lambda_{pb} = \left(\frac{3}{4\pi^2}\right) L\, \sigma_R\, T \left(\frac{E_g}{kT} + 4\right)^2 \qquad (5)$$

Magomedov et al (1987) reported that the Wiedemenn-Franz law can be used to calculated λ_e in the studied limited range of temperatures. Therefore, the electronic part of thermal conductivity was given by the equation. (Magomedov et al 1987 and Bellabarab et al 1981) :

$$\lambda_e = \sigma_R\, L\, T \qquad (6)$$

Where L is the Lorenz number (L = 2.44 x 10^{-8} WΩ/K^2) and σ_R is the electrical conductivity at room temperature. λ_{bp} and λ_e are calculated in Table (1) for the two samples Ge_{25} Bi_{40} Te_{35} and Ge_{25} $Bi_{40}Sb_{35}$ at the two different temperatures 313 and 333k respectively.

Table (1) Shows the calculated values of λ_{bp}, λ_e, σ_R and Eg with the measured thermal conductivity for both samples at 313K and 333 K :

Sample	T(K)	λ_e (w/m.k)	λ_{bp} (w/m.k)	λ (w/m.k)	σ_R (Ω.cm)-1	E_g (eV)
Ge_{25} Bi_{40} Te_{35}	313 333	0.8 x 10^{-9} 0.2 x 10^{-8}	0.29 x 10^{-8} 3.7 x 10^{-8}	1.182 2.38	1.05x10^{-4}	0.08
Ge_{25} Bi_{40} Sb_{35}	313 333	0.1 x 10^{-8} 0.1 x 10^{-8}	0.75 x 10^{-8} 0.1 x 10^{-9}	1.032 1.75	1.96x10^{-4}	0.15

From these results, it is observed that the values of λ_e and λ_{bp} are very small with respect to the measured values of λ, therefore one can neglected these values in the measurements. Both λ_e and λ_{bp} increase and decrease with temperature respectively, while both λ_e and λ_{bp} for Ge_{25} Bi_{40} Te_{35} are larger than λ_e and λ_{bp} for Ge_{25} $Bi_{40}Sb_{35}$.

The contribution of the atomic motion λ_a also can be calculated and is given by (Sharaf 1997) :

$$\lambda a = \frac{9\,k\,\nu}{\pi\,a} \qquad (7)$$

Where k is Boltzmann's constant, (ν) is the vibration frequency $\cong 3 \times 10^{12}$ Sec^{-1} and (a) is the atomic radius. ($a \simeq 4A^{o}$) for Ge_{25} Bi_{40} Te_{35} and ($a \simeq 4.8A^{o}$) for Ge_{25} $Bi_{40}Sb_{35}$. From eq. (7) λ_a is about 0.63 W/m.k for Ge_{25} Bi_{40} Te_{35} but for Ge_{25} $Bi_{40}Sb_{35}$ λ_a is about 0.59 W/m.k.

From the measured values of the thermoelectric power S, electrical conductivity σ (Sharaf et al 2001) and (Abd Rabo et al 2003), and the measured thermal conductivity λ it can be calculated the thermoelectric figure of merit (Z) for both samples in the solid and liquid states, by using the expression (Magomedov et al 1987) :

$$Z = S^2 \sigma / \lambda \qquad (8)$$

The theoretical calculated results of (Z) for both samples are given in Tables (2) and (3).

Table (2): Temperature dependence of the thermoelectric conversion (Z) for Ge_{25} Bi_{40} Te_{35} Chalcogenide glass:

In the Solid State	**T (K)**	**415**	**425**	**457**	**483**
	Thermoelectric Q- Factor Z $(deg)^{-1}$	0.091	0.093	0.157	0.197
	ZT	37.765	39.525	71.749	95.151
In the Liquid State	T (K)	563	685	723	757
	Thermoelectric Q- Factor Z $(deg)^{-1}$	0.287	0.577	0.582	0.669
	ZT	161.572	395.459	420.598	506.189

Table (3): Temperature dependence of the thermoelectric conversion (Z) for Ge_{25} Bi_{40} Sb_{35} chalcogenide glass.

In the Solid State	T (K)	208	225	234	260
	Thermoelectric Q- Factor Z $(deg)^{-1}$	1.175	2.465	3.761	8.987
	ZT	244.4	554.625	880.074	
	Thermoelectric Q- Factor Z $(deg)^{-1}$	$1.986x10^{-3}$	$4.226x10^{-3}$	$5.463x10^{-3}$	$11.247x10^{-3}$
	ZT	1.644	3.567	4.660	9.706

Tables (2) and (3) show that the figure of merit or the thermoelectric conversion (Z) increases with temperature for both samples. These data are very important in some applications, such as heat diffusion pumps.

CONCLUSION

The thermal conductivity of Ge_{25} Bi_{40} Te_{35} and Ge_{25} Bi_{40} Sb_{35} in the solid state varies with temperature. The variation of thermal conductivity is attributed mainly to phonon components. The phonon component decreases in the liquid state because of the increase of the distance between molecules and the weakening of the bonds between them.

The values of λ_e and λ_{bp} were estimated with temperature for the two samples. From these results it can be seen that λ_e and λ_{bp} are negligible compared with the measured values of λ. Also λ_a was calculated for each sample and found to be equal to 0.63 W/m.k for Ge_{25} Bi_{40} Te_{35} and 0.59 W/m.k for Ge_{25} $Bi_{40}Sb_{35}$.

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