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HARDNESS AND THERMAL CONDUCTIVITY OF As-Se-Te CHALCOGENIDE GLASSES

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Abstract.- The results of the Vickers Hardness (VH) and the thermal conductivity (K) of the As-Se-Te glasses containing: 28.5 - 50 at % As, 5 - 41.4 at % Se, and 0.0 - 57 at % Te are given. A trend in the variation of VH (room temperature) with composition has been observed. The difference in nature and concentration of the chemical bonds between the stoichiometric system, As$_2$Se$_2$-As$_2$Te$_3$, and the other two alloy systems, AsSe-AsTe and As$_2$Se$_2$-As$_2$Te$_3$, are used to explain the contrasting results. Below T$_g$ (the glass transition temperature) the thermal conductivity of the glasses increase with temperature. Such increase is pronounced at some compositions. The compositional variation of K for the chalcogenide systems all exhibit a dip in the conductivity at equal proportions of Se and Te. The value of K(20°C) of the As$_x$Se$_y$Te$_{2-y}$ glasses varies between 0.18 - 0.95 cal/cm.sec.deg. The electronic contribution of the thermal conduction in each system is stimulated with Te, whereas the main mechanism of heat transport is by phonons. So, the increase in K toward the composition ends is controlled by the number of scattering centres in the glass matrix.

Introduction.- Chalcogenide glasses are of interest for both basic researches and technological applications because of their unique optical and electrical properties. One explanation of the observed conduction changes accompanying mono and bistable switching is thermal avalanching initiated when Joule heating exceeds the heat transfer rate /1/. Hence, the compositional variation of the thermal conductivity of the chalcogenide glasses should affect the voltage necessary for the onset of switching. Mixed systems of binaries such as the As$_2$Se$_2$-As$_2$S$_3$ and As$_2$Se$_2$-As$_2$Te$_3$ have been the subject of detailed investigations /2-5/. However, there have been only a few data on thermal properties of the chalcogenide glasses /4-7/.

The interrelation between the electronic properties and nature of the chemical bonds in an alloy system As-Se-Te has been studied /8/. The present work represents a data on the hardness and thermal conductivity of different As-Se-Te compounds having the general formula As$_x$Se$_y$Te$_{2-y}$, with $y = 2.5$ (system A), 1.5 (system B), and 1 (system C), and $x$ with $0 < x < y$. Samples preparation and the measuring techniques were described in previous publications /4,8,9/.
Results and discussion

Hardness.- The change of the sample hardness $V_H$ associated with the introduction of Te is shown in fig. 1. It shows that the effect of Te on $V_H$ differs among the different systems. Such behaviour might be correlated with the concentration and strength of the different bonds formed in the network structure of the materials investigated.

In the parent glass of system A, As$_2$Se$_5$, there are two types of chemical bonds As-Se and Se-Se with a ratio 3:1. The introduction of Te in the alloy system As$_2$Se$_5$-As$_2$Te$_5$ leads to the consecutive formation of As-Te, Se-Te, and Te-Te bonds with their relative concentration depend on Te %. The formation of Te-Te bonds starts at compositions having $>35$ at % Te. In fig. 1, addition of Te upto 28 at % (AsSe$_2$.Te) leads to an increase in $V_H$ from 76 (AsSe$_2$.5) to 88 k.g.m/mm$^2$. Further addition of Te, which leads to the formation of Se-Te and then Te-Te bonds, is accompanied by a decrease in $V_H$ till it reaches 81 k.g.m/mm$^2$ at the rich Te sample, AsSe$_2$.5Te$_5$ (57 at % Te). This is likely to be due to the decrease in the strength of the Se-Te and Te-Te bonds than that of the Se-Se ones, whereas the respective values of these bonds are: 48, 46.5 and 49.5 K.cal/mole.

The observed increase of $V_H$ with Te for the stoichiometric system B, fig. 1, is attributed to the formation of As-Te bonds at the expense of the As-Se ones /4/.

In the composition AsSe$_2$, two types of chemical bonds As-Se and As-As exist having a ratio 4:1. The introduction of Te upto 45 at % (AsSe$_2$.Te$_0$.9) will cause the formation of As-Te bonds at the expense of As-Se bonds, while the concentration of As-As (69.4 K cal/mole) bonds remain constant /8/. The As-As bonds cause the increase of $V_H$ in a way more detectable than those produced in the other two systems. In system C, $V_H$ increases from 163 to 350 k.g.m/mm$^2$ with Te-content for the compositions investigated.

Thermal conductivity.- Figure 2 shows the temperature dependence of the measured thermal conductivity $K$ for the investigated compositions of the systems A and C. It shows an increase for $K$ with the temperature below $T_g$. This suggests the amorphous behaviour of the samples. However, the increase is small for most compositions and pronounced for others, particularly the rich Te samples, e.g. AsSe$_{0.5}$Te$_2$ in system A and AsSe$_{0.1}$Te$_{0.9}$ in system C.

In addition to lattice conductivity, $K_L$, in semiconducting materials, there can be electronic contribution to the thermal conductivity, but the photon contribution is excluded in the measured temperat-
ure range. The electronic contribution is due to thermal motion of free electrons $K_e$ and, also, to thermal electron-hole motion (of bipolar type) $K_{bp}$. Here, $K_e$ is evaluated in terms of the total electrical conductivity $\sigma$ from Wiedmann-Franz law: $K_e = L \sigma T$, where $T$ is the absolute temperature and $L$ the Lorentz number; $L = 1/3 \pi^2 (K_\text{B}/e)^2$. The calculated values of $K_e$ for AsSe show an increase from $1.5 \times 10^{-19}$ at $20^\circ C$ to $2.3 \times 10^{-18}$ cal/cm.sec.deg at $100^\circ C$. This corresponds to an increase from $1.2 \times 10^{-21}$ to $5.0 \times 10^{-17}$ cal/cm.sec.deg for AsSe. The electronic contribution of thermal current shows an increase with Te-content, and its values at $20^\circ C$ for the Te rich samples AsSe$_{0.5}$Te$_2$ and AsSe$_{0.1}$Te$_{0.9}$ are $6.5 \times 10^{-11}$ and $6.2 \times 10^{-11}$ cal/cm.sec.deg, respectively.

The bipolar thermal conductivity $K_{bp}$ caused by electron-hole pairs with energy $E$ diffusing down the temperature gradient, is given for a well-compensated intrinsic semiconductor with an ordinary parabolic band and current carrier scattering due to acoustic phonons by the formula $/11/$; $K_{bp} = (3k_B/4\pi)(E/k_B T + 2)^2$, where $k_B$ is Boltzmann constant. The calculated values of $K_{bp}$ for the parent glasses As$_2$Se$_3$ and AsSe increased, respectively, from $2.4 \times 10^{-17}$ to $2.4 \times 10^{-14}$, and from $3.3 \times 10^{-17}$ to $3.7 \times 10^{-15}$ cal/cm.sec.deg in the temperature range of $20 - 100^\circ C$. It is seen that $K_{bp}$ exceeds $K_e$ by about two orders of magnitude. Also, $K_{bp}$ shows an increase with Te-content.

For any As-Se-Te composition the calculated lattice component $K_L$ of the thermal conductivity, using the formula suggested by Turnbull $/12/$, was found to be of the order of the experimentally obtained value.

Fig. 2: Temperature dependence of thermal conductivity of As-Se-Te glasses.

Fig. 3: Dependence of $K_{20^\circ C}$ on Te-content.
Thus, one may conclude that the main contribution of heat transport in the investigated glasses is due to phonons. Apart from the compositions of the highest Te-content where the change in $\kappa$ with $T$ is large, one may assume that the specific heat $C_v$ has the same qualitative features as the thermal conductivity. That is, $\kappa$ is related to $C_v$. So, an estimation for the mean free path $\lambda$ of the phonons can be obtained from the formula proposed by Kittel /13/:

$$\lambda = \frac{3k}{C_vv}. $$

This corresponds to $12 - 13 \text{Å}$ for the parent glasses $\text{AsSe}$ and $\text{As}_2\text{Se}_5$ at room temperature, when the values of the average velocity $v$ and $C_v$ are assumed to be unchanged from the values of $\text{As}_2\text{Se}_3$ /6/. This value of $\lambda$ which is of the order of the unit cell dimensions /14/ for the glasses considered, suggesting that phonon scattering occurs as the wave propagates an interatomic distance, or less.

As seen from fig. 3, the thermal conductivity at 20°C changes with Te-content, having a minimum value at concentration of equal proportion of Se and Te; $\text{AsSe}_{0.5}\text{Te}_{0.5}$ (0.95x10^{-2} cal/cm.sec.deg) and $\text{AsSe}_{0.6}\text{Te}_{0.4}$ (0.3x10^{-2} cal/cm.sec.deg) for $\text{As}_2\text{Se}_3$-$\text{AsTe}_3$, where a dip in $\kappa$ was observed for the composition of $\text{AsSe}_{0.5}\text{Te}_{0.5}$. The decrease of the phonon conductivity might be explained by the increase of the number of scattering due to dissolving Te atoms in the parent glass matrix. As Te-content increase to more than Se-content, Se atoms will play the role of scattering centres in the As-Se-Te glassy alloy. Additional increase in Te-content leads to the decrease of the concentration of the Se scattering centres, leading to an increase in thermal conductivity, fig. 3.

References