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DENSITY AND VISCOSITY OF $AgGaSe_2$ SEMICONDUCTOR COMPOUND IN SOLID AND LIQUID STATES

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The density and kinematic viscosity of $AgGaSe_2$ were investigated in the solid and liquid states in the temperature range 690 – 930 °C. Density and dynamic viscosity measurements were carried out using the thermometer method and the rotating cylinder method. Experimental data show that the dependence of viscosity on temperature has an activation character and that logarithm of viscosity vs. reciprocal absolute temperature can be approximated by two straight lines corresponding to activation energies 0.36 eV and 0.19 eV in the solid and liquid states, respectively. The temperature dependence of the free volume was calculated and it was found that it decreases linearly with temperature. The results are explained on the basis of the free-volume model.

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1. Introduction

I-III-VI_2 chalcopyrite semiconductors are ternary analogs of the II-VI zinc blende compounds [1]. These ternary compounds are now well known as important semiconducting materials for use in optoelectronic devices. $AgGaSe_2$ is one of the least exploited compounds holding much promise for non-linear optics and solar cells [1-4].

The most important parameter characterizing the physical properties of liquid and melts is the viscosity, which is dependent on temperature and molecular mass.

The aim of the present work is to study the effect of temperature in vacuum on the density and viscosity in the solid and liquid states for ternary semiconductor compounds $AgGaSe_2$.

2. *Experimental*

$AgGaSe_2$ material was prepared by direct fusion of stoichiometric amounts of Ag, Ga and Se (purity 99. 999%) in a sealed, evacuated silica tube (at 10^{-7} Pa). The tube was heated at 1000 °C for 48 h with continuous rocking to ensure homogeneity of the sample. The tube was quenched in ice to obtain the sample in glassy state. The melting point of the $AgGaSe_2$ compound is about 850 °C.

Density measurements were carried out using the thermometer method [5–7], with the material placed inside an evacuated quartz ampoule. The measurements of the temperature dependence of density were carried out with a calibrated pyrometer (minimum error), and a specially shaped silica ampoule whose middle part is a capillary with a scale allowing for measurements of volume at different temperatures. The density of the sample is calculated as mass/volume.

Viscosity measurements were carried out using the rotating cylinder method [5–7] in which damped oscillations of a cylinder filled with liquid sample and suspended by an elastic filament were used. The viscosity, η, was calculated by the method of successive approximations using the Shvidkovskii equation [8]

$$\eta = \nu d$$

where

$$\nu = \frac{0.8225(MR^2/2)R^2\sigma}{2\tau[(I - MR^2/2)\,\delta - I(\tau/\tau_0)\,\delta_0]}\,, \tag{1}$$

is the kinematic viscosity, M is the mass of the liquid, I is the moment of inertia of the empty cylinder, R is the radius of the cylinder, δ and δ_0 are the logarithmic decrements of the damped oscillations of the filled and empty cylinders, τ and τ_0 are the oscillation periods of the filled and empty cylinders, σ is the correction factor and d is the density of the sample.

3. *Results and discussion*

Figure 1 shows the temperature dependence of the density of solid and liquid $AgGaSe_2$ sample. The decrease of density with temperature may be attributed to a large thermal expansion coefficient, i.e., the increase of the interatomic spacing which causes a net increase in volume.

Figure 2 shows the temperature dependence of the calculated kinematic viscosity ν, while Fig. 3 shows the temperature dependence of the calculated dynamic viscosity η of $AgGaSe_2$. At low temperature, the kinematic viscosity slightly decreases with temperature, passes through a minimum at about 1100 K, increases to a maximum at about 1150 K and then decreases again. The dynamic viscosity-temperature relationship for many liquids over a limited temperature range can be represented by a simple Arrhenius law [9] of the form

$$\eta = \eta_0 \exp(W/kT)\,, \tag{2}$$

where W is the activation energy for viscous flow, η_0 is a constant, k is the Boltz-

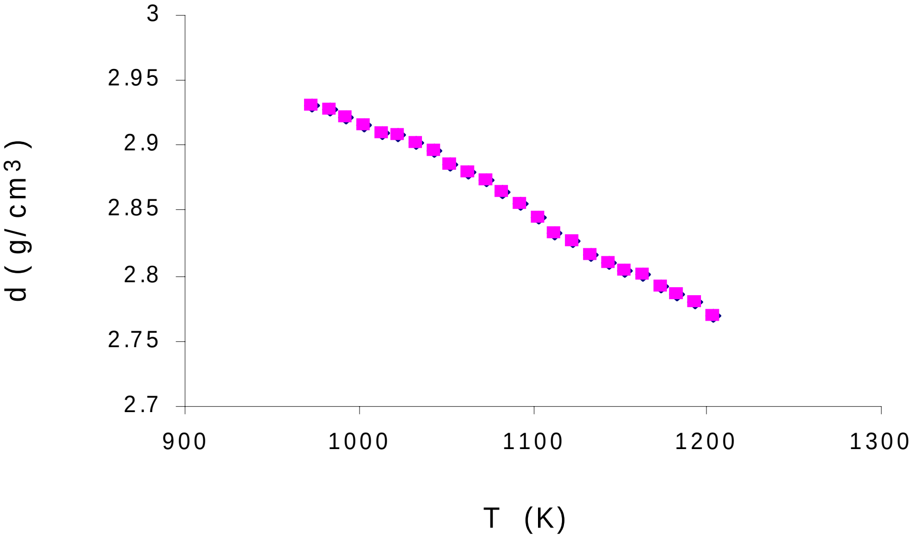

Fig. 1. Temperature dependence of density d of $AgGaSe_2$.

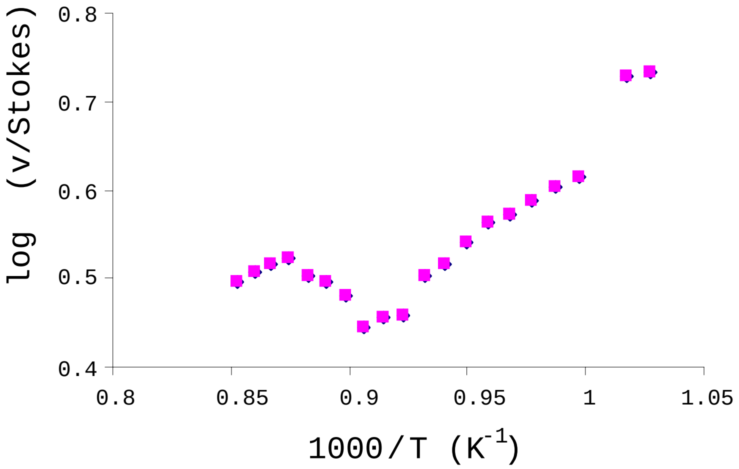

Fig. 2. Temperature dependence of the kinematic viscosity ν of $AgGaSe_2$.

mann constant and T is the absolute temperature. The experimental data shown in Fig. 3 in the temperature regions below 1100 K and above 1150 K were fitted by straight lines using the least squares method, and from the fits we derived the activation energies of the viscous flow of the solid and liquid states of 0.39 eV and 0.19 eV, respectively. These flow data may be discussed in terms of the standard theoretical models for liquid viscosity [5,10,11]. The free volume model [11] is representing the flow behaviour from 850 °C to 930 °C. In this model, the molecules are confined to a cage bounded by their immediate neighbours. Occasionally there is a fluctuation in density which opens up a hole within a cage large enough to permit considerable displacements of the molecules contained by it.

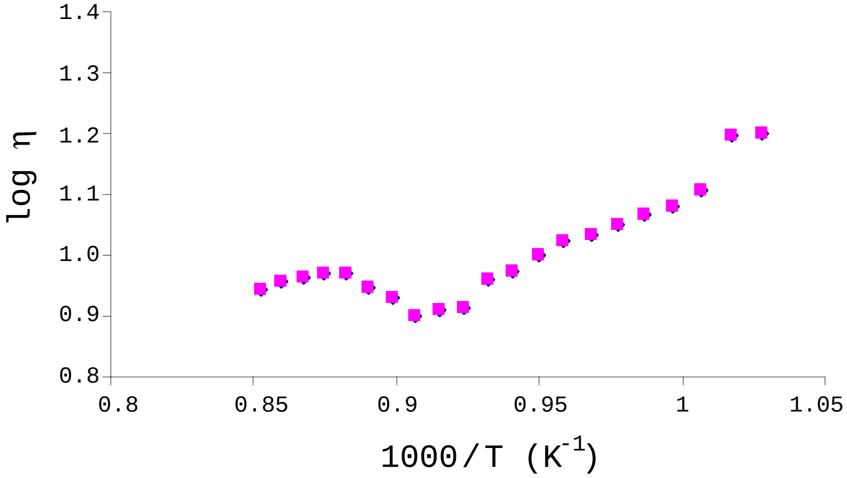

Fig. 3. Temperature dependence of the dynamic viscosity η *of* $AgGaSe_2$.

The diffusive motion occurs as a result of the translation of the molecules across the void in its cage, and diffusion occurs as a result of an activation rather as a result of redistribution of the free volume within the liquid [12,13]. The free volume of a given molecule is the volume within its cage less than the volume of the molecule and it should exceed a critical volume v^* just large enough to permit another molecule to jump in after the displacement. If the total range of volume of the free volume per molecule can be divided into small region having the average value v_i, and N_i is the number of molecules having free volume in i-th region, one has for the total free volume [13]

$$V_f = \gamma \sum N_i v_i \, , \tag{3}$$

where $\sum N_i = N$ is the total number of molecules, and γ is a numerical factor introduced to correct for the overlap of the free volume ($\gamma = 0.5$) and the average free volume per molekule $v_f = V_f/N$. The segmental friction factor is expressed in the free volume formalism by

$$F = A\sqrt{T}\,\exp(\gamma v^*/v_f)\,, \tag{4}$$

At temperatures above the glass-transition temperature, extensive molecular transport can occur. This implies the presence of a considerable number of holes, and the magnitude of the free volume is determined by the excess volume arising from the holes. The total free volume can be approximately obtained from the expression [14]

$$V_f = V_g[0.025 + \alpha(T - T_g)]\,, \tag{5}$$

where V_g is the volume at glass temperature, T_g is the glass transition temperature obtained by the differential thermal analysis (DTA) and α is the difference between the thermal expansion coefficient of the liquid and the glass.

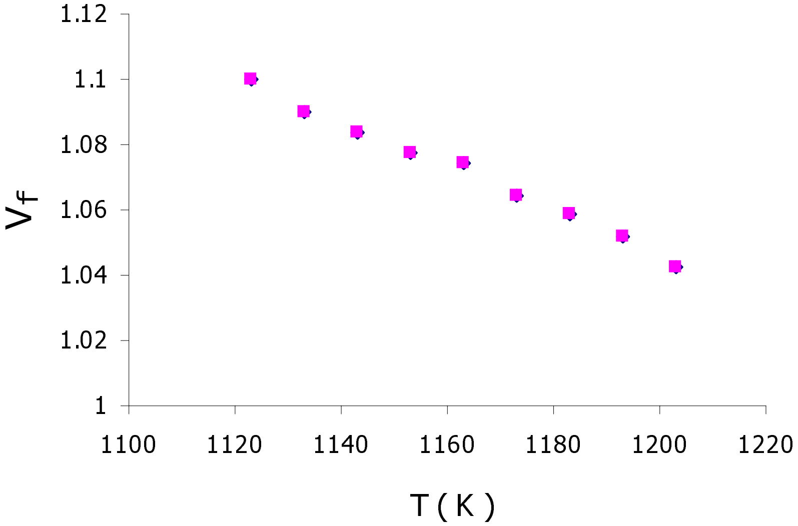

Fig. 4. Temperature dependence of the free volume of AgGaSe$_2$.

Figure 4 shows the relation between the free volume and the temperature. As can be seen from the figure, the free volume decreases with temperature, which may be attributed to the decrease of interatomic spacing and holes.

Doolittle [15] found the relation between the fluidity ϕ ($\phi = 1/\eta$) and the free volume in liquids

$$\phi = A\exp(-bV_0/V_f)\,, \tag{6}$$

where A is a constant and b is a constant of the molecules of the sample of the order of unity. From Eq. (6), we can determine the van der Waals volume V_0 of the molecules of the sample by plotting the relation between log ϕ versus $1/V_f$. From Fig. 5, $V_0 = 2.73 \times 10^{-23}$ cm^3 for the compound AgGaSe$_2$.

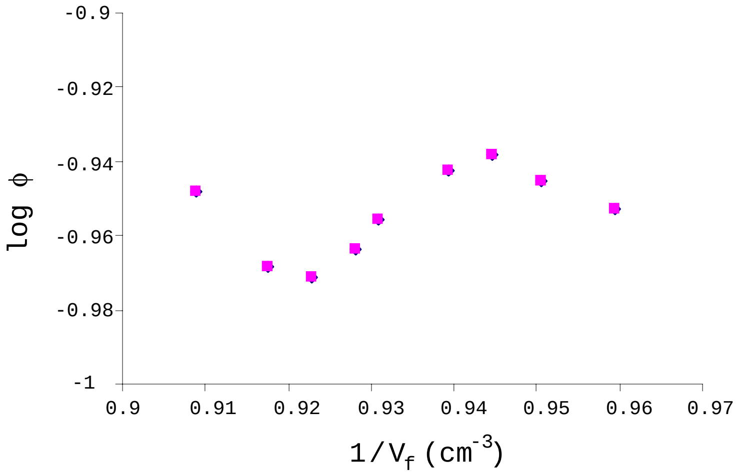

Fig. 5. The dependence of $\log\phi$ *on* $(1/V_f)$ *of* AgGaSe$_2$.

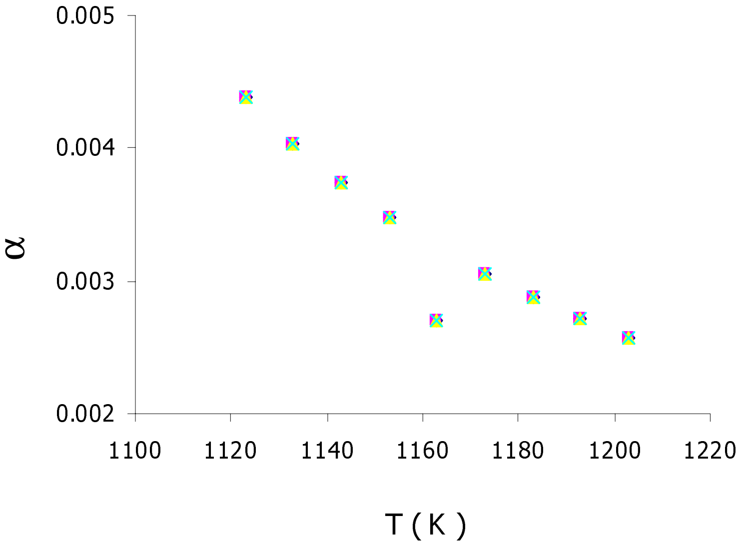

Fig. 6. Temperature dependence of the coefficient of thermal expansion α *of* AgGaSe$_2$.

Cohen and Turbull [12] have shown that the dynamic viscosity can be expressed by

$$\eta = C\sqrt{T}\,N\exp\left[\frac{\gamma V^*}{\alpha V_f(T-T_g)}\right]. \tag{7}$$

N is the number of molecules, $V^* \simeq 10V_f$ and $C = \sqrt{8mk/(9\pi^3)}/a^2$, where m is molecular mass and a is the molecular diameter.

Figure 6 shows the temperature dependence of the coefficient of thermal expansion α. One can see that α decreases when temperature increases.

4. Conclusion

The density of AgGaSe$_2$ decreases with temperature, while the dynamic viscosity of this semiconductor compound above the melting point at about 850 °C in the liquid state increases with temperature. The calculated activation energies for viscous flow are 0.36 eV and 0.19 eV in the solid and liquid states, respectively. The density d, the coefficient of thermal expansion α and the total free volume decrease with increasing temperature. The van der Waals volume of the molecules of the sample AgGaSe$_2$ was derived and found to be 2.73×10^{-23} cm^3.

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GUSTOĆA I VISKOZNOST POLUVODIČKOG SPOJA AgGaSe$_2$ U ČVRSTOM I TEKUĆEM STANJU

Istraživali smo gustoću i kinematičku viskoznost AgGaSe$_2$ u čvrstom i tekućem stanju na temperaturama 690 – 930 °C. U mjerenjima gustoće i viskoznosti primijenili smo termometrijsku metodu odnosno metodu rotirajućeg valjka. Mjerni podaci ukazuju da ovisnost viskoznosti η o temperaturi ima aktivacijske značajke, te se ovisnost log η o temperaturi može aproksimirati pravcima koji odgovaraju aktivacijskim energijama 0.36 eV and 0.19 eV za čvrsto odnosno tekuće stanje. Izveli smo i temperaturnu ovisnost slobodnog volumena i našli da se linerno smanjuje s temperaturom. Ishodi mjerenja tumače se na osnovi modela slobodnog volumena.