DIELECTRIC RELAXATION STUDY OF CuTlTe$_2$ IN THE SOLID AND LIQUID PHASES

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Measurements of the dielectric properties of CuTlTe$_2$ in the solid and liquid phases were carried out in a wide range of frequencies (10^4 to 10^7 Hz) at different temperatures (165 to 506 °C). The material displays dielectric dispersion and two loss peaks are observed. The curves log ε' vs. temperature, ε' and tan δ vs. frequency, give a direct evidence of the existence of a Debye-type relaxation having a wide distribution of relaxation times.

1. Introduction

Cole-Cole diagrams are used to determine the distribution parameter (α) and molecular relaxation time (τ) and Eyring's relaxation rate equations are used to determine the free energy of activation. The high frequency loss peak is attributed to charged defect states and Elliott's theory for *ac* conduction in chalcogenide glasses is used to calculate the density of defect states.

Much theoretical and experimental effort has been devoted to understanding the electronic relaxation phenomena in amorphous and liquid semiconductors. Various models[1−4] have been proposed to explain the conductivity behaviour and it has been demonstrated that some semiconductors retain their predominantly covalent semiconducting properties in the amorphous and liquid states, whereas other semiconductors acquire metallic properties above the melting point. Measurements of the frequency and temperature dependences of the dielectric proper-

ties of amorphous and liquid semiconductors allow to obtain critical information concerning the electronic structure as well as the conduction and relaxation mechanisms. The aim of the present work is to investigate the dielectric properties and ac conduction of $CuTlTe_2$ ternary semiconductor in the solid and liquid phases. $CuTlTe_2$ crystallizes in the chalcopyrite structure[5,6] and its melting point is 375 °C. Ternary chalcopyrite semiconductors are of technological interest because of their peculiar nonlinear optical properties. They show promise for application in the areas of visible and infrared detection parametric oscillators and far infrared generation.

2. Experimental

The samples were prepared by melting the proper amounts of highly pure component elements (99.999%). The material was sealed in a quartz tube at 10^{-3} Pa and heated at 1200 °C for 12 h with frequent rocking to ensure homogenization of the melt. Then the tubes were quenched in ice to obtain the sample in the amorphous state. The solid material is then heated in inert atmosphere until it melts and then transferred to the measuring cell.

A cylindrical measuring cell was used which consists of two coaxial graphite cylinders. The cell contains a temperature controlled heater, a chromel-alumel thermocouple for accurate measurements of temperature and was fitted with a guard ring electrode[7].

Measurement of the dielectric constant were carried out in an inert atmosphere at different frequencies and temperatures using a well shielded ac bridge connected according to the Schering principle in conjunction with a Farnell ESG2 oscillator, and a sensitive broad band oscilloscope type Trio CS-1560A was used as a null indicator.

3. Theory of measurements and experimental results

Fig. 1 shows the frequency dependence of the real part of the dielectric constant (ε') measured at different temperatures below and above the melting point in the high frequency range. It is clear from the figure that all the curves exhibit dielectric dispersion in the high frequency range and ε' apart from the dispersion regions remains constant.

Fig. 2 shows the frequency dependence of the energy loss parameter (tan δ) at different temperatures. It is clear that all curves of tan δ exhibit two energy loss peaks in the high frequency range and the frequency at the peak maximum shifts towards higher frequencies on increasing the temperature. Moreover, the height of the loss peak (tan $\delta)_{max}$ increases with temperature.

4. Distribution parameter and relaxation time

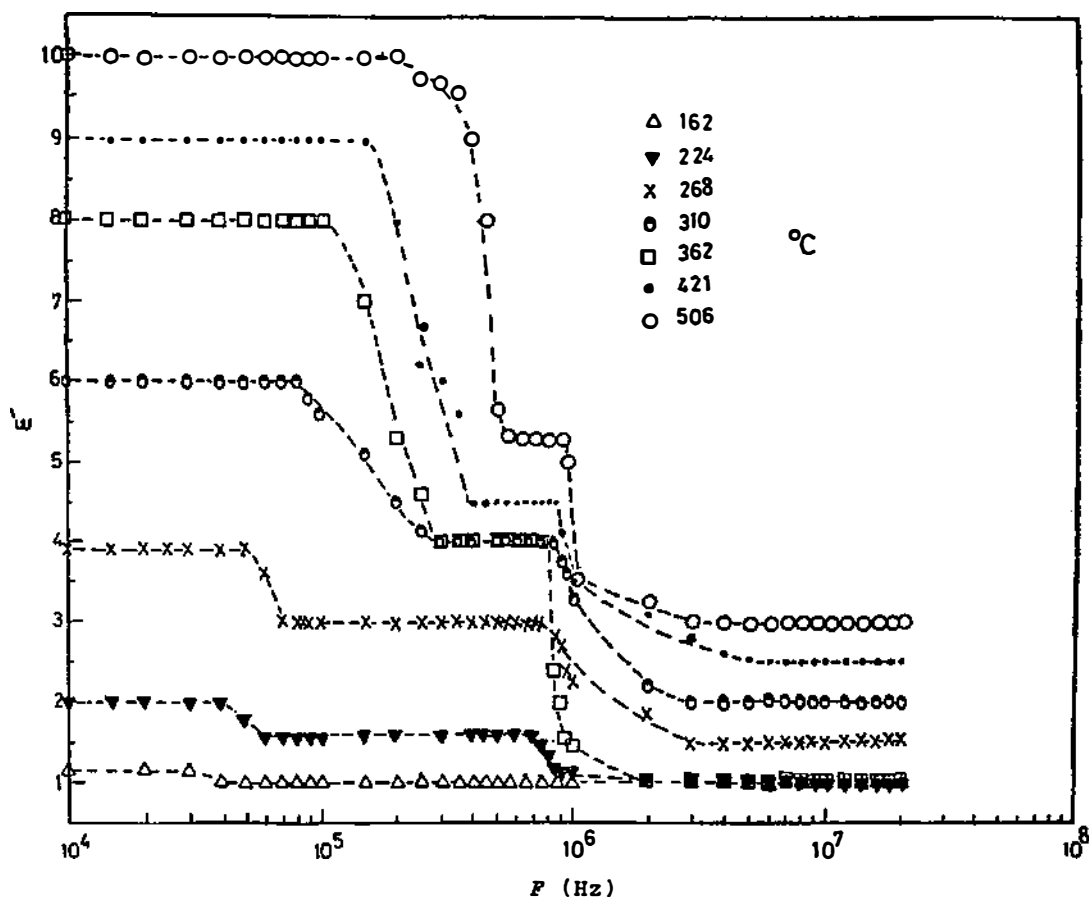Cole and Cole[8] showed that if a dielectric system has a distribution of relaxation times then the complex plane locus, obtained by plotting ε'' versus ε', is gene-

Fig. 1. The frequency dependence of the real part of the dielectric constant ε' at different temperatures for $CuTlTe_2$.

rally an arc of a circle intersecting the abscissa axis at the values ε_∞ and ε_s and having its center lying below the abscissa axis, where ε_s and ε_∞ are the static and optical dielectric constants, respectively. The diameter drawn through the center from ε_∞ makes an angle $\alpha\,\pi/2$ with the ε' axis; then $(\alpha\,\pi/2)$ being determined from the plots and α is calculated. Knowing α, one can determine the macroscopic relaxation time τ_0 by using the relation[8]

$$V/U = (\omega\,\tau_0)^{1-\alpha} \qquad (1)$$

where V is the distance on the Cole-Cole diagram between ε_s and the experimental point; U is the distance between that point and ε_∞, and ω is the angular frequency. The parameter α is equal to zero when the dielectric has only one relaxation time
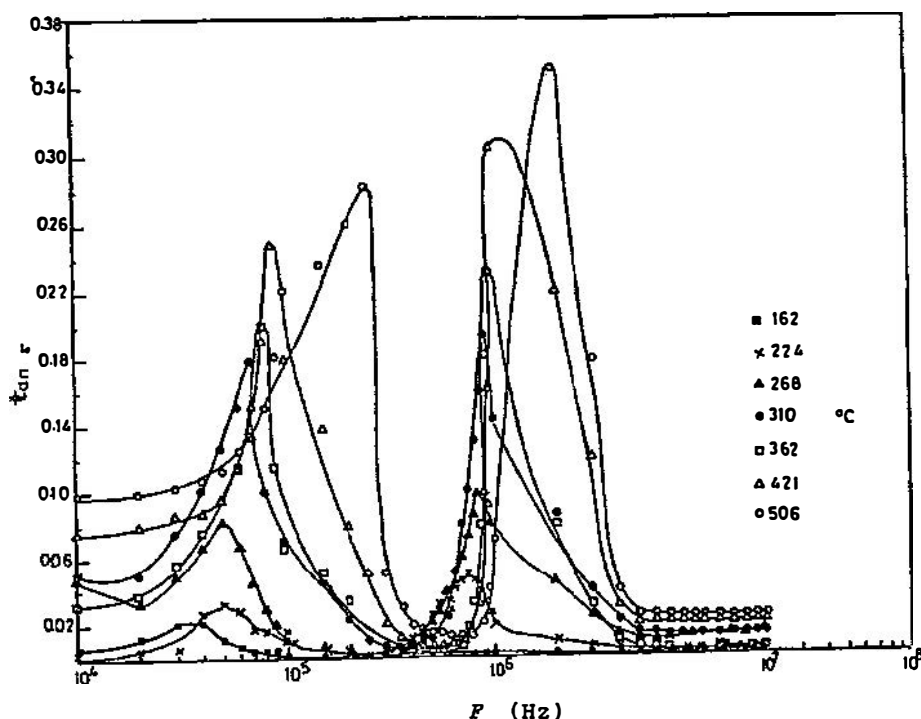
Fig. 2. The frequency dependence of tan (loss angle) δ at different temperatures for CuTlTe$_2$.

and the larger α the larger is the extent of the distribution of relaxation times $(0 < \alpha < 1)$.

The molecular relaxation time (τ) can be estimated from τ_0 using[9]

$$\tau = \tau_0 \frac{2\varepsilon_s + \varepsilon_\infty}{3\varepsilon_s}. \tag{2}$$

Cole-Cole diagrams for different temperatures for the high frequency peak are shown in Fig. 3 and the estimated values of ε_s, ε_∞, α, τ_0 and τ are indicated in Table 1. The data show that the molecular relaxation time decreases with temperature while the static dielectric constant increases.

5. Activation energy for dipole relaxation

Eyring[10-12] has shown that the molecular relaxation time is given by

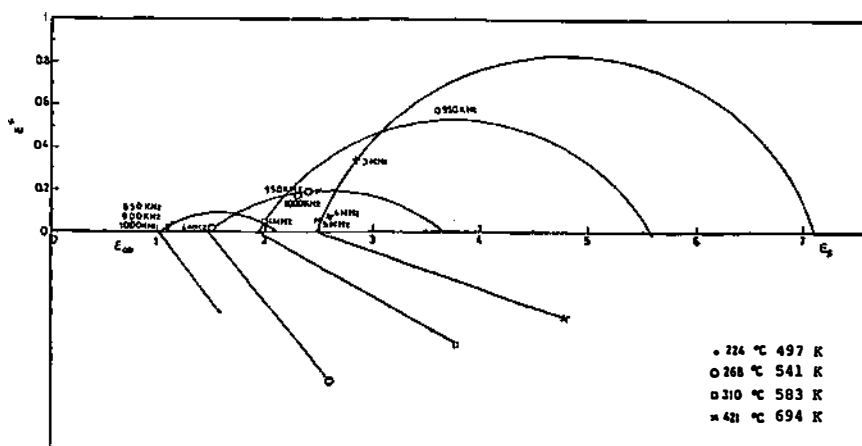$$\tau = \left(\frac{h}{KT}\right) \exp\left(\frac{\Delta F}{RT}\right) \tag{3}$$

Fig. 3. Cole-Cole plots at 224 °C, 268 °C, 310 °C and 421 °C for $CuTlTe_2$.

TABLE 1.

Temperature (K)	ε_s	ε_∞	α	Macroscopic relaxation time τ_0 (s), Eq. (1)	Molecular relaxation time τ (s)		Free energy of activation (k J/mole) ΔF
					Cole-Cole, Eq. (2)	$\tau = \dfrac{1}{\omega_m}$	
497	2.12	1.02	0.59	1.6×10^{-5}	1.32×10^{-5}	2.1×10^{-7}	60.39
541	3.68	1.48	0.55	3.2×10^{-7}	2.56×10^{-7}	1.87×10^{-7}	65.55
583	5.76	1.94	0.33	2.0×10^{-7}	1.56×10^{-7}	1.77×10^{-7}	70.73
694	7.12	2.48	0.21	4.8×10^{-7}	3.76×10^{-7}	1.38×10^{-7}	83.77

The values of the static dielectric constant, the optical dielectric constant, the distribution parameter, the macroscopic and molecular relaxation times and the free energy of activation deduced from the high frequency dispersion peak.

where ΔF is the free energy of activation for dipole relaxation, K is Boltzmann's constant and h is Planck's constant. Therefore, the free energy of activation can be calculated from

$$\Delta F \text{ [kJ/mole]} = 2.303 \, RT \log (\tau \, TK/h). \tag{4}$$

The calculated value of ΔF at different temperatures are shown in Table 1. The data show that ΔF increases with the temperature.
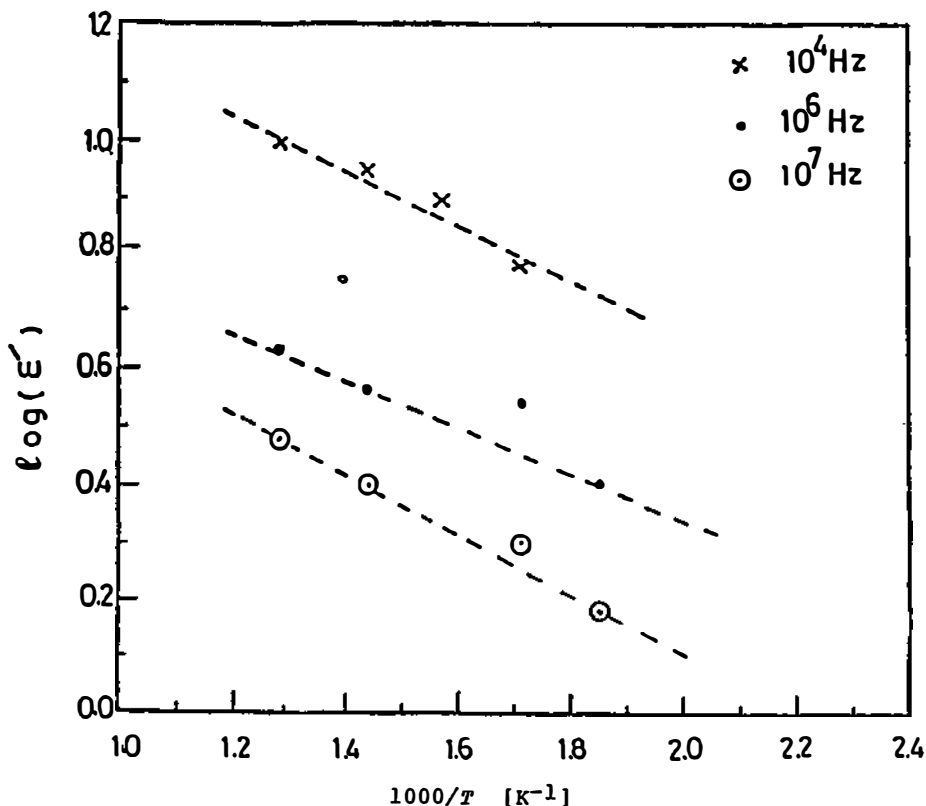
Fig. 4. Temperature dependence of log ε' at different frequencies.

6. Discussion

Fig. 1 shows that the dielectric constant (ε') increases with the temperature, the rate of increase being different at different frequencies. This indicates that the system exists in the form of molecular dipoles, as the temperature increases the relative influence of the molecular interaction energy decreases with respect to that of the thermal energy and the dipoles slowly get activated and attain freedom of rotation.

The existence of multi-relaxation times can be investigated by plotting Cole-Cole diagrams as shown in Fig. 3. It is clear from Fig. 3 that ε'' versus ε' curves represent the arcs of circles having their centres lying below the abscissa axis which confirms that there exists a distribution of relaxation times in the material. By measuring the angle $\alpha \pi/2$ and using Eqs. (1) and (2) and Cole-Cole diagrams (Fig. 3) the values of α, ε_s, ε_∞, τ_0 and τ have been calculated and are presented in Table 1.

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According to the Debye theory the curves tan δ versus ω must be symmetrical. Fig. 2 does reveal that the curves are nearly symmetrical around ω_m, where ω_m corresponds to the maximum absorption

$$\omega_m = \frac{1}{\tau} \tag{5}$$

where τ is the most probable value of a spread of relaxation times. The values of τ calculated from Eq. (5) are inserted in Table 1. From Table 1 it is clear that there is a close proximity in the values of relaxation times determined from Cole-Cole diagrams and those obtained by using Eq. (5). This is to be expected because both methods provide an average or most probably value of τ. Moreover, the molecular relaxation time τ decreases on increasing the temperature, and the rate of decrease is faster in the liquid phase than in the solid phase. This may be attributed to the effect of thermal energy, which tends to weaken the forces of intermolecular interaction.

In general, dielectric relaxation does not follow exactly Debye's equations and is often represented by the Cole-Cole equation[9,13]

$$\varepsilon^* = \varepsilon' - i\,\varepsilon'' = \varepsilon_\infty + \Delta\varepsilon'/[1 + (i\,\omega\,\tau_0)^{1-\alpha}] \tag{6}$$

where $\Delta\varepsilon'$ is the magnitude of the dielectric dispersion. The height of the loss peaks should represent the density of the corresponding dipoles,

$$(\tan\delta)_{max} \sim \left(\frac{N\,\mu^2}{\varepsilon\,\varepsilon_0\,KT}\right), \tag{7}$$

where N is the number of dipoles per unit volume and μ is the dipole moment. Therefore, the observed increase in the height of the loss peak with temperature suggests an increase in the density of the dipoles. The measured dielectric loss data can be adequately interpreted in terms of the theory developed by Elliott[16] for ac conductivity and dielectric loss in chalcogenide glasses. This theory is based on the charged defect concept suggested by Mott et al.[14,15] in which dangling bonds can exist in paired states ($D^+ D^-$) and are responsible for the density of states in the gap pinning the Fermi level. Elliott's theory[16] considers hopping of carriers between two sites over a barrier separating them, and the distribution of relaxation times for this process arises from the exponential dependence of the relaxation time on the barrier height. The hopping species was considered to be the doubly occupied bipolaron state[15,17] and the defect states were assumed to be sufficiently close (intimate valence alternation pairs) that appreciable interaction occurs, thereby giving rise to a distribution of barrier heights separating them. Carriers are ejected from a D^- site into one of the excited levels and then drop into the D^+ centre, converting it to a D^-.

The theory predicts a dielectric loss peak when $\omega\,\tau_{max} \approx 1$, and the ac conductivity is given by the formula[16]

$$\sigma(\omega) = \frac{\pi^2\,N^2\,\varepsilon'}{24}\left(\frac{8e^2}{\varepsilon'\,W_M}\right)^6\left(\frac{\omega^s}{\tau_0^\beta}\right) \tag{8}$$

where W_M is the energy required to take two electrons from the D^- state to the continuum (the conduction band) in the absence of a nearby D^+ centre, τ_0 is the effective relaxation time, N the concentration of localized sites, ε' the bulk dielectric constant,

$$\beta = 6KT/W_M \quad \text{and} \quad S = 1 - \beta.$$

According to the theory the *ac* conductivity has a slightly sublinear frequency dependence and W_M is given by

$$W_M = B - W_1 + W_2$$

where B is the band gap of the material, and W_1 and W_2 are approximately the distortion energies associated with the neutral D^0 and D^+ states, respectively.

Following Elliott's assumption that $W_1 = W_2$ as a first approximation, then $W_M = B = 0.32 \text{ eV} = 2E_a$ measured from the slope of the temperature dependence of the *dc* electrical conductivity[19]. Eq. (8) can be used to calculate the density of defects N at different temperatures using the experimental values of ε', ω and $\sigma(\omega)$ where the *ac* conductivity was calculated directly from the experimental data using[18]

$$\sigma_{ac}(\omega) = \frac{\omega\, C \tan \delta}{1 + (\tan \delta)^2} \frac{1}{A} (1 - 2D_0 \tan \delta)$$

where C is the sample capacitance, $\dfrac{1}{A}$ is the geometric factor, D_0 is a correction factor[18]. Table 2 gives representative data for the estimated values of N calcu-

TABLE 2.

T (K)	N (m^{-3})
497	5.56×10^{19}
541	5.16×10^{20}
583	1.74×10^{21}
694	$1.8 \ \times 10^{21}$

The calculated values of the spatial density of charged defects at different temperature.

lated at different temperatures and at the loss peak $(\tan \delta)_{max}$. From Table 2 it is clear that the density of defects N increases with the temperature, moreover the deduced values of the spatial density of defects N are similar in magnitude with estimates for other semiconductor materials[16].

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STUDIJ DIELEKTRIČNE RELAKSACIJE SPOJA CuTlTe$_2$ U ČVRSTOJ I TEKUĆOJ FAZI

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Izvršena su mjerenja dielektričnih svojstava spoja CuTlTe$_2$ u čvrstoj i tekućoj fazi u širokom intervalu frekvencija (10^4 do 10^7 Hz) na različitim temperaturama (165 do 506 °C). Spoj pokazuje dielektričnu disperziju a opažena su i dva maksimuma kod određivanja tan δ u ovisnosti o frekvenciji. Krivulje log ε' u ovisnosti o temperaturi, zatim ε' i tan δ u ovisnosti o frekvenciji direktno pokazuju postojanje relaksacije tipa Debye-a sa širokom raspodjelom relaksacijskih vremena.