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DIELECTRIC RELAXATION AND ELECTRICAL CONDUCTION IN LIQUID SELENIUM AND Se -Tl -S ALLOYS

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Original scientific paper

Measurements of the dielectric properties of liquid selenium and Se-Tl-S alloys were carried out at different frequencies and temperatures. It was found that the frequency at the maximum dielectric loss shifts towards high frequencies and increasing temperature. The dielectric relaxation activation energy was calculated and correlated with the electrical conduction activation energy.

1. Introduction

Much time and research have been devoted to understanding the electronic relaxation phenomena in amorphous and liquid semiconductors. One of the most interesting features of electrical conduction in glasses is that conduction is usually accompanied by dielectric relaxation. Recently, it was found a quantitative relation between the electrical conduction and dielectric relaxation irrespective of composition and conduction mechanism, ionic or electronic[1-3]. However, in liquid state such a correlation was not yet investigated. Therefore, simultaneous measurements of the dielectric properties and the electrical conductivity of liquid semi-

conductors allow to obtain information about the mechanism of the dielectric relaxation.

In the present contribution, the dielectric properties and the electrical conductivity of liquid selenium and its alloys with thallium and sulphur are investigated in a wide range of temperatures and frequencies.

2. *Experimental procedure*

Meausurements of the dielectric constant were carried out at different frequencies using an ac bridge connected according to Schering-principle (Fig. 1), where a sensitive oscilloscope was used as a null indicator.

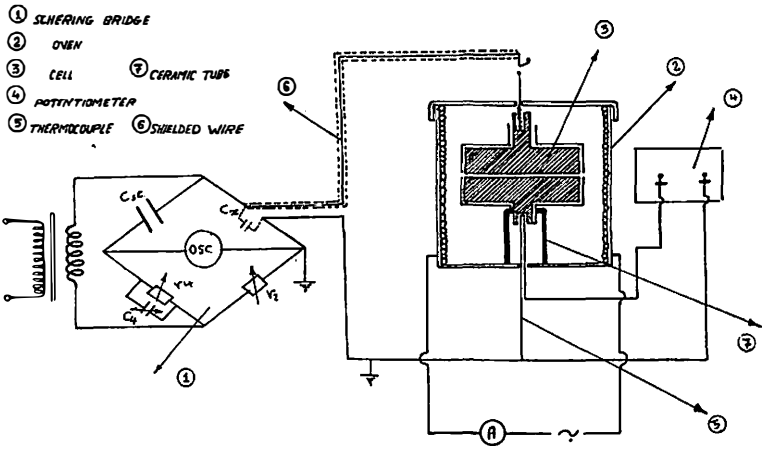

Fig. 1. Experimental arrangement and Schering bridge.

The samples were prepared from highly pure elements (99.999 %) and two Se-Tl-S alloys were prepared with the following composition (atom. %):

	Se	Tl	S
System (1)	54.2	3.3	42.5
System (2)	66	8.1	25.9

The synthesis of the samples was carried out under high vacuum in silica tubes at 450°C for more than 6 hours. Then the tubes were quenched in air at room temperature to obtain the samples in a glassy state. The solid glassy material is than heated in inert atmosphere untill it melts and then transferred to the measuring cell. The cell was made from ceramic material and fitted with graphite electrodes, the spacing between the electrodes is 0.1 mm.

Measurements of the electrical conductivity in the liquid state were carried out in the measuring cell, using a dc stabilized power supply (0—300 volt), a sensitive voltmeter and a sensitive galvanometer capable of measuring currents as low as 10^{-9} Ampere.

3. *Experimental results*

The frequency dependence of the dielectric constant ε' for liquid selenium at different temperatures is shown in Fig. 2. Typical dielectric dispersion curves were obtained, the frequency at the maximum dielectric loss f_m shifts towards high frequencies on increasing temperature. Fig. 3 and 4 show the frequency dependence of the dielectric constant ε' for Se-Tl-S liquid alloys. The dielectric constant varies with the frequency in a stair case manner and three loss peaks are observed. The

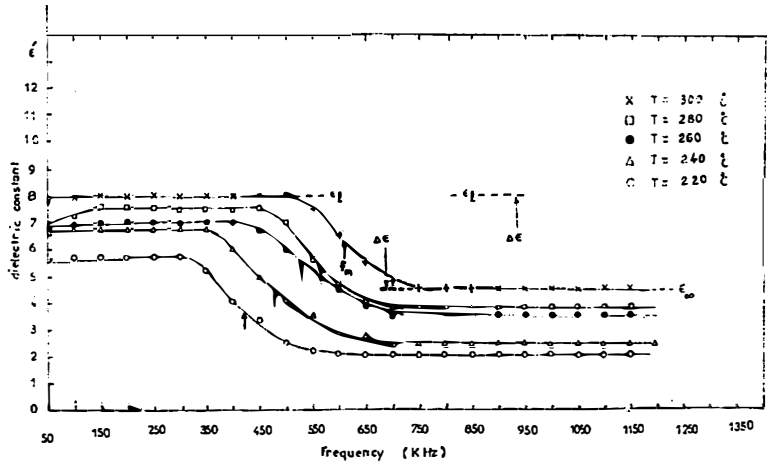

Fig. 2. Frequency dependence of the dielectric constant ε' for liquid selenium at different temperatures.

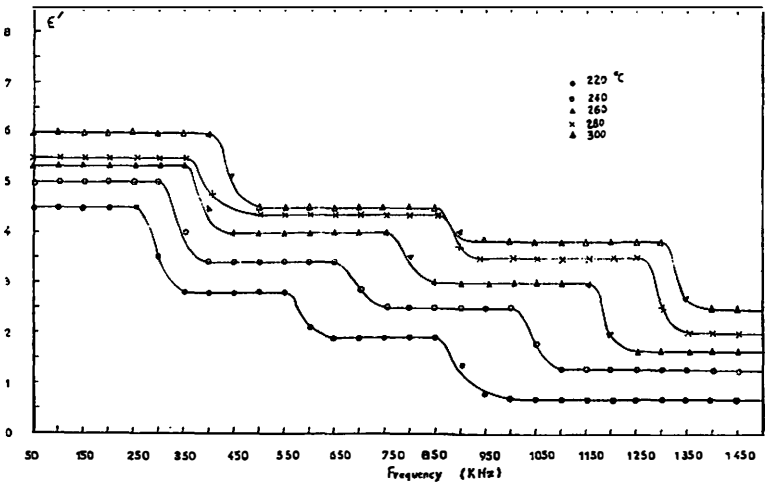

Fig. 3. Frequency dependence of the dielectric constant ε' for liquid $Se_{0.542}\ Tl_{0.033}\ S_{0.425}$ at different temperatures.

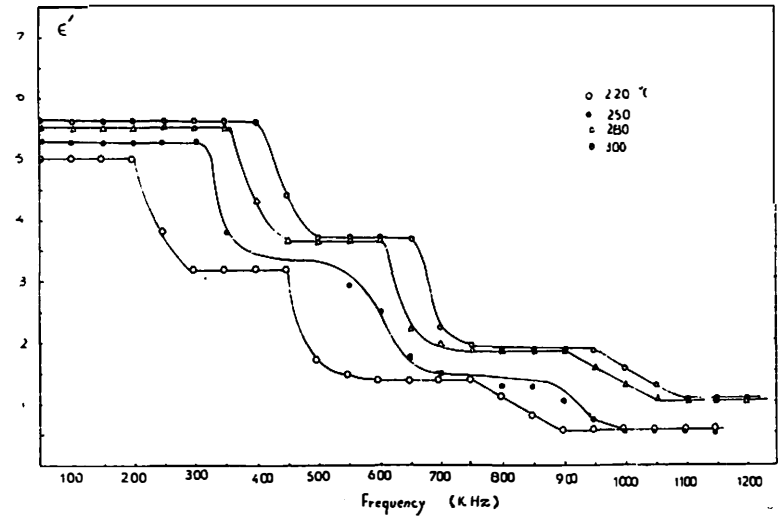

Fig. 4. Frequency dependence of the dielectric constant ε' for liquid $Se_{0.66}$ $Tl_{0.081}$ $S_{0.259}$ at different temperatures.

location of the first (f_{m1}) is close but lower than that of pure selenium, while the third one is close to that of pure sulphur (Fig. 5). The frequencies at the first f_{m1}, second f_{m2} and third f_{m3} loss peaks shifts towards high frequencies on increasing temperature.

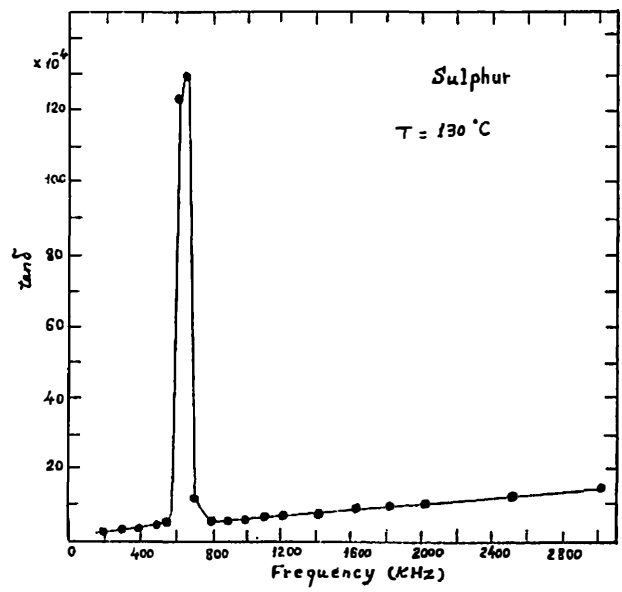

Fig. 5. Frequency dependence of the dielectric loss for liquid sulphur at 130 °C.

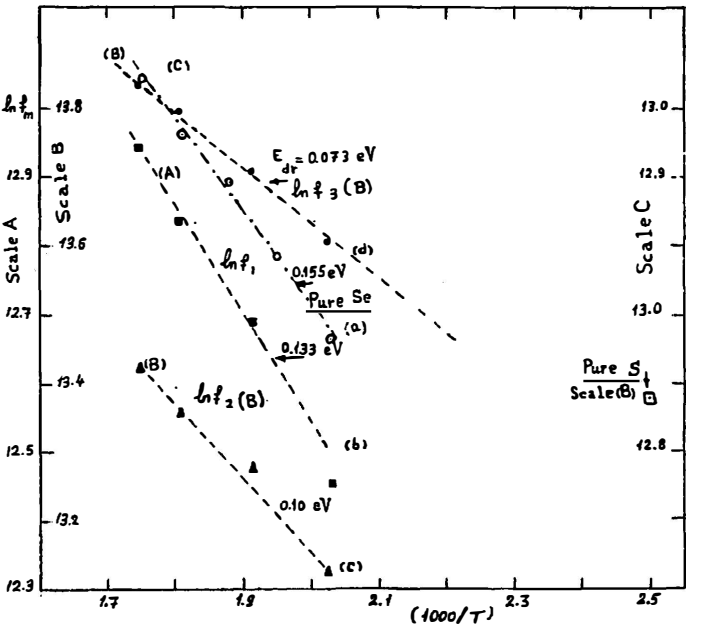

Fig. 6. Temperature dependence of the dielectric loss peak frequency f_m for liquid curve (a) selenium and for liquid $Se_{0.66}$ Tl_{081} $S_{0.259}$ curves (b, c, d).

The temperature dependence of the dielectric relaxation spectra for pure selenium and Se-Tl-S alloys are plotted as $\log f$ versus $1/T$ in Figs. 6 and 7. The los-

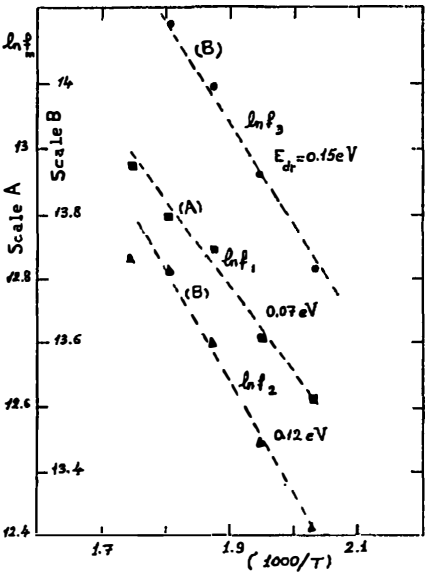

Fig. 7. Temperature dependence of the dielectric loss peak frequency f_m for liquid $Se_{0.542}$ $Tl_{0.033}$ $S_{0.425}$.

ses are linear within the observable temperature and frequency range, so the temperature dependence of the relaxation spectrum may be written as

$$f_m = f_{m0} \exp(-E_{dr}/kT)$$

where E_{dr} is the activation energy of the dielectric relaxation. The calculated values of the activation energy E_{dr} for each loss peak are shown in Table 1.

TABLE 1

System	E_{dr} (eV)			E_σ (eV)		f_{m1} (kHz) at 280 °C
	for f_{m1}	for f_{m2}	for f_{m3}	above 450 C	between 240—540 °C	
Liquid Se	0.155			1.6	0.54	575
System (1)	0.07	0.12	0.15	1.2	0.7	400
System (2)	0.133	0.101	0.073	0.7	0.5	375

The activation energy of the dielectric relaxation E_{dr} and the electrical conductivity E_σ for liquid selenium and Se-Tl-S alloys

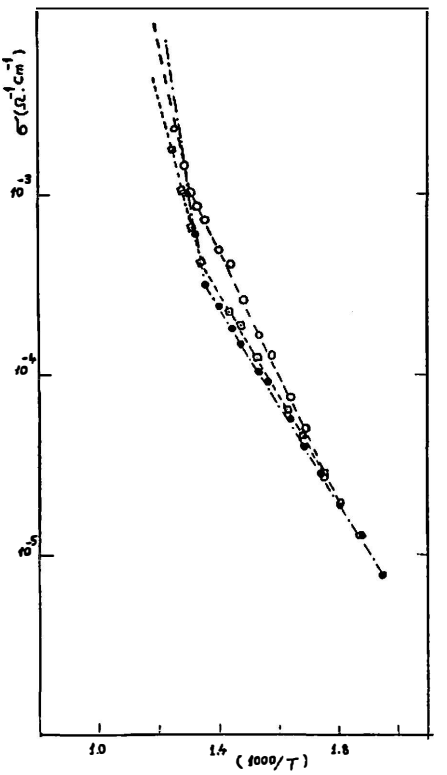

Fig. 8. Temperature dependence of the electrical conductivity of liquid selenium and Se-Tl-S alloys:
● Liquid selenium, ⊙ $Se_{0.542}$ $Tl_{0/033}$ $S_{0.425}$, □ $Se_{0.55}$ $Tl_{0.081}$ $S_{0.259}$

The temperature dependence of the electrical conductivity ($\log\sigma$ vs. $1/T$) for pure selenium and Se Tl S alloys are shown in Fig. 8. Two rectilinear parts are shown with different activation energies. The values of the activation energy for the electrical conductivity E_σ in the liquid state are shown in Table 1. The value of E_σ for liquid selenium is in good agreement with that measured by Gobrecht et al.[4] ($E_\sigma = 1.7$ eV).

4. *Discussion*

First, special attention should be given to the observed linear relations between $\log\sigma$ vs. $1/T$ and $\log f_m$ vs. $1/T$, which suggest a close correlation between the electrical conduction and dielectric relaxation. For a dielectric material the total induced charge accumulated per unit electrode area and unit interelectrode distance at an applied field $\mathscr{E}$, for any particular polarization is

$$Q = \varepsilon_0 \, \Delta\varepsilon \, \mathscr{E} \tag{1}$$

where ε_0 is the permittivity of free space and $\Delta\varepsilon$ is the magnitude of the dielectic dispeision $\Delta\varepsilon = \varepsilon_l - \varepsilon_\infty$, and ε_l, ε_∞ are the dielectric constants at frequencies lower and higher than the frequency range where any dielectric dispersion takes place, assuming τ_m is an average relaxation time ($\tau_m = 1/2\,\pi\,f_m$) of charge carriers for related polarization, therefore, the average electrical conductivity σ_{av} will be

$$\sigma_{av.} = Q/\tau_m \mathscr{E} = 2\,\pi\,\Delta\varepsilon\, f_m. \tag{2}$$

From Eq. 2 it is clear that any polarization should be accompanied by electrical conduction and the corresponding dielectric loss, even if any of them is nondetected.

Namikawa[5] had shown that for thermally activated relaxation mechanism of migration loss in amorphous solids

$$f_m = f_{m0} \exp(-E_{dr}/kT) \tag{3}$$

where E_{dr} is he apparent activation energy of dielectric polarization. Moreover, a similar relation is valid for the electrical conductivity

$$\sigma = \sigma_0 \exp(-E_\sigma/kT) \tag{4}$$

with $E_{dr} \cong E$. Namikawa had found that

$$f_m\,(\mathrm{Hz})/\sigma\,(\Omega^{-1} \cdot \mathrm{cm}^{-1}) = (5 - 30) \times 10^{10}. \tag{5}$$

Furthermore, Tomozawa[6] had derived a more accurate relation between the dielectric loss peak frequency f_m and the dc conductivity σ_{dc}

$$f_m = \frac{1}{2\pi}\left(\frac{\sigma_{dc}}{\varepsilon_0\,\varepsilon_\infty + 1/2\,\varepsilon_0\,\Delta\varepsilon\,\{1 - \cos(\pi\,a/2)\,[1 + \sin(\pi\,a/2)]\}}\right) \tag{6}$$

where α is a constant parameter ranging between zero to 1 in the Cole-Cole's dielectric relaxation equation[7]

$$\varepsilon^* = \varepsilon' - j\,\varepsilon'' = \frac{\Delta\varepsilon'}{1+(j\omega\tau_0)^{1-\alpha}} + \varepsilon_\infty \tag{7}$$

where τ_0 is the most probable relaxation time.

For $\alpha = 0$, Eq. (6) becomes

$$f_m = \frac{1}{2\pi}\frac{\sigma_{dc}}{\varepsilon_0\,\varepsilon_\infty}. \tag{8}$$

In the present work, linear plots of $\log f_m$ vs. $\frac{1}{T}$ and $\log\sigma$ vs. $\frac{1}{T}$ were obtained, however the activation energy values E_{dr} and E_σ are different, and the ratio $f_m/\sigma \cong$ $\cong 4 \times 10^{10}$ which lies close to the lower limit of relation (5). The difference between E_{dr} and E_σ may be explained if we assume that some of the charge carriers are localized and cannot contribute to the electrical conductivity. Such localized carriers may arise by submicroscopic heterogenity of the liquid sample. Moreover, other dielectric relaxation mechanisms which may act in this frequency range should be considered, the easy saturation of the polarization at higher frequencies leads us to conclude that jumping polarization takes place, which is due to the jumping of charge carriers from one site to some nearest-neighbour site in the direction of the applied field over the potential barrier in an average time τ_m. Moreover, the presence of heterogenities in the liquid samples which may be attributed to internal structural effects such as microscopic fluctuations in density or other effects, will act as a physical barrier that inhibits charge migration and charges pile up at the barrier producing a localized polarization of the material (space charge or interfacial polarization).

Maxwell-Wagner-Sillars theory[8-10] shows that, if the heterogenities are in the form of small particles of average conductivity σ_2 and permittivity ε_2 in a matrix of conductivity σ_1 and permittivity ε_1, and the phase boundary between the particles and the matrix serves as a barrier to charge migration, the frequency at peak loss is

$$f_m = 1/2\,\pi\,\tau_m = \frac{\sigma_2}{2\,\pi\,[\varepsilon_1'\,(\lambda-1)+\varepsilon_2']\,\varepsilon_0} \tag{9}$$

where λ is a parameter which depends on the dimensions and the concentration of heterogenities. It is clear from Eq. (9) that f_m decreases with λ, this may explain the downward shift of f_{m1} for selenium and f_{m3} for sulphur in the composite alloy system with respect to their values for pure selenium and sulphur.

Several investigators had established for liquid selenium[11] and liquid sulphur[14] that a chain structure is preserved with a strong temperature dependence. The upward shift of f_m with temperature may be attributed to the effect of temperature on the chain lenght of the molecules. The average chain length becomes shorter with increasing temperature[13-14] and smaller molecules are formed and a smaller relaxation time is involved. Moreover, it is known that thallium atoms tend to termi-

nate the chain length of selenium molecules[11], naturally the number of terminated chains will increase with thallium concentration and this is another additional factor that may explain the decrease of f_{m1} with thallium concentration (Table 1).

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DIELEKTRIČNA RELAKSACIJA I ELEKTRIČNA VODLJIVOST U TEKUĆEM SELENU I Se-Tl-S LEGURAMA

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Izvedena su mjerenja dielektričnih osobina tekućeg selena i S-Tl-S legura na različitim frekvencijama i temperaturama. Nađeno je da se frekvencija najvećeg dielektričnog gubitka pomiče naviše sa temperaturom. Izračunata je aktivaciona energija dielektrične relaksacije i stavljena u vezu sa aktivacionom energijom električne vodljivosti.