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# Photoconductivity studies of gallium sesquisulphide single crystals

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**Abstract.** Photoconductivity studies were carried out on  $\text{Ga}_2\text{S}_3$  single crystals prepared from melt. We studied the effect of light intensity, applied voltage, and ambient temperature on both the spectral distribution of photoconductivity and the lifetime of carriers. We found that the mode of the spectral characteristics was practically independent of the light intensity and applied bias voltage, but shifted to higher values of the photocurrent with increase light intensity and applied bias voltage. It was also noticed that the photocurrent decreases with the increase of temperature up to 200 K and increases above this temperature. The  $(E_g-T)$  behaviour was in agreement with behaviour described by the Varshni equation; its constant was found to be  $\alpha = 6.021 \times 10^{-4} \text{ eV K}^{-1}$ ,  $\beta = -167 \text{ K}$  and the temperature coefficient  $dE_g/dT = -5.33 \times 10^{-4} \text{ eV K}^{-1}$ . It was shown that the lifetime  $\tau$  decreases with an increase of light intensity and applied voltage, increases with a decrease in temperature and, below 200 K, the lifetime decreases with an increase in temperature.

## 1. Introduction

The  $\text{Ga}_2\text{S}_3$  compound is representative of  $\text{A}_2^{\text{III}}\text{B}_3^{\text{VI}}$  imperfect crystals and crystallizes into a wurtzite-type lattice [1]. Every third lattice site in the cationic sublattice of  $\text{Ga}_2\text{S}_3$  is vacant so that defects of the order of  $10^{21} \text{ cm}^{-3}$  concentration are found in these structures [2].

The influence of temperature on the electrical conductivity and Hall effect has been previously investigated [3]. We found the energy gap and the ionization energy to be 2.38 eV and 0.71 eV respectively and also studied the scattering mechanism of the charge carriers.

Experimental results on the fundamental absorption edge of  $\text{Ga}_2\text{S}_3$  single crystal, which were grown by the closed tube chemical transport method, have been described [4]. The measurements were made at a temperature range between 1.6 and 293 K by means of a common technique [5]. The properties of the absorption bands, along with the peak in the reflection spectrum, affirm that the structure observed near the fundamental absorption edge is related to the basic lattice of the  $\alpha$ - $\text{Ga}_2\text{S}_3$  crystal rather than to its defects or deviations from stoichiometric composition, and is of excitonic character.

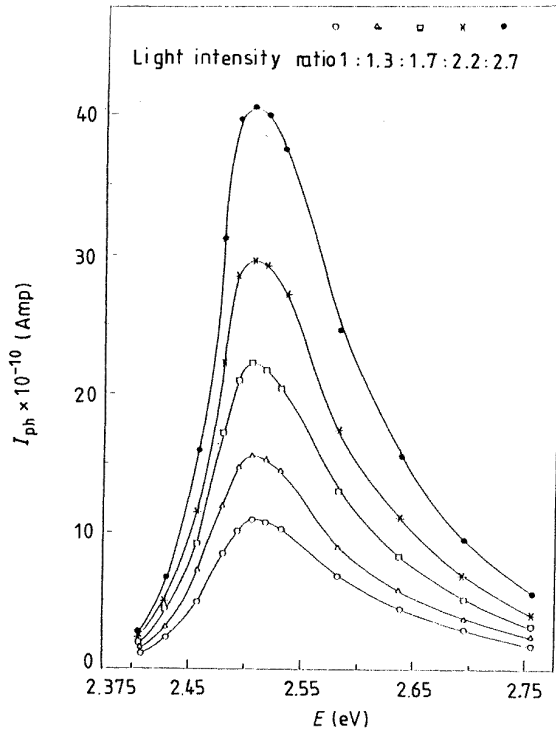
Aono and Kase [6] studied green luminescence of  $\text{Ga}_2\text{S}_3$  crystals and observed that characteristic green emission occurs at 2.38 eV in  $\text{Ga}_2\text{S}_3$  single crystals. In the same work it was stated that the green emission appears also in thermoluminescence. In addition, it was concluded from the results of infrared absorption and photoexcitation measurements, that the emission centre for the green emission band exists at about 0.4 eV above the valence band.

## 2. Experimental details

A new design for crystal growth from melt, using the Bridgman technique, was constricted locally by our group in the solid state laboratory at Aswan Faculty of Science, Egypt.  $\text{Ga}_2\text{S}_3$  single crystals were grown by this technique as previously reported [7]. The DC photoconductivity measurements were considered when a beam of light was perpendicularly incident to the sample surface without a chopper. The chopper controller (type SR540) used in the AC photoconductivity measurements had a square pulse of monochromatic light. The sample was connected in series with a stable DC voltage and a load resistance equal to  $13 \times 10^6 \text{ ohm}$ .

The variation of potential difference across the load resistance due to the modulated photoconductivity was observed on a double beam oscillograph (COS 5020) and measured by an AC value microvoltmeter TM3B (Level Electronic Ltd, England). DC photoconductivity was measured by a Keithley electrometer (610C). The light source was a 1000 W tungsten lamp and a monochromator (MUG11) (C Z Scientific Instruments, England). The product obtained was confirmed by x-ray diffraction carried out in the Central Metallurgical Research and Development Institute (CRMDI) to ensure the proper crystal structure and stoichiometry.

A  $\text{Ga}_2\text{S}_3$  single crystal was prepared in the form of thin mirror-like layers having a rectangular cross section of dimensions  $4.5 \times 1.3 \times 0.2 \text{ mm}^3$ . The sample was fixed in an optical cryostat DN1704 (Oxford Instruments, England) and the temperature of the specimen was maintained at a constant value during each measurement by using a



**Figure 1.** The spectral distribution of the photocurrent for  $\text{Ga}_2\text{S}_3$  at different light intensity ratios.

digital temperature controller (DTC2 Oxford Instruments, England).

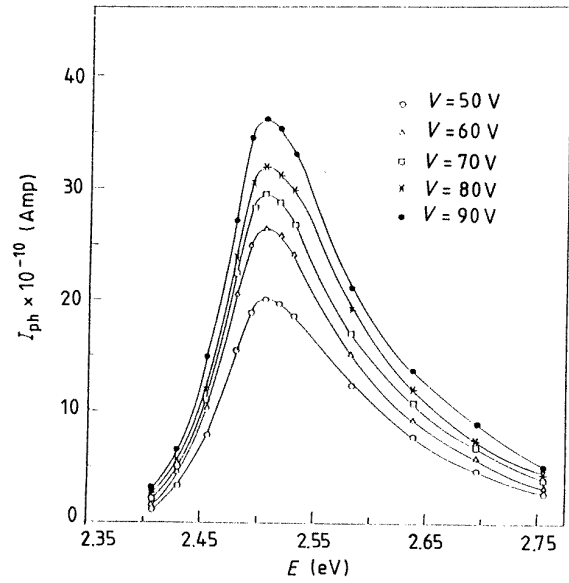
In our experiment we used a luxmeter (type LX-101) for measuring the intensity of the incident light. Also we examined the ohmic nature of the silver paste which was employed as an ohmic contact by recording the  $I$ - $V$  characteristics of the sample in two directions.

In the measurements of the photoconductivity (primary photoconductivity), the values of the dark conductivity were eliminated by subtraction from the total photocurrent.

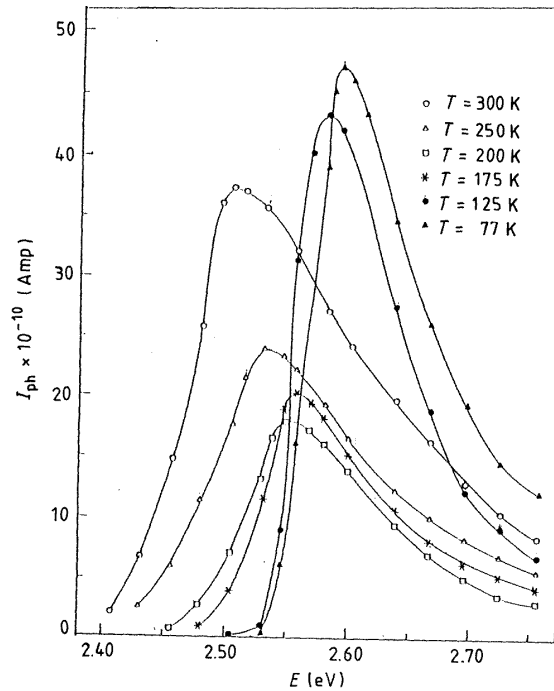
### 3. Results and discussion

Figures 1 and 2 depict the spectral distribution of photoconductivity of p-type  $\text{Ga}_2\text{S}_3$  single crystal in the photon energy range (2.76 to 1.41 eV) at room temperature. The shape of the spectral distribution characteristics was practically independent of the light intensity and applied bias voltage. The peak position shifted toward higher values of the photocurrent with increasing light intensity and applied bias voltage. The photocurrent rises continuously with photon energy, and reaches a certain maximum value at 2.51 eV, then a steep fall is found at high photon energy. The spectral dependence of the photocurrent agreed with previous measurements of the DC photoconductivity of similar compounds [8, 9] from the same group  $\text{A}_2^{\text{III}}\text{B}_2^{\text{VI}}$ .

The absorption coefficient is extremely low at  $h\nu < E_g$  and the excitation involves transition from impurity state to band states. For photon energies larger than the gap, the absorption coefficient increases rapidly. Therefore, the



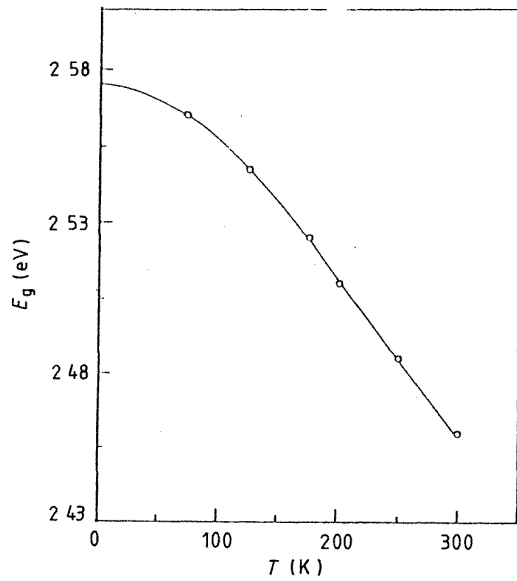
**Figure 2.** The spectral distribution of the photocurrent for  $\text{Ga}_2\text{S}_3$  at different bias voltage.



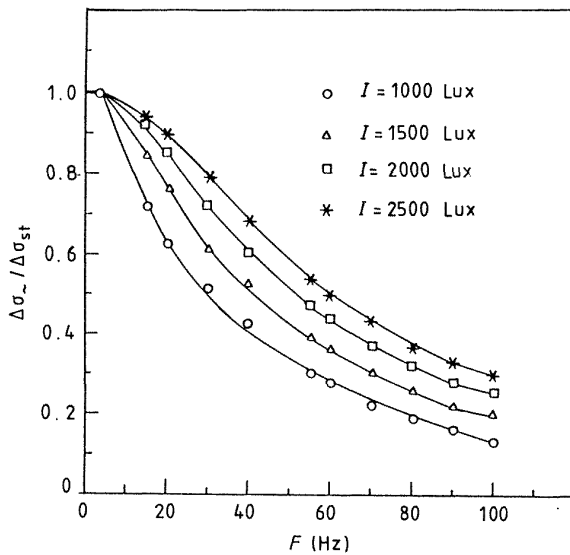
**Figure 3.** The spectral distribution of the photocurrent for  $\text{Ga}_2\text{S}_3$  at different temperatures.

cross section for transitions involving impurities becomes negligible and the dominant transitions are band-to-band transitions.

The effect of temperature on the spectral distribution of the photoconductivity ( $i_{ph}$  versus  $h\nu$ ) of  $\text{Ga}_2\text{S}_3$  single crystal is represented in figure 3. This shows that the position of the maximum photocurrent  $I_{ph}$  tends to shift towards lower values of photon energy when the

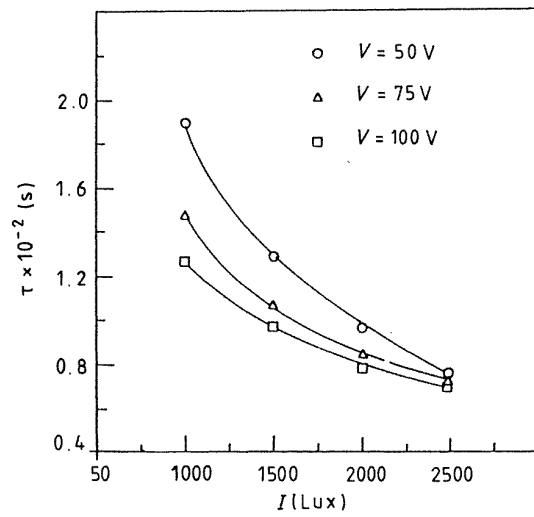


**Figure 4.** Dependence of energy gap on temperature for  $\text{Ga}_2\text{S}_3$  single crystal.

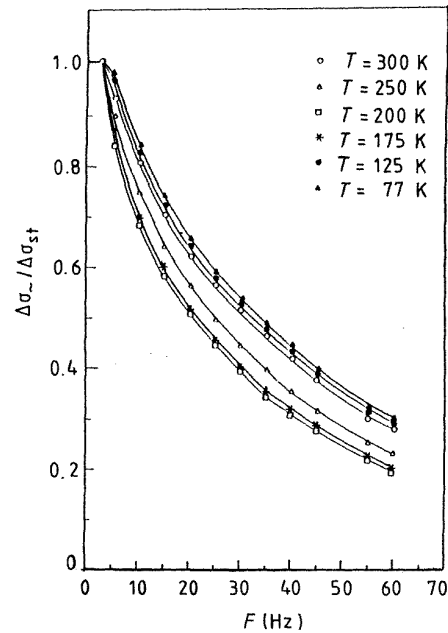


**Figure 5.** The variation of AC photoconductivity of  $\text{Ga}_2\text{S}_3$  with chopping frequency at  $V = 75$  V.

temperature ranges from 77 to 300 K. In the whole photon energy range (2.41–2.76 eV), the peak value of photocurrent spectra decreases until  $T = 200$  K and then increases again at temperatures above 200 K. The decrease of the maximum value from 77 K to 200 K may be due to a trapping process. The energy gap varies with temperature as shown in figure 4. It is observed that the dependence of  $E_g$  on temperature is nonlinear at low temperatures (below 125 K), whereas this dependence is linear up to 125 K and the temperature coefficient  $dE_g/dT$  calculated from the straight line portion was found to have the value  $-5.33 \times 10^{-4} \text{ eV K}^{-1}$ . The variation of energy gap  $E_g$  with



**Figure 6.** Dependence of carrier lifetime on light intensity for  $\text{Ga}_2\text{S}_3$ , at bias voltages of 50, 75 and 100 V.



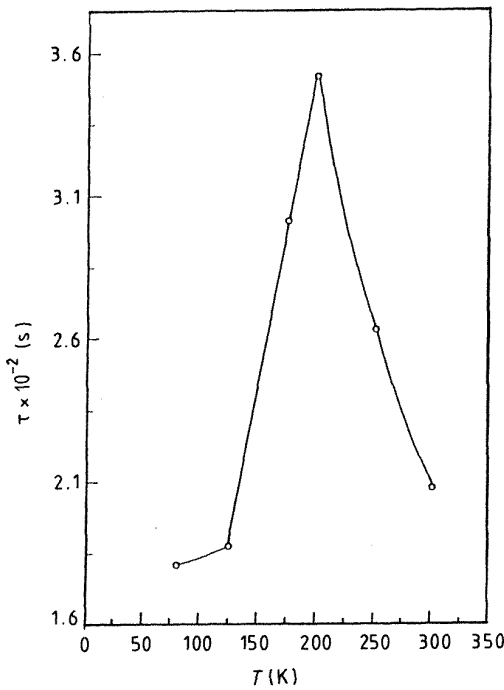
**Figure 7.** The frequency dependence of the photoconductivity of  $\text{Ga}_2\text{S}_3$  at different temperatures.

temperature can be described by Varshni equation [10].

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T - \beta}.$$

The value of  $E_g(0)$ , calculated from a  $(E_g-T)$  plot, was found to be 2.58 eV, and the constants  $\alpha = 6.021 \times 10^{-4} \text{ eV K}^{-1}$  and  $\beta = -167 \text{ K}$ . The gap determined here was estimated by applying the half maximum value [11].

A symmetrical square monochromatic light pulse for photoconductivity excitation was used in the case of AC photoconductivity measurements. The chopper frequency was varied from 3 to 100 Hz. The photoconductivity, as a function of chopping frequency of the modulation of the



**Figure 8.** The relation between carrier lifetime and temperature for Ga<sub>2</sub>S<sub>3</sub> single crystal.

incident light, was registered directly at different values of light intensity. Figure 5 represents the dependence of photoconductivity as a function of chopping frequency  $F$  at bias voltages of 50, 75 and 100 V. From the obtained dependence we observe that the behaviour of the curves in all the figures is similar and they have a general shape in which the photoconductivity decreases with increasing frequency in the whole range of investigated frequencies. The behaviour of these curves obeys the relation [12].

$$\Delta\sigma/\Delta\sigma_{st} = \tanh(1/4F\tau).$$

According to this relation, and making use of such curves, we can derive the lifetime of the carriers at different light intensities. The graphic representation of the relation between the carrier lifetime and light intensity is illustrated in figure 6 at different values of bias voltage. This dependence shows that the lifetime  $\tau$  is inversely proportional to the illumination intensity. The value of  $\tau$  was found to be of the order of  $10^{-2}$  s. In view of the high density of the vacant acceptor levels, photocarriers generated by illumination were captured almost immediately by these

levels. Therefore, phototransport could occur either by jumps between random centres or could involve capture by traps. Thus, we attempted to obtain a suitable interpretation of the diminution dose increase.

The same work was repeated whilst changing the temperature in order to establish the effect of the ambient temperature on the photoconduction behaviour of the Ga<sub>2</sub>S<sub>3</sub> single crystals.

The ratio  $\Delta\sigma/\Delta\sigma_{st}$  decreases with increasing frequency as shown in figure 7. At high chopping frequencies, the photoconductivity ratio decreases more slowly than in the low-frequency range. The effect of temperature on the photoconductivity ratio  $\Delta\sigma/\Delta\sigma_{st}$  is evident from these curves. Starting from room temperature, as the temperature decreases the photoconductivity also decreases. This is clear in the interval 300–200 K. With further cooling ( $T < 200$  K) the conductivity exhibits an unusual and unexpected behaviour when the temperature increases suddenly—the photoconductivity values are then greater than those obtained at room temperature. This was noticed at 125 and 77 K as seen in figure 7. The derivation of the carriers' lifetime leads to figure 8. It can be seen from the curve that  $\tau$  increases with increasing  $T$  up to 200 K and then decreases. This can be accepted only if we consider the trapping processes of the carriers which occur in this temperature range. Consideration of the results shown in figure 3 is also helpful here because in figure 3 we obtain two different modes of variation of the photocurrent—one of which is below 300 K (until 200 K) while the other is below 200 K. These two modes are quite similar to that already obtained in figure 8.

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