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Temperature- and photo-excitation effects on the electrical properties of $\text{Tl}_4\text{Se}_3\text{S}$ crystals

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Abstract

The extrinsic energy states and the recombination mechanism in the $\text{Tl}_4\text{Se}_3\text{S}$ chain crystals are being investigated by means of electrical and photoelectrical measurements for the first time. The electrical resistivity is observed to decrease exponentially with increasing temperature. The analysis of this dependence revealed three impurity levels located at 280, 68 and 48 meV. The photocurrent is observed to increase as temperature decreases down to a minimum temperature $T_m = 200$ K. Below this temperature the photocurrent decreases upon temperature lowering. Two photoconductivity activation energies of 10 and 100 meV were determined for the temperature ranges below and above T_m , respectively. The photocurrent (I_{ph}) versus illumination intensity (F) dependence follows the $I_{\text{ph}} \propto F^\gamma$ law. The value of γ decreases from ~ 1.0 at 300 K to ~ 0.34 at 160 K. The change in the value of γ with temperature is attributed to the exchange of roles between the monomolecular recombination at the surface near room temperature and trapping centers in the crystal, which become dominant as temperature decreases.

1. Introduction

Chain structured compound semiconductors such as TlS, TlSe, TlInSe₂, TlInTe₂ and TlGaTe₂ are promising candidates for photovoltaic and charge accumulating device applications [1–14]. Such types of crystals have attracted the attention of researchers. Tl₂S and Tl₂Se nanorods have been fabricated [15] and charge accumulating cells with a voltage of 2.1 V and a short-circuit current density of 100 mA cm⁻² have been made on the basis of a *p*-TlSe single crystal [16].

Most of the physical properties of the TlSe–TlS crystal system have been investigated. In particular, the x-ray and neutron diffraction, specific heat and dielectric measurements, nuclear magnetic resonance and electron paramagnetic resonance, dielectric sub-millimeter spectroscopy, infrared (IR) spectroscopy, Raman and Brillouin scattering, inelastic neutron scattering, Mossbauer spectroscopy, etc have all been investigated [1–7]. An inclusive review paper on the physical

properties of this system may be found in [2]. However, to our knowledge no articles have been published to report the physical properties of the $\text{Tl}_4\text{Se}_3\text{S}$ crystal which relate to the same system. For this reason, the main purpose of this paper will be to report the dark and light illuminated electrical properties of $\text{Tl}_4\text{Se}_3\text{S}$ crystal.

2. Experimental details

Single crystals of $\text{Tl}_4\text{Se}_3\text{S}$ crystals were grown by the Bridgman method from the stoichiometric melt of the starting materials sealed in evacuated (10^{-5} Torr) silica tubes with a tip at the bottom. The ampule was moved in a vertical furnace through a thermal gradient of 20 °C cm⁻¹, between the temperatures 375 and 150 °C at a rate of 6 mm h⁻¹. The analysis of x-ray diffraction data showed that $\text{Tl}_4\text{Se}_3\text{S}$ crystallized in a tetragonal unit cell, with lattice parameters: $a = 0.7975$ and $c = 0.6926$ nm. Typical dimensions of the crystals suitable for electrical measurements were $\sim 0.5 \times 0.5 \times 0.2$ cm³. Using silver paste, point contacts were fixed

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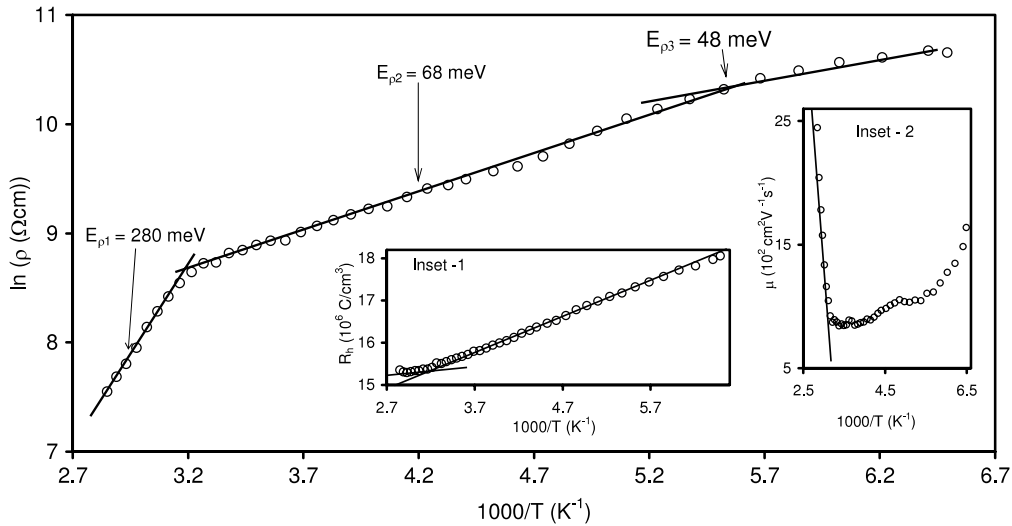


Figure 1. Variation of $\ln(\rho)-T^{-1}$ for $\text{Tl}_4\text{Se}_3\text{S}$ crystals. Insets 1 and 2 show the R_h-T^{-1} and $\mu-T^{-1}$ dependences, respectively.

at the top surface of the sample. The ohmic nature of the contacts was confirmed by the $I-V$ characteristics. The $I-V$ characteristics recorded parallel to the crystal c -axis (along the chain) are found to be linear for low applied voltages. Cooling of the sample was achieved by means of a closed cycle cryostat (Advanced Research Systems) and Lake Shore 340 temperature controller. The dark electrical resistivity and photocurrent were measured using a dc Keithley 6430 SUB-FEMTOAMP remote source/electrometer. The dark electrical resistivity measurements were performed using the Hall bar technique. The illumination was from a halogen lamp. The light intensity was altered by changing the value of the current through the lamp and was calibrated using an IL 1700 radiometer.

3. Results and discussion

For the purpose of investigating the dominant current conduction mechanism and identifying the impurity levels in the $\text{Tl}_4\text{Se}_3\text{S}$ crystals, the temperature dependence of the dark electrical resistivity (ρ_d) was measured in the temperature range of 150–350 K. A general view of the dark resistivity as a function of reciprocal temperature is displayed in figure 1. It is evident from the figure that ρ_d systematically increases upon temperature lowering. The measured data of ρ_d-T dependence is found to follow the relation

$$\rho_d = \rho_0 \exp\left(\frac{E_\rho}{kT}\right), \quad (1)$$

where ρ_0 is the pre-exponential factor and E_ρ is the resistivity activation energy of the crystal. According to equation (1), the slopes of the $\ln(\rho_d)-T^{-1}$ graph (solid lines in figure 1) reveal three different resistivity activation energies of 280, 68 and 48 meV being dominant in the temperature regions of 350–300 K, 290–210 K and 200–150 K, respectively.

Insets 1 and 2 of figure 1 display the Hall coefficient, R_h , and Hall mobility, μ_h , data for the $\text{Tl}_4\text{Se}_3\text{S}$ crystal, being recorded at a magnetic field of 1.4 T. The recorded Hall voltage

was positive, indicating p-type conduction of the samples under investigation. It is clear from inset 1 that the R_h-T^{-1} dependence is very like that of $\rho-T^{-1}$ except that it exhibits only two activation energies of 20 and 70 meV above and below 300 K, respectively. On the other hand, the $\mu_h - T^{-1}$ dependence follows an exponential law just above 300 K. The activation energy, E_μ , calculated from the Hall mobility data using the relation, $\mu = \mu_0 \exp(-E_\mu/kT)$, where μ_0 is the pre-exponential factor, above 300 K is found to be 260 meV. The Hall mobility below 300 K does not follow an exponential behavior, indicating that a more detailed study is required to investigate the scattering mechanism(s) in the crystal. Such a type of study usually needs temperature-dependent carrier concentration data analysis and theoretical fittings of the Hall mobility data. These types of analysis are out of the scope of the current work and will be considered elsewhere.

The numerical values of E_ρ are less than half of the energy band gap, E_g , which is reported as: 0.96 eV for Tl_4S_3 [8], 0.74 eV for $\text{TlSe}_{0.8}\text{S}_{0.2}$ [6], 0.71 and 0.94 eV for TlSe and TlS [2], respectively, reflecting the extrinsic type of conduction. The activation energy of resistivity being 280 meV above 300 K is just the sum of the Hall coefficient (20 meV) and Hall mobility activation energies (260 meV) in that region. The resistivity activation energy of 68 meV is very close to the 70 meV found from R_h data, indicating that such an energy state may be an impurity state.

Photocurrent (I_{ph}) measurements were carried out at different light intensities (F) in the range of 16.8–53.6 mW cm^{-2} in the temperature region of 300–150 K. The electric field was fixed at 4.9 V cm^{-1} . Figure 2 shows representative data of the experimental photocurrent as a function of reciprocal temperature for $\text{Tl}_4\text{Se}_3\text{S}$ crystals at different illumination intensities. The figure illustrates the exponential increment of photocurrent with temperature increase in the range of $150 \text{ K} \leq T < T_m$, where $T_m = 200 \text{ K}$ is the temperature corresponding to the maximum photocurrent value. In the temperature range where $T > T_m$, the photocurrent decreases with the increase of T . It is seen

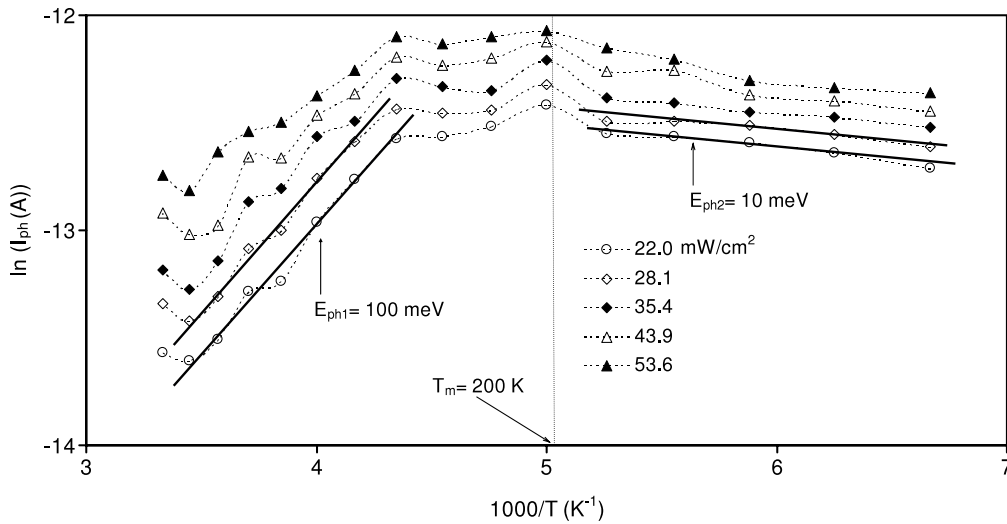


Figure 2. The $\ln(I_{ph})-T^{-1}$ dependence for Tl_4Se_3S crystals.

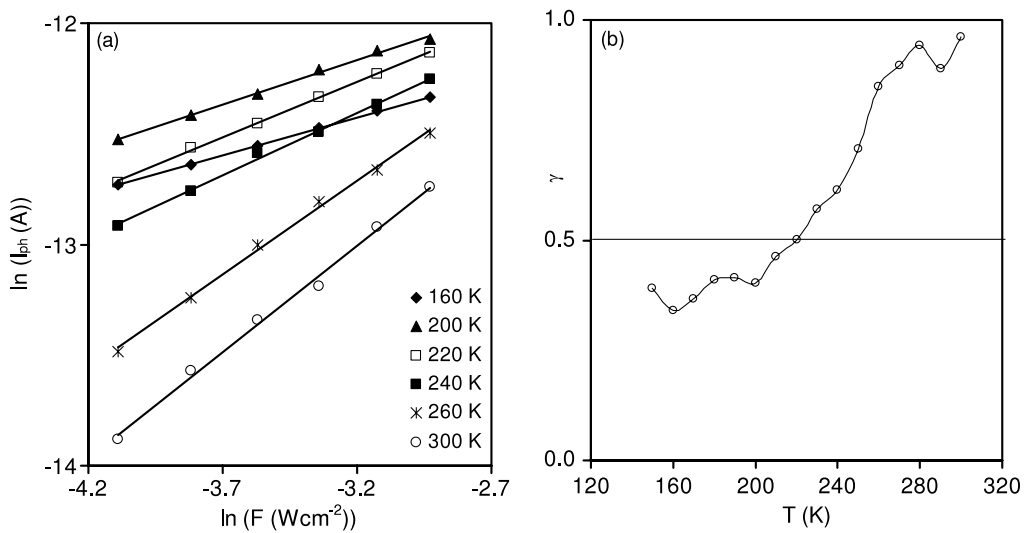


Figure 3. (a) The $I_{ph}-F$ dependence at various temperatures for Tl_4Se_3S crystals. (b) The $\gamma-T$ dependence.

from figure 2 that plots of $\ln(I_{ph})-T^{-1}$ consist of two distinct regions. In the first temperature region, $150\text{ K} \leq T < T_m$, the exponential increase of photocurrent with temperature, in accordance with the expression $I_{ph} \propto \exp(-E_{ph}/kT)$ displays photocurrent activation energy $E_{ph1} = 10\text{ meV}$. In the second region, $T > T_m$, the exponential decrease in photocurrent with temperature according to the relation $I_{ph} \propto \exp(E_{ph}/kT)$ reveals an average photocurrent activation energy of $E_{ph2} = 100\text{ meV}$. These values are different from those found through the dark electrical resistivity analysis as 280, 68 and 48 meV, indicating that the photocurrent originates from energy states which are detectable only under light excitation and can be regarded as recombination centers.

Figure 3(a) illustrates the typical representation of the photocurrent growth as a function of illumination intensity at different temperatures. It is evident from the figure that $I_{ph} \propto F^\gamma$. Generally, γ is observed to vary upon temperature change. The variation of γ with temperature is displayed in

figure 3(b). As shown in this figure, γ sharply decreases from a value of ~ 1.0 at 300 K to a value of 0.34 at 160 K. The behavior is consistent with that of $I_{ph}-T$ dependence.

Similar behavior of temperature-dependent photocurrent was also observed in $GaSe_{0.95}S_{0.05}$, Na mixed crystals [18] and $TlInS_2$ crystals [19]. For these crystals, the photocurrents were also observed to increase with increasing temperature up to critical temperatures of 357 K and 245 K, respectively. Above this temperature, I_{ph} decreases with increasing temperature. This type of variation of I_{ph} with temperature was explained assuming the existence of deep recombination centers and shallow traps [17]. These levels are electron trapping levels located at E_{ct} below the conduction band and hole trapping levels located at E_{vt} above the valence band. The levels are assumed to be in quasi-equilibrium with the corresponding band. In accordance with the above, the $I_{ph}-T$ variation in the Tl_4Se_3S crystal could be explained as follows: at fixed illumination intensity with increasing

temperature the maximum temperature T_m is reached at which the minority carriers (electrons) are thermally reactivated from their trapping level into the extended conduction band, providing additional free electrons. Therefore, these free electrons are easily captured in deep recombination centers where they recombine with free holes. Hence, the lifetime of the majority carriers (holes) are shortened leading to the decrease of the photocurrent, as observed in figure 2.

4. Conclusions

We have studied the dark and photocurrent properties of Tl_4Se_3S chain crystals grown by the Bridgman method in the temperature regions of 150–350 K and 150–300 K, respectively. The Hall effect measurements have shown that the crystals exhibit extrinsic p-type conduction. The dark electrical resistivity and Hall data allowed the determination of activation energy levels as 280, 68/70 and 48 meV, at high, moderate and low temperatures, respectively. The photocurrent analysis revealed the existence of two photoconductivity energy levels of 10 and 100 meV, being dominant at low and high temperatures, respectively. The photocurrent increases with temperature increment up to a maximum temperature of 200 K and thereafter decreases. The illumination intensity dependence of the photocurrent was found to exhibit linear and approximately sublinear characteristics in the studied different temperature regions. These features are indications of recombination mechanism change, which is attributed to the exchange in the role of trapping and recombination centers present in the crystal band gap.

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