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LOW-TEMPERATURE PHOTOLUMINESCENCE SPECTRA OF $TlIn_xGa_{1-x}S_2$ LAYER MIXED CRYSTALS

K.R. Allakhverdiev* and N.M. Gasanly†

Department of Physics, Middle East Technical University, 06531 Ankara, Turkey

and

A. Aydinli

Department of Physics, Bilkent University, 06533 Ankara, Turkey

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Low-temperature photoluminescence spectra of $TlInS_2$, $TlIn_{0.95}Ga_{0.05}S_2$ and $TlIn_{0.8}Ga_{0.2}S_2$ layer crystals were studied in the temperature range 14–220 K. The temperature dependencies of bands 2.374 eV (A), 2.570 eV (E) and 2.576 eV (F) for $TlInS_2$ are interpreted by supposing that the crystal undergoes structural phase transitions. Band A is considered to come from a donor–acceptor recombination channel.

Keywords: A. semiconductors, A. ferroelectrics, D. optical properties, D. phase transitions, E. luminescence.

1. INTRODUCTION

IN THE LAST few years increasing interest has been shown to the study of the luminescence and non-linear properties of the layered crystal $TlInS_2$ [1–4]. A number of luminescence bands have been observed at 1.8 K and they were attributed to the recombination of free and bound excitons [1]. Second harmonic generation at successive phase transitions was reported in [2]. According to [2] a sequence of at least five phase transitions takes place in $TlInS_2$ with decreasing temperature: the transition from the paraelectric phase with $C2/c$ symmetry to the incommensurate phase takes place at $T_{i1} = 216\,K$; ferroelectric phase transition with spontaneous polarization in the layer plane along the second order axis takes place at 200 K. Besides the above mentioned transitions, $TlInS_2$ undergoes additional phase transitions: an incommensurate one at $T_{i2} = 206\,K$, an antipolar one at $T_{c1} = 204\,K$ and a weak ferroelectric one at $T_{c2} = 79\,K$. The transition at $T_{c2} = 79\,K$ was considered as isomorphic [2]. The photoluminescence bands were observed for 2.36 eV (A), 2.5 eV (B), 2.545 eV (D), 2.55 eV (E), 2.554 eV (F) and 2.559 eV (G) at 20 K and for 2.54 eV (C) at 10 K [3]. The temperature dependencies of the intensities of these bands were interpreted by a variation in the crystal structure and the coexistence of several polytypes. The bands D, E, F and G were interpreted as due to excitons and the bands A and B were interpreted as due to non-local lattice defects. Among different thallium chalcogenides the properties of $TlInS_2$ were studied rather extensively [5]. However there are still many controversies regarding the interpretation of its physical properties. The most probable reason for this controversy is that $TlInS_2$ crystallizes in different polytypes [1].

* On leave from the Institute of Physics, Azerbaijan Academy of Sciences, Baku, Azerbaijan.

† On leave from Baku State University, Baku, Azerbaijan.

2. RESULTS AND THEIR INTERPRETATION

In the present paper we report the experimental results of the photoluminescence spectra of undoped $TlInS_2$ crystals excited at different temperatures and excitation intensities. The temperature dependencies of the luminescence spectra of $TlIn_xGa_{1-x}S_2$ mixed crystals for compositions $x = 0.95$ and 0.8 are also reported in the temperature range 14–220 K.

Undoped $TlIn_xGa_{1-x}S_2$ mixed crystals were grown by the modified Bridgman method [6].

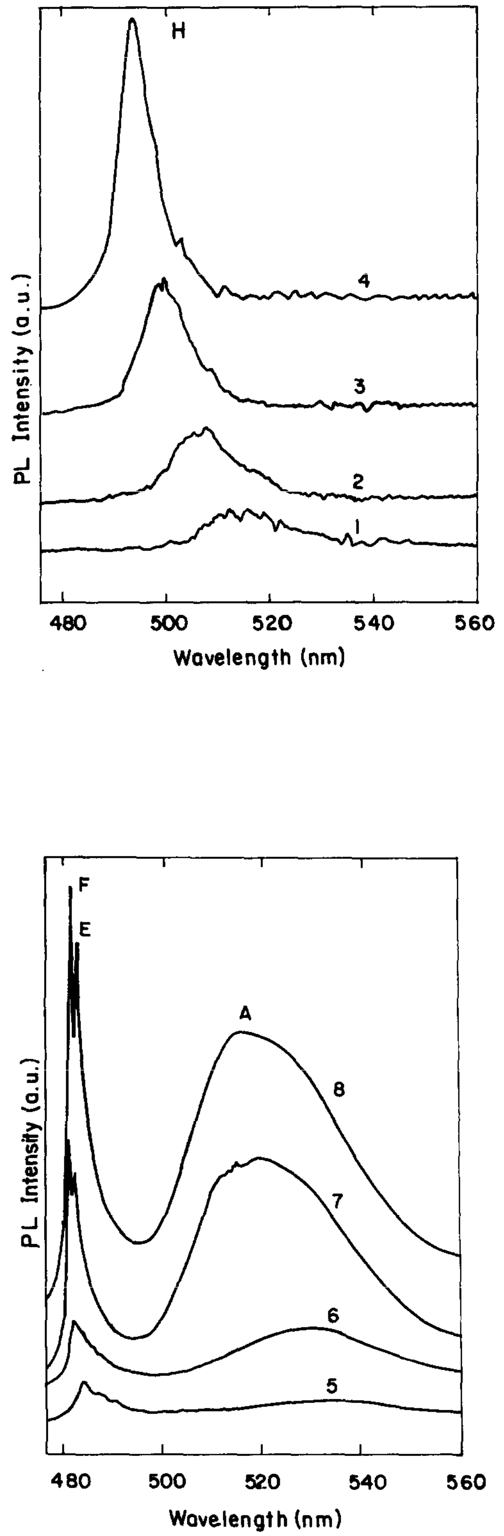

Fig. 1. Photoluminescence spectra of $TlInS_2$ crystal at different temperatures: (a) 1, 2, 3, 4 – 220, 180, 150, 120 K; (b) 5, 6, 7, 8 – 60, 45, 20, 14 K. Excitation density for (a) and (b) $I_0 = 9\,W\,cm^{-2}$. The intensity of bands shown in (b) is about ten times stronger than that shown in (a).

Crystals suitable for measurements were obtained by easy cleavage along the (0 0 1) plane perpendicular to the optical c-axis. In the photoluminescence measurements samples of a typical size $6 \times 6 \times 2\,mm^3$ were used. The photoluminescence, excited by the 476.5 nm line of a Spectra-Physics argon ion laser, was investigated from the side of the laser-illuminated surface of the samples in a direction close to the normal to the layers. A "CTI-Cryogenics M-22" closed-cycle helium cryostat was used to cool the crystals. The temperature was controlled within an accuracy of ± 1 K. The photoluminescence spectra in the wavelength range 477–560 nm were analysed using a U-1000 "Jobin Yvon" double grating spectrometer and a cooled GaAs photomultiplier supplied with the necessary photon counting electronics.

The photoluminescence spectra of $TlInS_2$ in the temperature range 220–14 K are shown in Fig. 1. No bands were observed at temperatures higher than ≈ 220 K. At ≈ 220 K (according to [2] at $T_{i1} = 216$ K the crystal undergoes a transition from the paraelectric phase to the incommensurate one) a weak broad band appears at 2.39 eV (band H). The peak intensity of this band increases with decreasing temperature and the band shifts to higher energies (Fig. 2). No noticeable changes were observed in spectra down to temperature $T = 60$ K. At $T = 60$ K a new broad band appears at 2.31 eV (band A). With decreasing temperature the intensity of this band increases and band shifts to higher energies. Almost at the same temperature new structures appear at the high energy side of the spectra. These bands are named according to [3] as: 2.374 eV (A); 2.570 eV (E); 2.576 eV (F) at 14 K. From the temperature dependencies described above, one can suppose that the phase transitions occur in $TlInS_2$ at temperatures near 220 K and 60 K.

When comparing our results with that published in [3] one can see noticeable differences:

(1) We did not observe bands B (2.5 eV) and C (2.54 eV).

(2) The temperature dependence of band A (2.374 eV) was completely different. In our spectra this band grew in intensity with lowering of the temperature. According to [3] the intensity of this line decreased with decreasing temperature.

(3) All the bands observed in the present work were slightly shifted to the blue side of the spectra in comparison with that published in [3].

We attribute this controversy mainly to the different kind of polytypes studied in [3] and in the

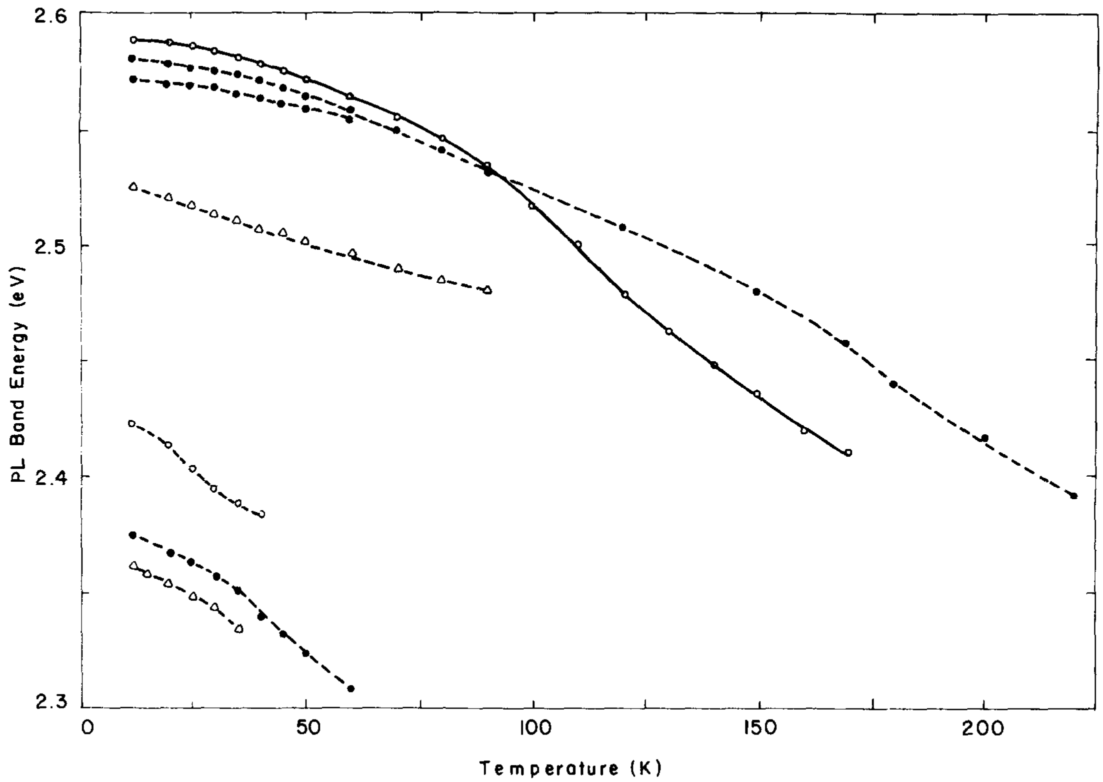

Fig. 2. Energy positions of the photoluminescence bands of $TlIn_xGa_{1-x}S_2$ mixed crystals vs temperature under excitation density $I_0 = 9\,W\,cm^{-2}$. ●, $x = 1$; ○, $x = 0.95$; △, $x = 0.8$. Lines are only a guide for the eye.

present work. In case of GaSe, for example, the difference in the band gap of the β- and ϵ-modifications is about 50 meV [7]. According to [3] band A may originate from lattice defects causing a distortion or deformation of the lattice or from uncontrolled impurities. Our results are in accordance with such a point of view. The temperature and density behavior of band A are very similar to those of bands α_i and ϕ_i, which was published for the layered crystal GaSe [8] and may be due to a donor–acceptor recombination channel favoured by low pumping power and high defect (impurity) content. It seems that the electron–hole recombination in the case of $TlInS_2$ can take place via two competing channels, the first one involving the exciton states and the second one the donor and acceptor states. Due to the wide band gap of $TlInS_2$ (≈ 2.58 eV at 14 K) a third recombination channel may also exist involving the lowest electron traps and acceptor states. The existence of these three recombination channels is well supported by the results of electrical and photoelectrical measurements in $TlInS_2$ [9–11] and the optical results reported in [12].

With substitution of a part of the InS_4 complexes in $TlInS_2$ by GaS_4 complexes, i.e. in $TlIn_xGa_{1-x}S_2$ mixed crystals, the phase transition at 220 K (for pure $TlInS_2$) is displaced towards lower temperatures: at 170 K (for $x = 0.95$) and at 90 K (for $x = 0.8$) (Fig. 2). This result is in agreement with that obtained in [13] where the temperature dependence of the IR reflection was measured. No luminescence was observed for crystals with composition $TlIn_{0.7}Ga_{0.3}S_2$. In [14] by studying the Raman spectra of mixed crystals $TlIn_xGa_{1-x}S_2$ under pressure it was shown that the crystals with $0 \leq x \leq 0.6$ have the structure of $TlGaS_2$. The absence of luminescence for crystals with $x = 0.7$ may be due to the fact that for this composition a highly disordered system is formed. The other possibility is the concentration quenching of the luminescence with increasing Ga content in mixed crystals.

An interesting feature was observed when studying the intensities of the bands of $TlInS_2$ at a fixed temperature ($T = 14$ K) vs the excitation density in the high energy side of spectra (Fig. 3). At low excitation density ($0.27\,W\,cm^{-2}$) four bands were observed: 2.547 eV (D), 2.570 eV (E), 2.576 eV (F) and 2.581 eV (G) and 2.565 eV (E′) as a weak shoulder. With increasing excitation density the intensities of all bands increased. The intensities of the weak shoulder (E′) and band D were too low to be reliably analyzed with increasing excitation

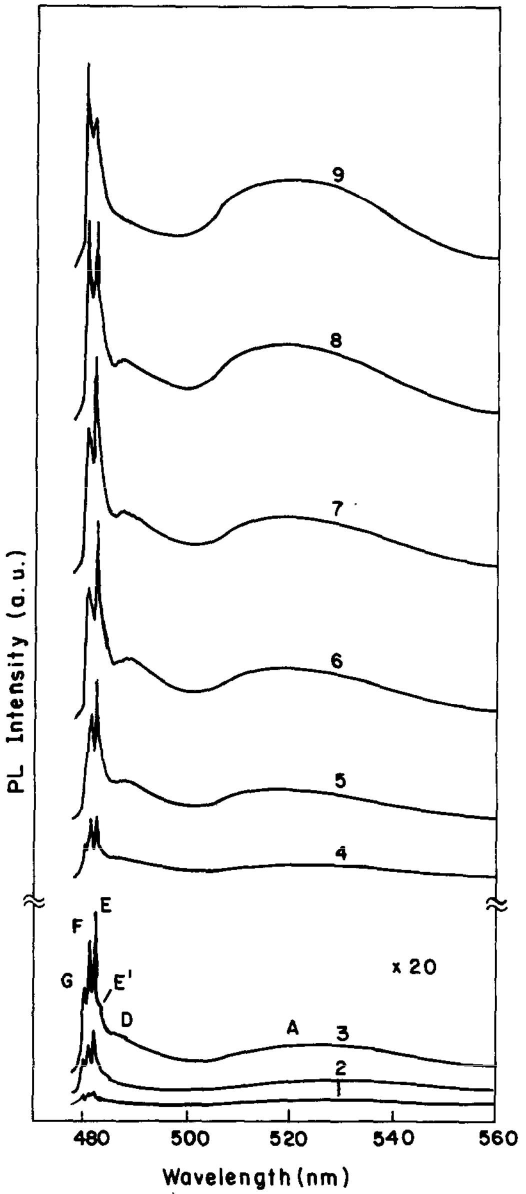

Fig. 3. Photoluminescence spectra of $TlInS_2$ crystal at $T = 14\,K$ at various excitation densities: 1, 0.027; 2, 0.135; 3, 0.27; 4, 1.17; 5, 2.25; 6, 3.6; 7, 4.5; 8, 6.3; 9, $9\,W\,cm^{-2}$. Note that the first three spectra have been multiplied by a factor of 20.

density. That is why we considered only density dependencies for E, F, and G bands. With increasing excitation density the intensities of all three bands increased up to $1.17\,W\,cm^{-2}$. At a density of about $2.25\,W\,cm^{-2}$ band G appeared as a weak shoulder on the high energy side of the triplet and only the two bands F and E were well resolved, the intensity of band E being higher than that of band F. At about $6.3\,W\,cm^{-2}$ the intensity of both bands are almost the same. Further increase in the excitation density results in a redistribution of the intensities of these two bands; the intensity of band E becomes also lower than that of band F. These bands can originate from excitons in different $TlInS_2$ polytypes.

Dependencies of the luminescence intensity vs the excitation power for $TlInS_2$ at 14 K are shown in Fig. 4. It is worthwhile to note that all the density experiments in the present work were performed for low excitation densities at which the excitonic interaction was not screened and the system did not become metallic. We used the formula given in [15] $n_M \approx 3/4\pi\alpha_x^3$, where α_x is the exciton Bohr radius, and the value of $\alpha_x = 23\,Å$ for $TlInS_2$ given in [16], and obtained $n_M \approx 2 \times 10^{19}\,cm^{-3}$. This estimation showed that at the highest density used for exciting $TlInS_2$ in our work ($9\,W\,cm^{-2}$) the density of excited electron–hole pairs was not more than $N \approx 10^{15}\,cm^{-3}$, which is much lower than the Mott limit. It was found that the relative intensities of all photoluminescence lines were not depending on the excitation density at 14 K up to $9\,W\,cm^{-2}$. This result is in agreement with that published in [3] and also denies the possibility of the appearance of molecular excitons.

3. CONCLUSIONS

In conclusion, the largest change in the photoluminescence spectra of $TlInS_2$ with the temperature occurs at about 220 K at which this crystal has an incommensurate phase with $\mathbf{q}_i = (\delta;\ \delta;\ 0.25)$ [5]. A low-temperature structural transformation at about 60 K induces the appearance of a new broad band at 2.31 eV (A). Substitution of InS_4 complexes in $TlInS_2$ by GaS_4 [$TlIn_xGa_{1-x}S_2$ mixed crystals ($x = 0.95$, 0.8)] results in a displacement of the phase transition at 220 K ($x = 1$) to lower temperatures: 170 K ($x = 0.95$) and 90 K ($x = 0.8$). No luminescence was observed for $TlIn_xGa_{1-x}S_2$ mixed crystals with $x = 0.7$.

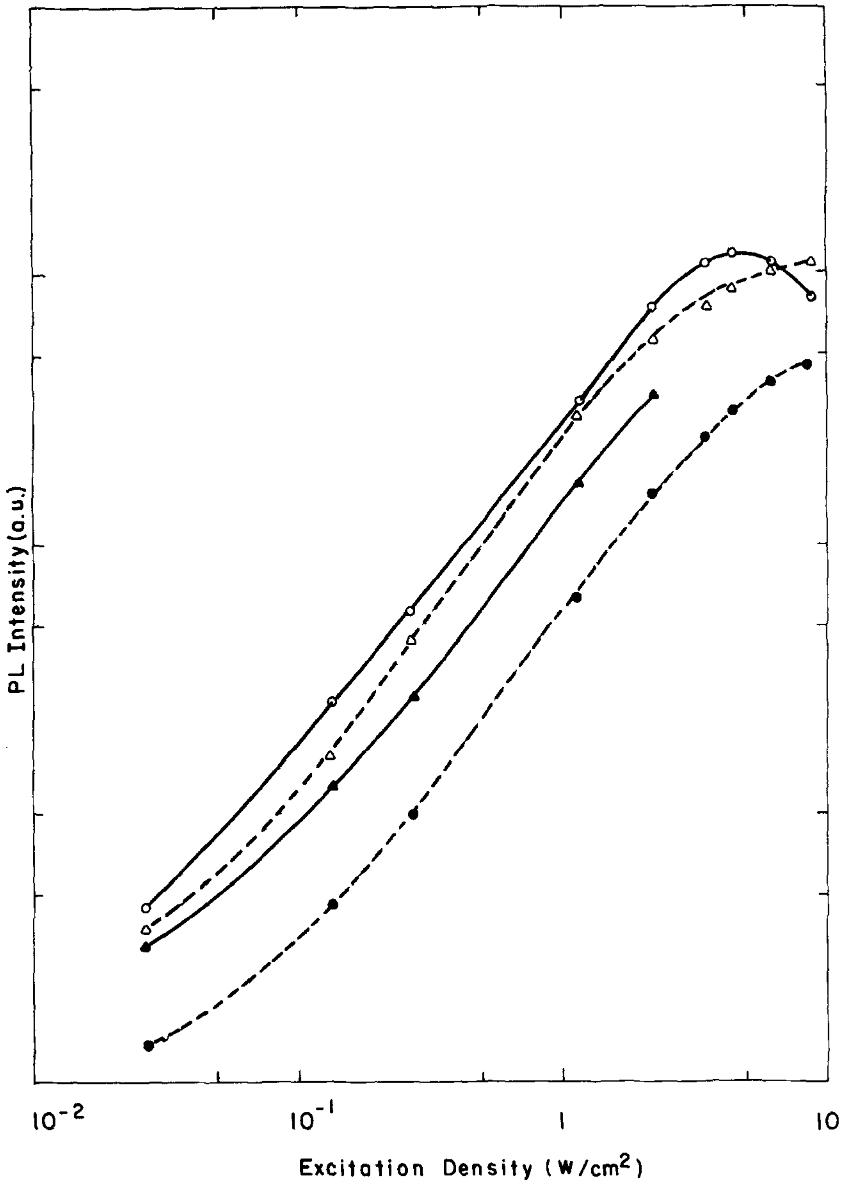

Fig. 4. Dependence of the photoluminescence intensity on the excitation density for $TlInS_2$ crystal at $T = 14$ K for different bands: ●, A; ○, E; △, F; ▲, G. Lines are only a guide for the eye.

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REFERENCES

1. G. Abdullaev, G. Abutalybov, A. Aliev, L. Larionkina, I. Neiman-zade & E. Salaev, *JETP Lett.* **38,** 632 (1983).
2. F. Salaev, R. Fischer, D. Haarer & K. Allakhverdiev, *Ferroelectrics* (submitted).
3. T. Arai, J. Aoyagi, Y. Maruyama, S. Onari, K. Allakhverdiev & E. Bairamova, *Japan J. Appl. Phys.* **32,** Suppl. 32-3, 754 (1993).
4. M. Hanias, A. Anagnostopoulos, K. Kambas & J. Spyridelis, *Physica* **B160,** 154 (1989).
5. K. Allakhverdiev, T. Mamedov, B. Akinoglu & S. Ellialtioglu, *Turkish J. Phys.* **18,** 1 (1994).
6. N. Gasanly, A. Goncharov, N. Melnik, A. Ragimov & V. Tagirov, *Phys. Status Solidi (b)* **116,** 427 (1983).
7. Landolt–Börnstein, *Zahlenwerte und Funktionen aus Naturwissenschaften und Technik. Festkörperphysik, Band 17, Halbleiter,* p. 530. Springer Verlag, Berlin (1983).
8. J. Voitchovsky & A. Mercier, *Phys. Status Solidi (a)* **18,** 545 (1973).
9. M.P. Hanias, A.N. Anagnostopoulos, K. Kambas & J. Spyridelis, *Mat. Res. Bull.* **27,** 25 (1992).

10. N. Kalkan, M.P. Hanias & A.N. Anagnostopoulos, *Mat. Res. Bull.* **27,** 1329 (1992).
11. N. Kalkan, D. Papadopoulos, A.N. Anagnostopoulos & J. Spyridelis, *Mat. Res. Bull.* **28,** 693 (1993).
12. J.A. Kalomiros & A.N. Anagnostopoulos, *Phys. Rev.* **B50,** 7488 (1994).
13. S. Nurov, V. Burlakov, E. Vinogradov, N. Gasanly & B. Dzhavadov, *Phys. Status Solidi (b)* **137,** 21 (1986).
14. E. Bairamova, K. Allakhverdiev, B. Akinoglu, T. Arai & T. Mamedov, *Turkish J. Phys.* **18,** 497 (1994).
15. N. Mott, *Phil. Mag.* **6,** 287 (1961).
16. G. Abutalybov, S. Abdullaeva & N. Zeinalov, *Sov. Phys. Semicond.* **16,** 1348 (1982).