

INVESTIGATION OF OPTICAL AND PHOTOCONDUCTION PROPERTIES OF TiGaSSe AND TiInSSe CRYSTALS

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ABSTRACT

Spectral distribution of the absorption coefficient α and the spectral dependence of photoconductivity were studied at temperature range 80-350K for TiGaSSe and TiInSSe single crystals in the photon energy range 1.55-2.75 eV. The direct and indirect transition took place at this range for both samples. Two photoconductivity maxima were observed at temperature above 150 K for TiGaSSe , while for TiInSSe there was a sharp maximum at $h\nu = 2.29$ eV which shifts towards lower energy with increasing temperature.

INTRODUCTION

Complex semiconductor compounds $\text{TlA}_{2x}^{\text{III}}\text{B}_{2(1-x)}^{\text{VI}}$ are attracting and of increasing attention in the present time. Single crystals of these compounds are anisotropic, optically active, having a high photosensitivity over a wide spectral range and may find application in optoelectronics.[1,2]

A continuous series of solid solution $\text{TiGaS}_{2x}\text{Se}_{2(1-x)}$ and $\text{TiInS}_{2x}\text{Se}_{2(1-x)}$ compounds crystallizes in a monoclinic structure with $\text{O}x\text{ssL}$.[3-6] The crystal lattices changes from monoclinic to tetragonal structure in the compounds of $\text{TiInS}_{2x}\text{Se}_{2(1-x)}$ solid solution as the sulfur content at $x < 0.3$ decreases.[7,8]

Optical properties and structure of the absorption edge of $\text{TiGaS}_{2x}\text{Se}_{2(1-x)}$ with $x = 0$ and I have shown that the band gap varies from 2.03 to 2.46 eV as x changed from 0 to 1 at 300 K. The long wavelength edge was due to indirect transitions, and as $h\nu$

increases, direct transition began to predominate[5,6,9,13]. The fundamental absorption edge of TiInS_2 [14-18] and TiInS_2 [18-19] is due to allowed indirect and direct transitions. The energy gap of TiInS_2 equals to 1.44 eV, and 2.38eV for TiInS_2 at 300K. As the temperature decreases the threshold energy of indirect transition grows[20].

It was observed, from the photoconductivity measurements of $\text{TiInB}_2^{\text{VI}}$ (where $B = \text{S, Se, Te}$)[16] that, in passing from Te to S (at 300 K) the forbidden gap width increases in the following sequence : TiInS_2 - 2.2 eV, TiInSe_2 - 1.12 eV and TiInTe_2 - 0.62 eV[16].

Since the physical properties of the single crystals TiGaSSe and TiInSSe still very little studied[21]. The present paper reports the results of measurements of optical absorption coefficient and spectral distribution of photoconductivity of these crystals in the energy interval 1.55 to 2.75 eV at temperature range from 80 to 350 K.

EXPRIMENTAL

TiGaSSe and TiInSSe single crystals were grown from the melt by Bridgman - Stockbauer method. Pure semiconductor elements of purity 99.999% were introduced, in stoichiometric ratio, into silica glass crucible (12 mm diameter and 120 mm length) with a tip at the bottom. The two crucible were evacuated to 10^{-5} Torr and sealed, then heated in a temperature gradient furnace, so that the sulphur condensed at the cold end and slowly reacted with the heated metals at the hot end.

After complete reaction the crucible were kept at 1000 K for 10 hours to maintain homogeneity of compounds.

The growth was achieved by lowered each crucible, in a two zone furnace; from the hot side, at 1203 K for TiGaSSe and at 1153 K for TiInSSe , to the cold side at 973 K at a speed of 0.10 mm/h. In the cold zone, the crystals were cooled down slowly within a couple of days.

The samples have a layered structure and were easily split along the cleavage planes.

The sample used in the absorption measurements were prepared by splitting crystal along the cleavage planes. The resultant surface were mirror-like and there was no need for any mechanical polishing. The thickness of samples varied between 100 and 300 μm . Light was incident perpendicularly to the cleavage planes. The sample used in measurements of the photoconductivity and electrical conductivity were prepared in a similar manner.

Contacts were made by a silver paste for photoconductivity measurement. The room temperature resistivity of TiGaSSe and TiGaSSe were of order 10^7 and $10^9 \Omega\text{cm}$ respectively.

Optical measurements were performed with spectrophotometer (spectronic 601, Milton Roy), with wavelength range 195-999nm and accuracy $\pm 1.0 \text{ nm}$. The temperature investigation were carried out with a cryostat type DNI704 (Oxford instrument - England). The temperature was controlled by the digital temperature - England). The temperature was controlled by the digital temperature controller DTC2 (Oxford instrument - England) with an accuracy of 0.1 K in the temperature range 77-500 K. Measurements were carried out under vacuum of about $1.5 \times 10^{-4} \text{ Torr}$. The current was measured by a 610C Keithley electrometer with the accuracy $\pm 2\%$.

RESULTS AND DISCUSSIONS

The absorption coefficient [$\alpha \text{ (cm}^{-1}\text{)}$] were determined from both absorbance and transmittance measurements by the following relation[22,23].

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T}$$

where R is the reflectance, T the transmittance, α the absorption coefficient and d the sample thickness.

The absorption coefficient of TiGaSSe and TiInSSe crystals in the photon energy ranges 1.55 - 2.37 and 1.55 - 2.22 eV respectively were studied at temperature range 80-350 K.

The general feature of the spectral distribution of optical absorption coefficient shows that the absorption coefficient increases slowly with increasing $h\nu$ and then increases rapidly determining the fundamental absorption edge. Fig. (1) shows the spectral distribution of optical absorption coefficient for TiGaSSe and TiInSSe crystal.

Fig. (2) represent the dependence of the absorption coefficient $(\alpha h\nu)^{1/2}$ on the photon energy $h\nu$ at 80 K (curve 1,3) and 300 K (curve 2,4) for TiGaSSe (curve 1,2) and TiInSSe (curve 3,4) single crystals. It can be noticed the weak-absorption range indicated that indirect allowed transitions took place. At long wavelength side, we observe that two straight lines intersect the $h\nu$ axis. The intersect at $h\nu = \Delta E_v^i + E_p$, gives the emission of phonon. The second intersects $h\nu$ axis at $h\nu = \Delta E_g^i + E_p$, indicates absorption of phonon.

The minimum energy of the indirects transition was found to be 2.25 eV for TiGaSSe and 2.12 eV for TiInSSe at 80 K. The average temperature coefficient of energy of these transitions in the 80 - 350 K range was -3.8×10^{-4} eV/K and -4.8×10^{-4} eV/K respectively. The average phonon energy was 45 and 34 meV for TiGaSSe and TiInSSe (curve 3,4) respectively. We also observed that the absorption edge shifts towards low photon energy with increasing temperature. The energy gap width was calculated and found to be 2.34 and 2.2 eV at 80 K for TiGaSSe and TiInSSe respectively.

With increasing $h\nu$, the TiGaSSe and TiInSSe exhibited direct allowed transitions with the dependence $(\alpha h\nu)$ on $h\nu$. The dependence of $(\alpha h\nu)^2$ on $h\nu$ at 80 K (curve 1,3) and 300 K (curve 2,4) are plotted in Fig. (3) for TiGaSSe (curve 1,2) and TiInSSe (curve 3,4) respectively. From the figures we observed that the absorption edge shifts towards low photon energy with increasing temperature. The energy gap

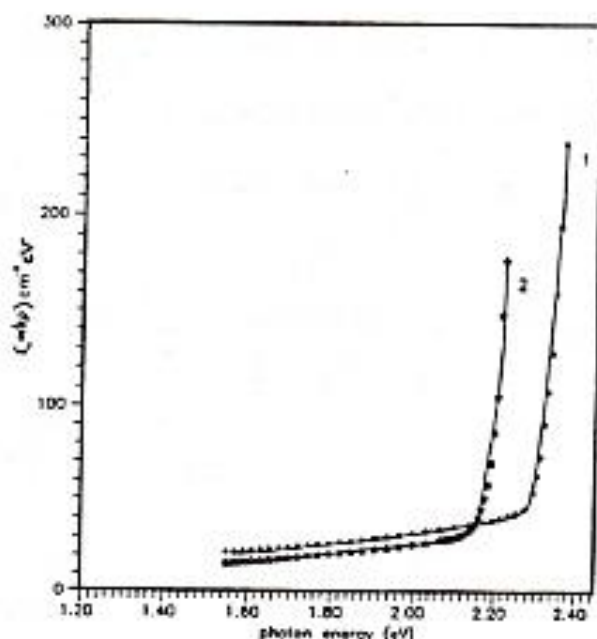


Fig. 1.: The dependence of absorption coefficient ($\alpha h\nu$) on the photon energy for TiGaSe (1) and TiInSe (2) Crystals.

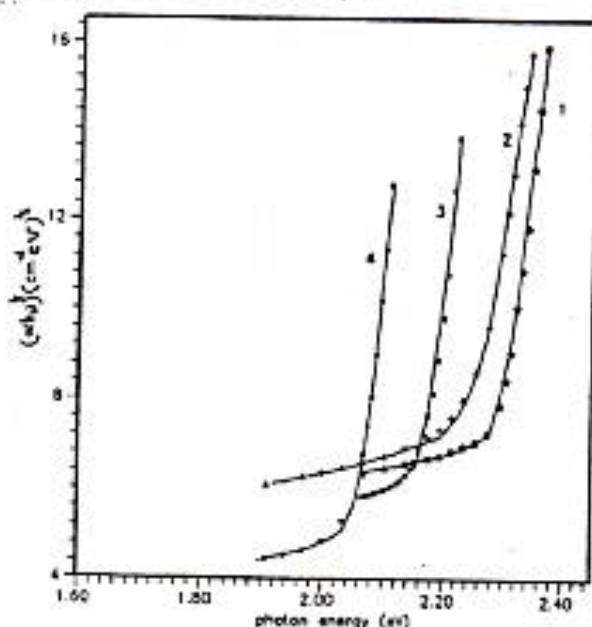


Fig. 2.: The dependence of absorption coefficient $(\alpha h\nu)^{1/2}$ on the photon energy for TiGaSe (1,2) and TiInSe (3,4) crystals at temperatures : 2, 4-300 K, 1.3-80 K.

width was calculated and found to be 2.34 and 2.2 eV at 80 K for TiGaSSe and TiInSSe respectively. The temperature coefficient of forbidden gap $\frac{\delta E_g}{\delta T}$ was found to be -2.1×10^{-4} and -4×10^{-10} eV/K for TiGaSSe and TiInSSe respectively in the temperature range 80-350 K.

Fig. (4) shows the band gap width for indirect optical transition smaller than that for direct ones for both samples as expected. The high photosensitivity of the crystals made it possible to study photoconductivity spectra in the impurity and intrinsic regions. The photoresponses in samples appeared at $h\nu = 1.55$ eV.

The spectral distribution of the photoconductivity has a sharp maximum at $h\nu = 2.36$ eV for TiGaSSe and 2.29 eV for TiInSSe. The fairly steep fall of the photoresponses on the short wavelength side indicated a considerable importance of the surface recombination processes.

Fig. (5) shows the spectral distribution of photoconductivity for TiGaSSe at different temperatures. It is shown that, the photocurrent decreases in the range from 80 to 150 K with increasing temperature. This behaviour may be because of the sensitization levels are converted back to trapping levels causing a reduction of photosensitivity. A further increase in temperature, above 150 K, causes liberation of carriers from the trapping levels and therefore the photocurrent increases. Two photoconductivity maxima clearly appeared at temperature more than 150 K. The above explanation for the first one at $h\nu = 2.35$ eV, which was clearly associated with direct band transition. The second peak which appeared approximately at $h\nu = 2.05$ eV could be related to ionization of deep impurities which may be considered as an evidence of the $\sigma = f(T)$ dependence [Fig. (6)].

Fig. (7) shows that the photocurrent of TiInSSe decreases with increasing temperature till 200 K and above 200 K the photocurrent increases with increasing temperature. This behaviour could be due to increasing carrier concentration by the liberation of carriers from the trapping levels. A slight shift in the position of peak

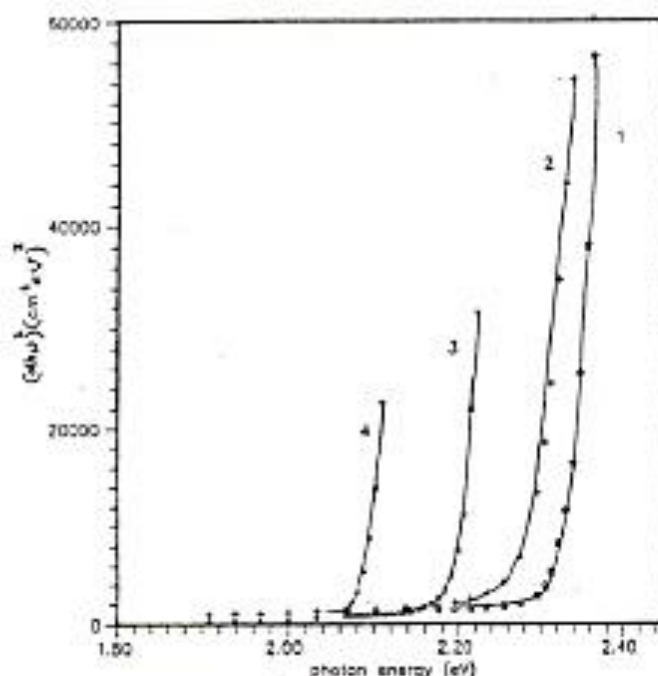


Fig. 3. : The dependence of absorption coefficient $(\alpha hv)^{1/2}$ on the photon energy for TiGaSSe (1,2) and TiInSSe (3,4) crystals at temperatures : T, K: 2.4 - 300, 1.3 - 80.

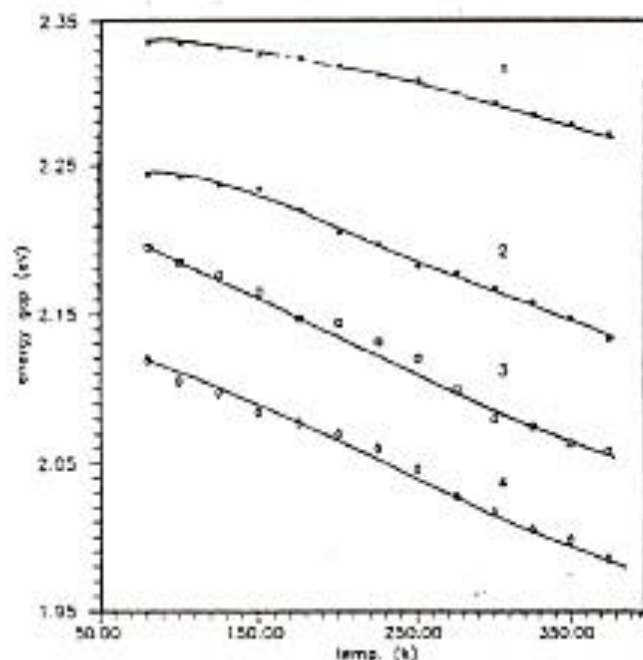


Fig. 4. : Temperature dependence of energy gap width for TiGaSSe (1,2) and TiInSSe (3,4).
1.3 - energy gap for direct transition,
2.2 - energy gap for indirect transition.

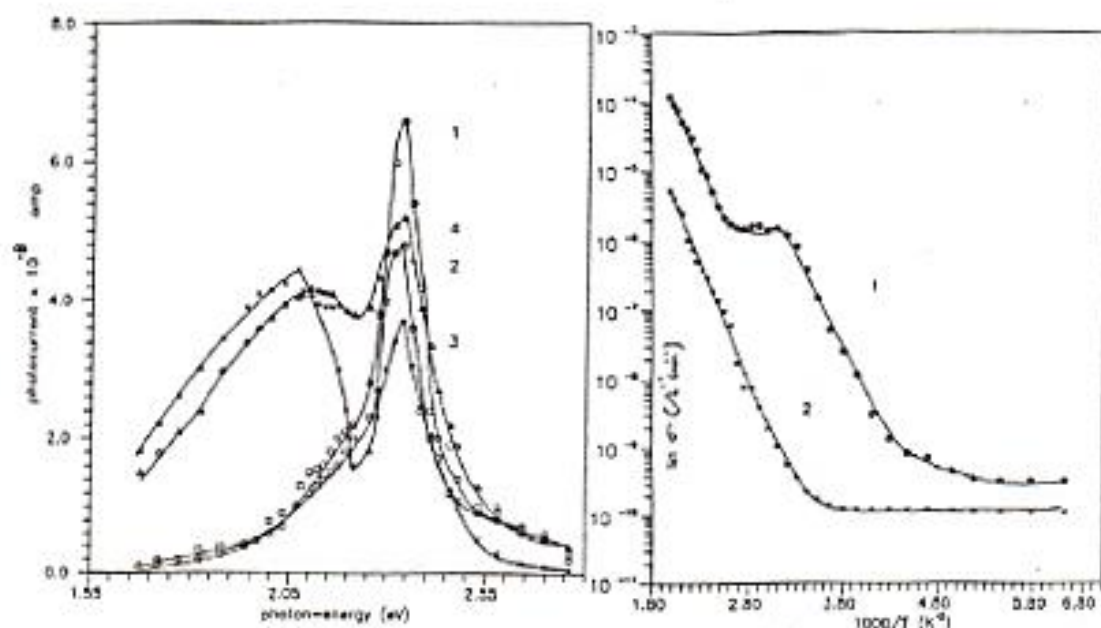


Fig. 5. : Spectral distribution of photoconductivity for TiGaSSe. temperatures : 1 - 80, 2 - 100, 3 - 175, 4 - 200 K.

Fig. 6. : Temperature dependence of the electrical conductivity of TiGaSSe (1) and TiInSSe (2) single crystals.

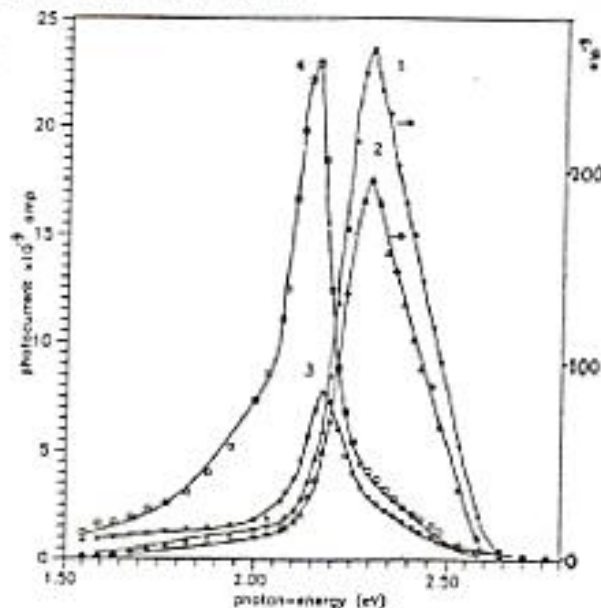


Fig. 7. : Spectral distribution of photoconductivity for TiInSSe. temperature : 1 - 80, 2 - 100, 3 - 200, 4 - 250.

towards low photon energy was observed with increasing temperature. The thermal coefficient of the maximum position was $\frac{\delta E_m}{\delta T} = -7.7 \times 10^{-4}$ eV/K. This shift is due to the temperature dependents of the forbidden energy gap width and it is not observed in TiGaSSe samples.

Finally, the fundamental absorption edge of these two compounds were formed by allowed indirect and direct transitions which agree with the previous study[1,3,20].

Growth and decay of the photoconductivity was slow (long time) specially in TiGaSSe crystal, and it may be associated with the trapping of carriers by deep levels which was found to be located at 0.2 - 0.44 eV from the conduction band.

The energy gap of TiGaSSe is greater than the energy gap of TiInSSe. Gallium atoms are replaced by Indium atoms, both are from the same group, but with a greater mass and bigger atomic radius. This results in any material with weaker binding force so that the energy required to excite a valence electron into conduction band is smaller.

REFERENCES

- 1- A.M. Akhmedov, A.E. Bakhyshov, A. A. Lebedev, and M. A. Yakobson, Sov. Phys. Semicond. 12 (3), 299 (1978).
- 2- F. Zernike and J. E. Midwinter, Applied Nonlinear optics : Basic and Application, Interscience New York (1973).
- 3- A. E. Bakhyshov, A. A. Lebedev, Z. D. Khalafov, and M. A. Yakobson, Sov. Phys. Semicond. 12 (3), 336 (1978).
- 4- D. Muller and H. Hahn, Z. anorg., Allg. Chem. 438, 258 (1978).
- 5- A. E. Bakhyshov, L.G. Musaeva, A.A. Lebedev, and M. A. Yakobson, Sov. Phys. Semicond. 9 (8), 1021 (1975).
- 6- A. E. Bakhyshov, A. A. Lebedev, Z.D.Khalafov, and M. A. Yakobson, Fiz, Tekh. Poluprovodn. 12, 555 (1978).
- 7- N. M. Gasanly, B.M. Dzhevandov, V.I. Tagirov, and E. A. Vinogradov, phys. stat. sol. (b) 95, k27 (1979).
- 8- N. A. Bakhyshov, N. M. Gasanly, B. M. Yavvadov, V. I. Tagirov, and Sh. M. Efediev, phys. stat. sol. (b) 91, k1 (1979).
- 9- G.I. Abutalybov, I. Kh. Akopyan, I. K. Neimanzade, B. V. Novikov, and E. Yu. Salaev, Sov. Phys. Solid State 27 (9), 1710(1985).
- 10- G. I. Abutalybov, and E. Yu. Salaev, Sov. Phys. Solid State 28 (7), 1231(1986).
- 11- A. E. Bakhyshov, A. A. Lebedev, Z.D. Khalafov, and M. A. Yakobson, Sov. Phys. Semicond. 12 (3), 320 (1978).
- 12- A. M. Darvish, A. E. Bakhyshov, and V. I. Tagirov, Sov. Phys. Semicond. 11 (4), 548 (1977).

13. Yu. Banis, A. Brilingas, J. Grigas, and G. Guselnov, *Sov. Phys. Solid State* 29 (11), 1906 (1987).
14. K. R. Allakhverdiev, T.G. Mamedov, E. Yu. Salaev, and I. K. Efendieva, *phys. stat. sol. (b)* 113, K43 (1982).
15. A. E. Bakhyshov, M. F. Ageeva, and A. M. Karvish, *Phys. Stat. Sol. (b)* 91, K31 (1979).
16. A. E. Bakhyshov, L.G. Gasanov, A.A. Lebedev, S.R. Samedov, and M. A. Yakhyshev, *Fiz. Tekh. Poluprov.* 15, 808 (1981).
17. A. E. Bakhyshov, L.V. Gasanov, A. A. Lebedev, S.R. Samicond., 15 (4) 462 (1981).
18. G.D. Gusieno, E. Mooser, E. M. Kermova, R. S. Gamidov, I. V. Alekseev, and M.Z. Ismailov, *phys. stat. sol.* 34, 33 (1969).
19. M. Ya. Bakirov, N. M. Zeinalov, S. G. Abdulayeva, V.A. Gajiyev, and E. M. Gojayev, *Solid State Communication*, 44 (2), 205-7 (1982).
20. A. E. Bakhyshov, Safuat Boules, F.E. Faradzhov, M. Sh. Mamedov, and V.J. Tagirov, *Phys. Stat. sol. (b)* 95, K121 (1979).
21. G.D. Guseinov, F.M. Seidov, and E.M. Kerimova, *Izv. Akad. Nauk. Az. SSR Ser. Fiz. Tekh. & Mat. Nauk. (USSR)*, 2, 62 (1981).
22. M. Becker and H.Y. Fan, *Phys. Rev.* 76, 1530 (1949).
23. T.S. Moss, "Optical properties of Semiconductors". Butterworths, London (1959).