

ABSORPTION NEAR THE ABSORPTION EDGE OF A $Tl_xAs_{2-x}S_{3-x}$ SYSTEM

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Received March 2nd, 1972

In this paper transmittance measurements in the vicinity of the absorption edge for glasses of a summary composition $Tl_xAs_{2-x}S_{3-x}$ for $x = 0-1$ are presented. The absorption edge has been proved to exhibit an exponential course up to $K \sim 10^3 \text{ cm}^{-1}$, for higher K the course is quadratic. From the quadratic part of the absorption edge energy E_g^{opt} for $TlAsS_2$ has been determined. With the increasing thallium content position of the absorption edge is shifted towards lower energy values and E_g^{opt} changes from 2.32 eV for As_2S_3 to 1.90 eV for $TlAsS_2$, respectively.

Formation of ternary glasses of composition $Tl_xAs_{2-x}S_{3-x}$, produced in the system $As_2S_3-Tl_2S$ was for the first time examined by Hawley¹. He found the solid solutions to be produced from 100 down to 62% As_2S_3 . Later on, data on the conditions of the synthesis as well as on the limit of glass-formation were made more precise by Gorjunova, Kolomijec, and Šilo². They established that during a slow 10 to 12 hours lasting cooling of the melts from 800°C downwards, homogeneous glasses containing max. 15 at% of thallium ($As_2S_3 - 67.4 \text{ mol.}\%$) could be prepared. The melts having a higher content of thallium required a sharp outer cooling usually achieved from a temperature of 600°C down with use of water, if quartz ampulas were employed. Stable glasses of up to 25 at% of thallium (50 mol% of As_2S_3) could be thus produced.

Total region of the formation of glass in a ternary system $Tl-As-S$ was studied by Flaschen and Pearson³, later on by Markova⁴. In accordance with paper² glasses of the above-given composition with $x = 0-1$ can be prepared in the plane section $As_2S_3-Tl_2S$. Markova⁴ examined, among others, dependence of electric conductivity on temperature and position of the absorption edge. She found a decrease of the conductivity energy E_σ with the increasing thallium content. On the basis of the optical measurements made on compact samples of these glasses she estimated energy values E_λ , which were established from the course of the absorption edge—of its centre corresponding to the half-value of the maximum transmittance. The E_λ value is by about 0.2 eV higher, when compared with E_σ . For $TlAsS_2$ ($x = 1$), Markova presents values E_σ and E_λ to be $1.6 \pm 0.1 \text{ eV}$ and $1.76 \pm 0.03 \text{ eV}$, respectively. Some further data on glass of the $TlAsS_2$ composition have been published by Dembovskij⁵. From the course of the absorption edge he estimated value of E_λ to be 1.6 eV.

In the present paper, which is a partial result of examining glasses of the composition given, we are concerned with the study of the position of the absorption edge over a wide range of energies up to values for $K \sim 10^5 \text{ cm}^{-1}$, and with determining width of the energy gap more precise.

EXPERIMENTAL

Samples of glasses, whose composition and numerical identification are given in Table I, were prepared by direct synthesis from the elements. Arsenic was of purity 99.9999%. The sulphur used was purified by the Murphy and Clabaugh⁶ method; after redistillation in a quartz apparatus under a nitrogen atmosphere, trace amounts of Ca, Si, and Mg were found by spectral analysis. Thallium of semiconductor purity contained traces of Pb, Cu, Cd, Zn, and Fe. All the three elements were weighed in corresponding ratios into the quartz ampulas. Thallium and arsenic were weighed under an argon atmosphere. On pumping off down to the residual pressure below 10^{-3} Torr, the ampulas were sealed and put into an electric resistance furnace the temperature of which was slowly increased up to 600°C. During the synthesis and subsequent 60 hours tempering the ampulas were maintained under rotation. After the components having been fully reacted and the mixture homogenized, the samples were cooled down to the room temperature at a rate of 220°C per hour. The sample with the highest thallium content only (sample No 5) was pulled out from the furnace and cooled in the air. The Debye-patterns of the samples thus prepared had no reflections.

The reflectivity measurements were carried out at normal temperature on polished samples using monochromator Zeiss SPM 2 with a glass prism. In terms of a source of continuous radia-

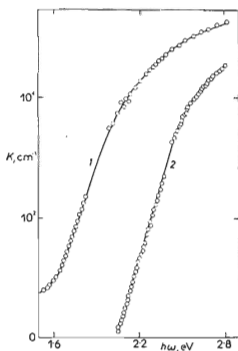


FIG. 1

Plot of the Absorption Coefficient K against Energy $h\omega$ for Amorphous TlAsS_2 (1) and As_2S_3 (2) at the Temperature of 293 K

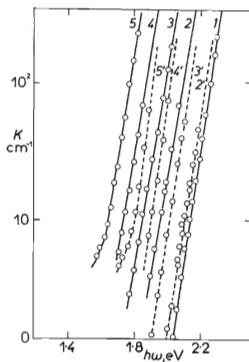


FIG. 2

Plot of the Absorption Coefficient K against Energy $h\omega$ for Samples of Composition $\text{Tl}_x\text{As}_{2-x}\text{S}_{3-x}$ for $x = 0.0495$, $x = 0.238$, $x = 0.652$, $x = 1.5$ at the Temperature of 293 K

Curve 1 is taken from paper⁸; dashed curves correspond to the measurement of K at 80 K.

tion, bulb of 6 V and 35 W with a tungsten wire was employed. The measurement was accomplished by means of the alternating method using frequency of 400 c. The sample along with the polished germanium single crystal, which served as the reflectivity standard, was held in a sliding holder. The incidence angle of radiation on the sample was no greater than 15° . Detection of radiation was achieved by photomultipliers M 12 FQS and M 13 Gek (Zeiss). The alternating signal from the photomultipliers was amplified and led to the input of a synchronous detector.

The transmittance measurement was carried out on polished samples of thicknesses 0.13–0.16 cm and 0.016–0.024 cm, respectively, and on thin 0.1–2.5 μm layers, vapour-deposited in vacuum. The vapour-deposition was accomplished in vacuum better than 10^{-4} Torr onto plane glasses. Thickness of the thinnest layers was determined by the Tolanski method⁷; for thicker vapour-deposited layers the thickness was calculated from positions of interferometric maxima and minima of transmittance over the range of 0.7–2.5 μm . Experimental arrangement was in case of the transmittance measurement the same as for the reflectivity measurement; the sample only was placed in a glass cryostat allowing measurements at low temperatures.

RESULTS AND DISCUSSION

The reflectivity measurement of separate samples showed that value of reflectivity rises with the increasing thallium content, the character of curves being equal.

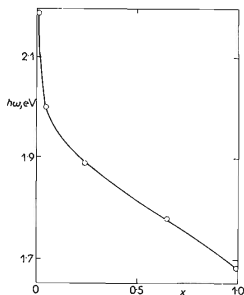


FIG. 3

Plot of Position of the Absorption Edge against Composition x

The energy values were read out for $K = 20 \text{ cm}^{-1}$ from curves in Fig. 2 for the temperature of 293 K.

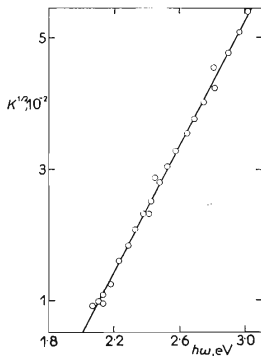


FIG. 4

Plot of the Absorption Coefficient $K^{1/2}$ against Energy of a Photon for Amorphous TiAs_2 at 293 K

With use of these curves, values of reflections over an appropriate range of wavelengths were read out to calculate coefficient of absorption K .

In Fig. 1 plot of $\log K$ against $h\omega$ is graphically presented for a sample of the highest thallium content, of composition TlAsS_2 (sample No 5), and compared with the same plot for As_2S_3 (ref.⁸). The absorption coefficient K was calculated from the relationship

$$T = [(1 - R)^2 \exp(-Kd)]/[1 - R^2 \exp(-2Kd)]. \quad (1)$$

It follows from Fig. 1 that the thallium content is responsible for a shift of the position of the absorption edge towards lower energies. The course of the curve of absorption coefficient K is similar to that of arsenic trisulphide and characteristic for glassy substances. On curve 1, the exponential part may be observed in region $K = 10$ to $5 \cdot 10^3 \text{ cm}^{-1}$, whereas the quadratic part for higher K values. The curves of the other samples (2, 3, 4) are of a similar character.

In Fig. 2, plots of $\log K$ against $h\omega$ for the samples (Nos 2, 3, 4, and 5) investigated are presented; for the sake of comparison, curve 1 for As_2S_3 (ref.⁸) is illustrated in the Fig. It follows from the measurements presented that all samples exhibit an exponential course of the absorption edge $K \sim \exp(h\omega/E_c)$, except for the curve of sample 5 for $K < 10 \text{ cm}^{-1}$. The sample of the highest thallium content (TlAsS_2) is concerned, in which formation of microcrystalline centres probably takes place, whose existence may be manifested at low K values. It also follows from Fig. 2 that tangents of the curves decrease with the increasing thallium content. The E_c constant changes from value 0.0535 eV for As_2S_3 to 0.0575 eV for TlAsS_2 . The values calculated for individual samples are given in Table II. From curves 1–5 in Fig. 2 energy values $h\omega$ were read out for $K = 20 \text{ cm}^{-1}$ (Table II).

In Fig. 2, measurements of the absorption coefficient of samples 2–5 at the temperature of 80 K (denoted with a dot-and-dash line) are simultaneously given.

TABLE I
Composition of the Glasses Examined (at %)

No of sample	Tl	As	S	$\text{Tl}_x\text{As}_{2-x}\text{S}_{3-x}$ x
1	—	40	60	0
2	1	39.4	59.6	0.0495
3	5	37	58	0.238
4	15	31	54	0.652
5	25	25	50	1.00

TABLE II

Energy Values $h\omega$ Read Out from Graph 2 for $K = 20 \text{ cm}^{-1}$ at 293 K, E_g Values at Temperatures of 293 K and 80 K, and Temperature Coefficient Values

No of sample	E_g , eV 293 K	$h\omega$, eV $K = 20 \text{ cm}^{-1}$	E_g , eV 80 K	β , eV/K
1	0.0535	2.19	0.0476	$6.7 \cdot 10^{-4}$
2	0.0613	2.00	0.0535	$7.1 \cdot 10^{-4}$
3	0.0637	1.89	0.0546	$7.6 \cdot 10^{-4}$
4	0.0602	1.78	0.0500	$7.5 \cdot 10^{-4}$
5	0.0575	1.68	0.0461	$7.2 \cdot 10^{-4}$

As evident, the exponential shape is maintained even at a low temperature. At 80 K the course is somewhat steep and the change of the curve tangents is with the increasing thallium content similar. The values calculated are given likewise in Table II. From these measurements for $K = 20 \text{ cm}^{-1}$ values of the temperature coefficient (Table II) were simultaneously calculated.

As follows from Fig. 3, dependence $h\omega$ for $K = 20 \text{ cm}^{-1}$ upon the thallium content in the samples exhibit a distinct nonlinear course; the greatest change lies in the region of low thallium concentrations for x up to the value of 0.238. A quite analogous course of the dependence is offered by the values achieved in the measurements at low temperatures. In Fig. 4, a measurement of the absorption coefficient K in a region of high values is graphically presented, the measurement being carried out on thin vapour-deposited layers of a sample having a composition of TlAsS_2 . The plot of $K^{1/2}$ against $h\omega$ is linear, this showing the dependence of K upon energy to be in this part of the absorption edge quadratic $K \sim (h\omega - E_g^{\text{opt.}})^2$. On the basis of this dependence, $E_g^{\text{opt.}} = 1.90 \text{ eV}$ at a temperature of 293 K has been determined.

Thallium arsenosulphidic glasses of composition $\text{Tl}_x\text{As}_{2-x}\text{S}_{3-x}$ produce for x up to 1 homogeneous systems, only for TlAsS_2 ($x = 1$), a certain tendency to crystallization during a somewhat slower cooling was found. On rapidly cooled samples even after a year no enhanced absorption was observed. By the vacuum vapour-deposition, the layers, however, are not homogeneous throughout its thickness, and amorphous TlAsS_2 offered layers of relatively best quality. It follows from the results of our measurements that for the series of the glasses studied, $E_g^{\text{opt.}}$ decreases from value 2.32 eV for As_2S_3 ($x = 0$) down to value 1.90 eV for TlAsS_2 ($x = 1$). Fig. 3 allows then to determine approximate values of $E_g^{\text{opt.}}$ for the other samples of composition lying inside this interval. Similarly as in earlier measurements⁸, the value $E_g^{\text{opt.}}$, determined from the dependence of $K^{1/2}$ upon $h\omega$ in the region of high K values, appears to be by about 0.2 eV higher when compared with $h\omega$ for $K =$

= 10 cm^{-1} . The E_λ values which have been presented by Markova⁴ or Dembovskij⁵ were determined in the region of lower K values, this means from the exponential part of the absorption edge which represents localized states in the energy gap^{8,9}. From this point of view comparison of the absorption edge position with the increasing thallium content in glasses is particularly interesting. The dependence proved by us (Fig. 3) appears to be in an apparent contradiction with a linear dependence up to 15 at.% which follows from the measurements of Markova⁴, or up to 25 at.% of Tl considering E_λ for TlAsS₂, presented by Dembovskij⁵.

We assume that the nonlinear course of a shift of the absorption edge position, as dependent on the thallium content (Fig. 3), excludes in these glasses presence of a simple mixture of individual chains of structural units AsS_{3/2} and TlAsS_{2/2}. As to a more distinct connection of these fundamental chains, we draw conclusions only for the region above 5 at.% of Tl; for glasses of a lower Tl content, splitting (As₂S₃)_n is likely predominating. In connection with E_g^{cl} presented by Markova⁴ it is necessary to point out that for glasses of the Tl_xAs_{2-x}S_{3-x} composition, E_g^{opt} is generally higher than E_g^{cl} , this fact being not in agreement with the results of the measurements, for example, with CdGeAs₂ (ref.⁹). For the latter glass-forming material, value $E_g^{\text{opt}} = 0.71 \text{ eV}$ was found by the authors, whereas $E_g^{\text{cl}} = 1.2 \text{ eV}$. This gives evidence of the fact that the glasses studied by us are in contradiction with the model suggested for CdGeAs₂.

REFERENCES

1. Hawley L.: J. Am. Chem. Soc. 29, 1011 (1907).
2. Gorjunova N. A., Kolomijec B. T., Šilo V. P.: Ž. Tech. Fiz. 28, 981 (1958).
3. Flaschen S. S., Pearson A. D., Northower W. R.: J. Am. Ceram. Soc. 42, 450 (1959).
4. Markova T. P.: Vest. Leningr. Gos. Univ. 1962, No 22, 96.
5. Dembovskij S. A.: Izv. Akad. Nauk SSSR, Neorgan. Mater. 4, 1920 (1968).
6. Murphy J., Claubaugh O.: J. Res. Nat. Bur. Std. A 64, 353 (1930).
7. Tolanski S.: *Multiple-Beam Interferometry of Surfaces*. Clarendon Press, Oxford 1948.
8. Kosek F., Tauc J.: Czechoslov. J. Phys. B 20, 94 (1970).
9. Tauc J., Štourač L., Vorlíček V., Závětová M.: Proc. Int. Conf. Semicond. Phys., p. 1251. Moscow 1968, Leningrad 1968.

Translated by J. Hejduk.