

## ELECTRICAL AND PHOTOELECTRICAL PROPERTIES OF INDIUM SELENIDE

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**Abstract:** Electrical conductivity, photoconductivity and X-ray measurements have been performed on indium selenide single crystals. It has been shown that the sample preparation procedure has great influence on the measured properties of InSe. The intrinsic energy gap from conductivity measurements was 0.95 eV and from photoconductive spectral response 1.18 eV. From the relaxation of photoconductivity a trapping level ( $E_t = 0.62$  eV) for holes was determined.

### *1. Introduction*

Although the existence of the compound InSe was established as early as 1934<sup>1)</sup> semiconducting properties were not reported until 1948<sup>2)</sup>. Results on the properties of InSe reported in later papers were very variable and incomplete.

Optical absorption and photoconductivity measurements gave the values 1.8<sup>3)</sup> and 1.2 eV<sup>4)</sup> for the band gap, whereas the energy gap determined from the thermal activation energy of the electrical conductivity was 1.6 and 0.95 eV<sup>5)</sup> and 1.0 eV<sup>6)</sup>. Several authors drew attention to difficulties in determining the carrier type<sup>6, 7)</sup>. The temperature dependence of the conductivity showed irreproducibility even at and above the room temperature<sup>8)</sup>.

The purpose of this paper is to present some experimental results on the synthesis, conductivity and photoconductivity of InSe, and to indicate the reasons for the conflicting results of different authors.

### *2. Sample preparation*

The compounds were prepared by direct fusion of stoichiometric amounts of high purity elements (Se 5N8 and In 6N) in sealed, evacuated silica tubes.

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First two fusions were performed, one with excess In and another with excess Se. The ingots obtained in this way showed n- and p-type conductivity measured by thermoelectric power on grounded surfaces. Ingots which were prepared from stoichiometric amounts of In and Se showed n-type conductivity with  $\sigma \sim 1.2 \cdot 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  at room temperature, but a very thin layer on the surface was p-type. This indicates that the vapour pressure of selenium at the melting point of InSe was significant. This of course, can cause different results in the determinations of carrier type if they are obtained by Hall (volume effect) and thermoelectric (by probes on surface) measurements. By adding a small quantity of selenium to prefusion stoichiometric amounts we obtained p-type ingots of very high resistivity.

Larger deviations from stoichiometry gave ingots with lower resistivities, such ingots were not used for these measurements.

According to many authors their samples of InSe had a mica-like structure with one cleavage plane. Assuming that this property would be more significant when a temperature gradient exists in the ingot during solidification, we adopted two ways of sample preparation. In the first way (denoted by A) silica tubes with molten InSe were very slowly cooled in a good isothermal furnace. In the second method molten InSe were cooled in a furnace in which there was a temperature gradient. In the first case large single crystal regions can be found in the ingot. In the second case these monocrystal regions have a very easy cleavage properties (such samples are denoted by B). As will be seen later such preparation procedures yield samples of different conductive and photoconductive properties.

Our X-ray diffraction measurements of ingots A are given below together with the results of other authors:

K. Schubert *et al.*<sup>8)</sup>, rhombohedral  $a = 4.02 \text{ \AA}$  and  $c = 25.05 \text{ \AA}$

S. A. Semiletov<sup>9)</sup>, hexagonal  $a = 4.04 \text{ \AA}$  and  $c = 16.9 \text{ \AA}$

Our measurements, hexagonal  $a = 4.00 \text{ \AA}$  and  $c = 16.6 \text{ \AA}$ .

### 3. Electrical conductivity

InSe single crystals are used for the investigation described in the present paper. Sample dimensions were about  $2 \text{ mm} \cdot 2 \text{ mm} \cdot 6 \text{ mm}$  from ingots type A and  $0.1 \text{ mm} \cdot 5 \text{ mm} \cdot 10 \text{ mm}$  from ingots type B. All specimens were ground to avoid the surface of the ingot. Good ohmic contacts were obtained

by soldering with indium. No photovoltaic effect was present in the whole temperature range used in our measurements indicating good homogeneity of the ingots.

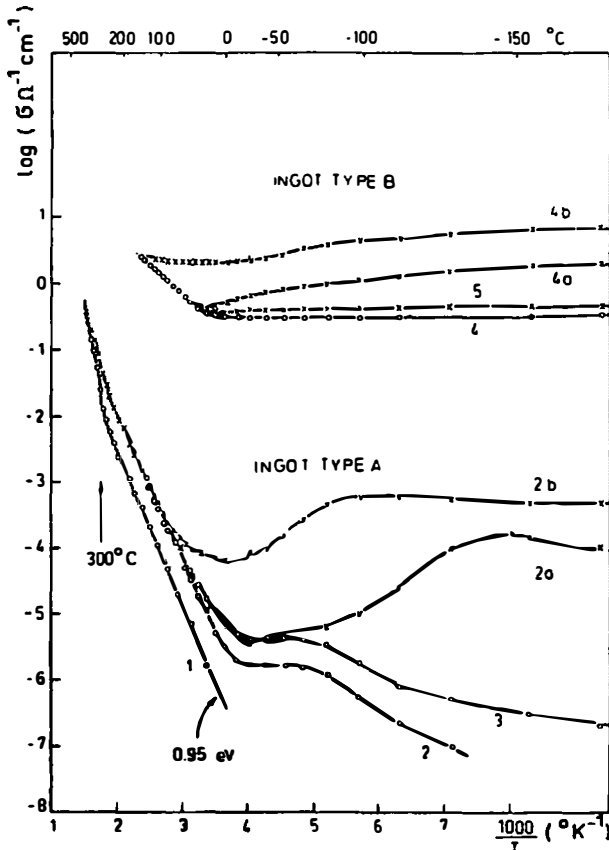


Fig. 1. Temperature dependence of dark conductivity in p-type (1) and n-type (2 and 3) samples from A ingots and n-type samples (4 and 5) from B ingots. Curves denoted with »a« were measured in the dark after illumination in liquid nitrogen. Curves »b« were measured under steady illumination.

Fig. 1 shows the temperature dependence of conductivity in several samples (curves 1, 2 and 3 for samples obtained from ingot type A and curves 4 and 5 for samples obtained from ingot type B). It can be seen that samples A have much lower conductivity than the samples from ingot type B.

Samples 2 and 3 are n-type and have a similar temperature dependence of the conductivity. At low temperatures the conductivity rises slowly with temperature, then it is constant and at higher temperatures the conductivity rises again. The last portion of the curve corresponds to the intrinsic acti-

vation of electrons and holes with the energy gap of 0.95 eV. P-type samples give the same slope (curve 1). The lower value of conductivity of this sample is probably due to different mobilities of electron and holes.

The very important point about these measurements is their reproducibility with increase and decrease of temperature. Conductivity vs temperature measurements were recorded on an XY-recorder and were reproducible in the temperature range from liquid nitrogen to 300 °C. On heating to 300 °C and above p-type sample were converted into n-type (Fig. 1, curve 1). N-type samples (Fig. 1, curve 2 and 3) showed an increasing conductivity at temperatures above 300 °C. These heat treatments resulted in an increase in the room temperature conductivity of the samples. Knowing the influence of excess In and Se on the conductivity it was concluded that selenium had been evaporated from the sample. It is interesting to note that the irreversible conductivity increase in n-type specimens heated above 300 °C could be reduced by 10 — 20 % by regrinding the sample surfaces. As the surface of the sample was n-type before grinding it is probable that this recovery was caused either by removing an oxide film from the surface or by removing a region of higher selenium content.

#### 4. Photoconductivity

Fig. 1 shows the temperature dependence of conductivity (curves 2b and 4b) under illumination from a small (4W) filament lamp at a distance of about 2 cm from the sample. As can be seen from these curves thermal

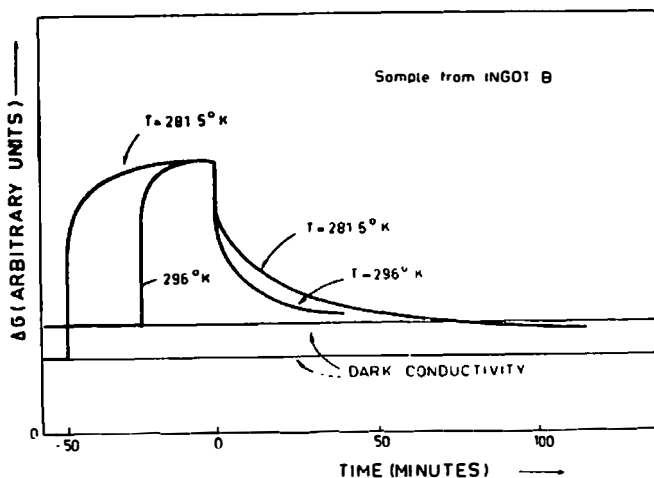


Fig. 2. Oscillograms of conductivity decay after a light pulse with  $\lambda = 0.97 \mu\text{m}$ .

quenching of photoconductivity was observed in samples made from ingot type A at temperatures of  $-73^{\circ}\text{C}$  and above. This can be explained by two levels in the forbidden gap<sup>10</sup>. Samples from ingot type A were very good photoconductors at low temperatures.

The photoconductive spectral response was also measured in sample obtained from both type of ingots. From the long wave drop of photoconductivity the width of the energy gap was found to be  $(1.18 \pm 0.02)$  eV for samples A and  $(1.18 \pm 0.01)$  eV for samples B.

Dynamic characteristics of photoconductive decay were also measured. The samples were exposed to monochromatic light of energy somewhat larger than that of the energy gap. The decay of photoconductive response after exposure to a light pulse shows two components; one short and one long. This shows that the response time is influenced by the combined effects of both recombination centres and traps. The long tail in the decay of photoconductivity is much more significant in specimens made from ingots type B. Fig. 2 shows the relaxation of the photoconductivity of a n-type specimen from ingot type B, measured at two temperatures  $T_1 = 281.5^{\circ}\text{K}$  and  $T_2 = 296.0^{\circ}\text{K}$ . It can be seen that the long time component of decay is very sensitive to temperature. Fig. 3 shows logarithm of photoconductivity vs time. The last part of the curve  $\log \Delta\sigma$  vs time is a straight line. This means that the excitation of holes from the trapping level is the only process which influences the decay of photoconductivity. As the difference between  $T_1$  and  $T_2$  is small it is possible to make a simple calculation which gives the position of the trapping levels of holes. The result of this calculation is that this level lies above the valence band at the distance

$$E_t = k \ln \frac{\text{tg } \alpha_1}{\text{tg } \alpha_2} \cdot \frac{T_1 T_2}{T_2 - T_1},$$

where  $k$  is the Boltzmann constant and  $\alpha_1$  and  $\alpha_2$  are angles of the slopes obtained from the end part of curves at temperatures  $T_1$  and  $T_2$ , respectively. Using this formula we obtained  $E_t = 0.62$  eV. The same experiment with samples A was not possible because the influence of the long-time decay component was too small.

An attempt was made to measure thermally stimulated currents on samples from ingots A and B. A maximum in the curve was found only in the case of n-type samples made from ingot type A (Fig. 1, curve 2a). This again means that at least two levels are present in the forbidden band gap. Since the maximum of thermally stimulated currents is at a low temperature, about  $-150^{\circ}\text{C}$ , the determination of the position of the lower level with the known methods gives only that it is less than 0.1 eV.

In samples made from ingots type B a maximum was not observed (Fig. 1, curve 4a) probably due to the very long time for the decay of photoconductivity.

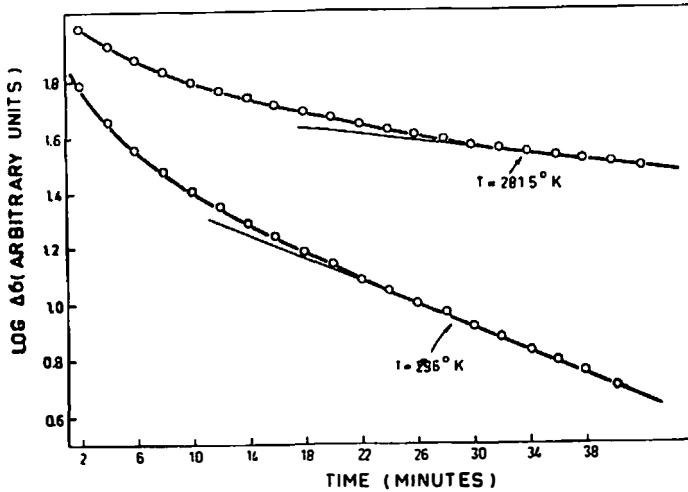


Fig. 3. The plot of  $\log \Delta\sigma$  vs time for the sample shown in Fig. 2.

### 5. Discussion

It seems that it is difficult to obtain specimens in the region of intrinsic conductivity. Evaporation or oxidation of selenium cause that conductivity increases with temperature more than intrinsic excitation predicts (See Fig. 1). This fact can explain why other authors obtained different results for the forbidden energy gap. The limitation at lower temperature comes from the influence of impurities and small deviations from stoichiometry. Our specimens made from ingots type A revealed a relatively wide region of intrinsic conductivity. Our value of 0.95 eV obtained from p- and n-type specimens (A ingots), together with one result in<sup>5)</sup>, is very probably the true energy gap. The values of 1.18 eV for the energy gap obtained from photoconductivity measurements is in agreement with<sup>4)</sup>. Thus the »optical« and »intrinsic« activation energies are not the same.

It is obvious that the crystallisation procedure has a great influence on the properties of InSe. Cleavage properties and the influence of trapping are pronounced in samples made from ingots type B. This means that a temperature gradient along the ingot during solidification prevents the growth of compact crystals. The samples made from ingots type A did not exhibit

cleavage properties. The very low conductivity of such samples, together with the small influence of trapping, indicates that their method of preparation can give large monocrystals.

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## ELEKTRIČNA I FOTOELEKTRIČNA SVOJSTVA INDIUM SELENIDA

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### S a d r ŷ a j

U radu su prikazana mjerenja električne vodljivosti, fotovodljivosti i rendgenska mjerenja na monokristalima indium selenida. Pokazano je da metoda preparacije ima utjecaj na spomenuta svojstva. Intrinzična veličina zabranjene zone, izmjerena pomoću temperaturne ovisnosti vodljivosti, iznosi 0.95 eV, dok veličina zabranjene zone, dobivena iz fotovodljivosti, iznosi 1.18 eV. Mjerenje relaksacije fotovodljivosti daje energetski položaj stupica za šupljine od 0.62 eV.