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Photodielectric investigations of zinc sulphide activated with copper

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Experimental investigations of the photodielectric effect in polycrystalline zinc sulphide (ZnS-Cu) activated with copper have been carried out. It has been pointed out that this effect is associated with the photoconductivity of phosphor grains. A proposal has been made to apply the photodielectric effect in ZnS-Cu for the construction of a detector for measuring UV-radiation.

1. Introduction

If a photoconductor is mounted as a dielectric in a capacitor in which an alternating electric field is applied, then the capacity and dielectric losses of such a capacitor increase during the absorption of electromagnetic radiation. This phenomenon, called the photodielectric effect, has been observed in the polycrystalline powders of ZnS, ZnO and CdS as well as in CdS and ZnS monocrystals. This effect depends upon the presence of activators in the above-mentioned photoconductors.

In order to explain the photodielectric effect several hypotheses have been put forward. They are exhaustively represented in papers [1–14].

Our own experiments on the polycrystalline ZnS-Cu powders, during which the capacity of capacitors, the dielectric loss factor and electrical conductivity were measured simultaneously, support the Kallmann's hypothesis [1–2]. The results of these investigations will be presented in the paper. Moreover, the application of the photodielectric effect in the construction of a detector for measuring UV-radiation will be proposed.

2. Experimental part

Experimental investigations of the photodielectric effect were performed on powdered electroluminophores of zinc sulphide (ZnS-Cu), activated with copper in concentration of 10^{-2}–10^{-1}%. The investigations were performed using flat (of thick 40–200 μm) capacitors with the area of 4 cm^2, in which polycrystalline zinc sulphide has been suspended in epoxy resin Epidian 5. One plate of the capacitor was formed by a thin electrically conducting transparent layer of SnO_2 deposited on Corning glass by the method of hydrolysis of activated $SnCl_4$ [15] and the other one — copper plate. The capacitors were obtained in the following way: fine-grained ZnS-Cu activated with copper was mixed with epoxy resin in the weight ratio of 1.5 : 1 and placed between the electrodes and then pressed to the required thickness. The structure of the capacitor is presented schematically in Fig. 1.

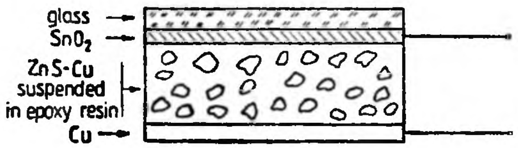

Fig. 1. Schematic diagram of the capacitor

The capacity C, dielectric losses $\tan\delta$, and the electrical conductivity G of the capacitor increase under action of the UV-light. Measurements of C, $\tan\delta$ and G were performed at room temperature by means of the Meratronik 315 A automatic bridge operating at the frequency of 1 kHz. The measuring voltage was 5 V.

As it is known, the quantities we have measured are related according to the formula

$$G = \omega C \tan\delta.$$

Thus, only two of them are mutually independent. However, in the diagrams presented in the sequel they will be shown as the functions of the illumination intensity, capacitor thickness, etc. This better illustrates the reliability of the hypothesis concerning the relation between the observed photodielectric effect and the photoconductivity of the substance.

Using a UV VIS spectrophotometer it has been found that Corning glass plates, on which a layer of SnO_2 and a layer of epoxy resin Epidian 5 were deposited, are transparent for UV-radiation down to 295 nm.

The capacitor was illuminated with UV-radiation emitted by an HBO-50 or HBO-200 mercury discharge lamp and filtered by an UG1 absorption filter. The intensity of UV-radiation was changed by changing the number of UG1 absorption filters mounted in the course of the light beam. During spectral measurements the inlet of a ZMR-3 monochromator was illuminated with light emitted by an XHP 150/GS xenon lamp. The tested capacitor was placed behind the outlet slot. The radiation intensity was measured by means of a VTh-1 vacuum thermo-couple.

The examined crystalline phosphors ZnS-Cu show a strong blue-green photoluminescence when exposed to UV-radiation, as well as an intensive electroluminescence in alternating electric field of the audio frequency.

3. Results of measurements

Figure 2 represents the increase in capacity C, dielectric loss factor $\tan\delta$ and electrical conductivity G of the capacitor depending on the relative intensity I/I_0 of UV-radiation ($I_0 = 172$ μW/cm²). The capacitor thickness was 60 μm.

It can be seen from the figure that the capacity C is a monotonic function of the intensity of UV-radiation. The changes of the capacity are accompanied by relatively fast changes of the electrical conductivity which reaches quite rapidly its saturation value with the increasing illumination intensity. The dielectric loss factor tan δ exhibits a maximum, thus, according to the classification of the photodielectric effect presented in papers [7, 11] the effect is associated with the increased conductivity of phosphor grains.

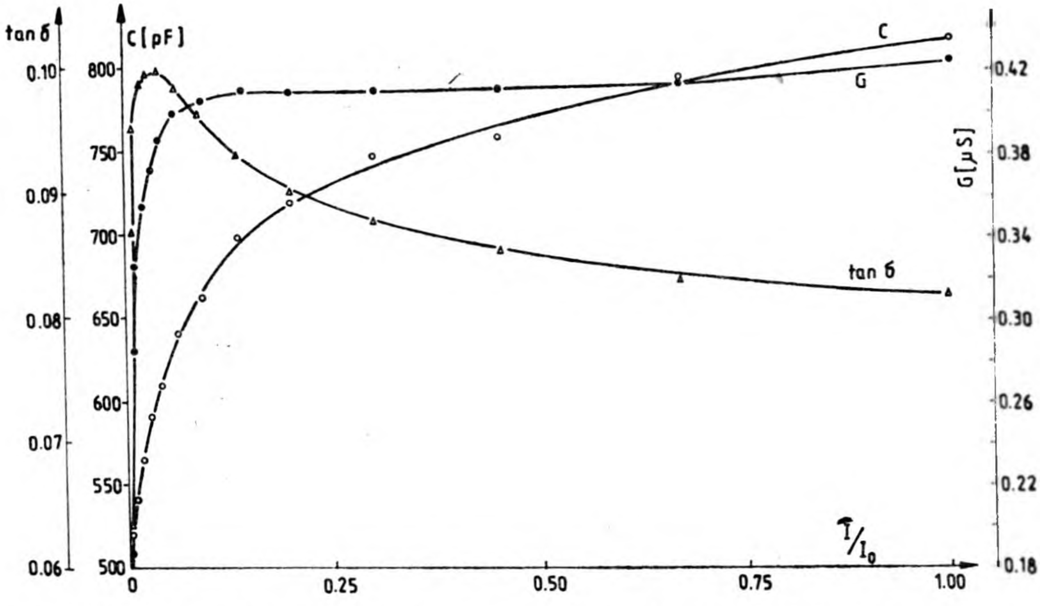

Fig. 2. C, tan δ and G of the capacitor as a function of the relative UV-radiation intensity I/I_0 ($I_0 = 172\ \mu W/cm^2$)

If the capacitor is illuminated with constant intensity of UV-radiation, then the relaxation of C, tan δ and G increases. After some time from switching off the illumination C, tan δ and G take again their initial value. These changes are presented in Fig. 3 for 40 μm thick capacitor illuminated with UV-radiation of the intensity of $I = 10\ \mu W/cm^2$. For zinc sulphides with various Cu concentration the relaxation time of the increments of ΔC, Δ (tan δ) and ΔG to the stationary value during the illumination of capacitors ranges from 20 to 80 seconds.

The stationary values of the capacity ΔC, dielectric loss factor Δ (tan δ) and electrical conductivity ΔG increments during the illumination of capacitors depend on their thickness d. These dependences are shown in Fig. 4. The capacitors were made of zinc sulphide with the same copper concentration of $5 \cdot 10^{-2}\%$ and were illuminated with monochromatic UV-light with the wavelength $\lambda = 360$ nm and the intensity of $I = 11\ \mu W/cm^2$. It can be seen from Fig. 4

that in a wide range of capacitor thicknesses d, the increments of dielectric loss factor Δ (tan δ) are almost constant, whereas the increments of the capacity ΔC and those of electrical conductivity ΔG decrease monotonically as a function of capacitor thickness d.

Measurements of the spectral sensitivity of the photodielectric effect have confirmed the hypothesis that in the examined phosphors ZnS-Cu this effect is caused by the increasing concentration of electrons in the conduction band of grains. For UV-radiation of low intensity ($I/I_0 \approx 0.1$), the curve depicting

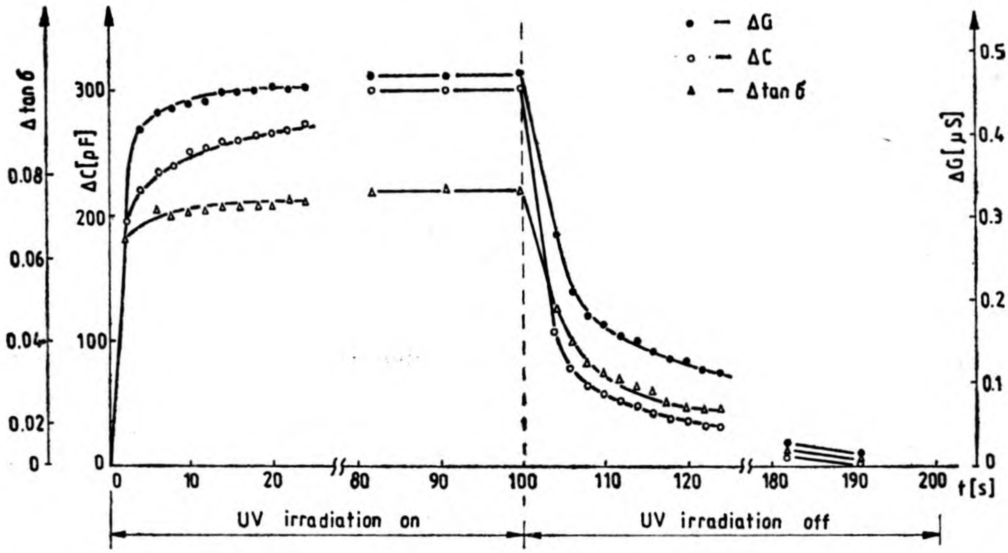

Fig. 3. The time dependences of ΔC, Δ (tan δ) and ΔG during and after illumination of the capacitor with UV-light of constant intensity $I = 10\ \mu W/cm^2$

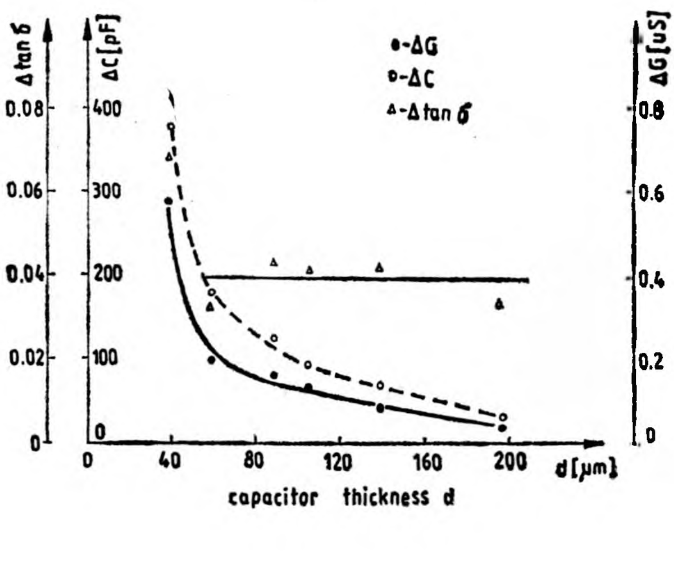

Fig. 4. Dependence of ΔC, Δ (tan δ) and ΔG on capacitor thickness d illuminated with monochromatic UV-light (360 nm) of the intensity $I = 11\ \mu W/cm^2$

the capacity increment (Fig. 2) may be approximated by a straight line. With this assumption the sensitivity of the capacitor is defined as the ratio of the increment of capacity ΔC or electrical conductivity ΔG in the stationary state to the intensity of illumination I of its surface. Spectral sensitivity of the photodielectric effect $\Delta C/I$ and electrical conductivity $\Delta G/I$ of the 60 μm-thick capacitor containing the ZnS-Cu phosphor with the concentration of Cu $5\cdot 10^{-2}$ % have been presented in Fig. 5. In these measurements the transmittance of glass plate with the deposited SnO_2 layer has been taken into account. From Fig. 5 it can be seen that the curves describing the $\Delta C/I$ and $\Delta G/I$ in function of wavelength are very similar, which means that the photodielectric effect may be attributed to the increase in electrical conductivity of phosphor grains due to the absorbed electromagnetic radiation.

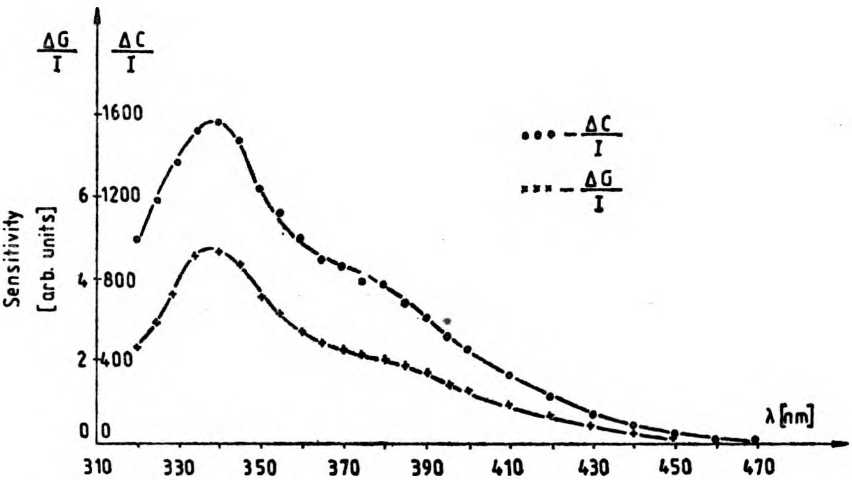

Fig. 5. Spectral distributions of the sensitivity of a photodielectric ZnS-Cu ($5\cdot 10^{-2}$ %) layer

The photodielectric effect in ZnS-Cu can be used for detecting the UV-radiation, where the capacity C of the capacitor is the quantity changing under the influence of radiation. From Fig. 2 it can be seen that the increase in the capacity is a monotonic function of the radiation intensity. In the narrow range of the radiation intensities ($I/I_0 \approx 0.1$), the increment of capacity ΔC of the capacitor may be approximated by a straight line. In order to apply the detector to the UV range instead of an SnO_2-deposited glass electrode of the capacitor an UG-1 absorption filter covered with an SnO_2 layer may be used. The transmittance values of UG-1 absorption filter alone and of that with the SnO_2 layer measured by means of a spectrophotometer are presented in Fig. 6. Spectral sensitivity $\Delta C/IS$ of the detector constructed in our laboratory is shown in Fig. 7 for the intensities I of order of several μW/cm². As can be seen, the detector is sensitive to the UV-radiation within the range of 410–300 nm and, after appropriate calibration, it can be used for measuring the radiation intensity in this range of spectrum. Unfortunately, the time-constant of the detector is rather large and depending on the concentration of Cu in the ZnS-Cu phosphors, it ranges from 20 to 80 seconds. The detector for UV-radiation measurements based on the photodielectric effect in polycrystalline ZnS-Cu can be constructed in various sizes. It seems that it could be applied to measurements of the low intensities of diffused UV-radiation, down to 10^{-2} $\mu W/cm^2$.

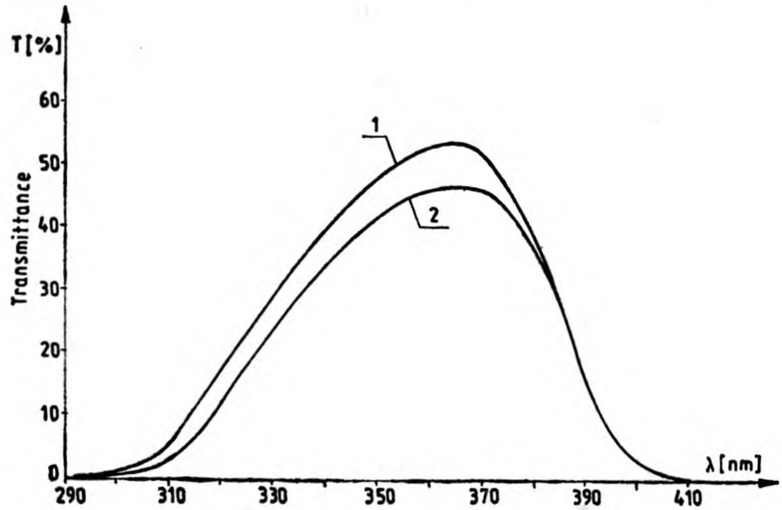

Fig. 6. Spectral distribution of the transmittance of the UG-1 filter (curve 1) and of the UG-1 filter covered with thin layer of SnO_2 (curve 2)

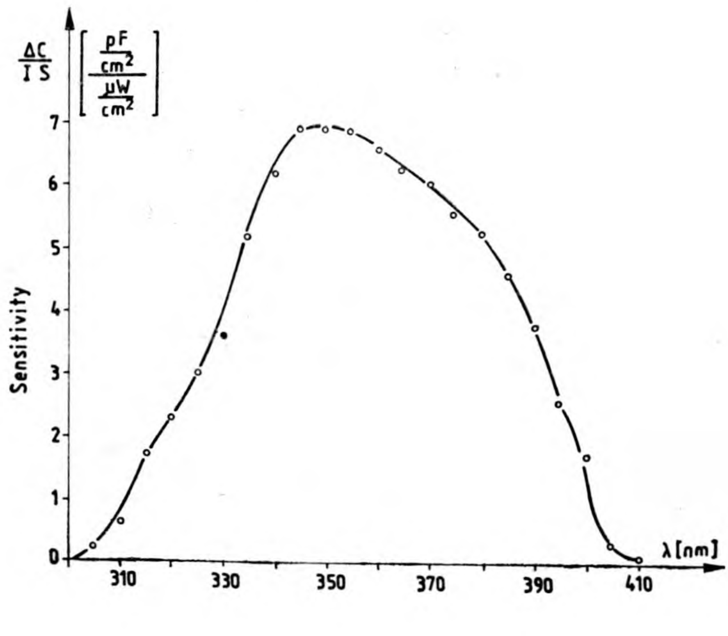

Fig. 7. Spectral sensitivity of the detector

4. Conclusions

The presented above studies on the photodielectric effect in polycrystalline ZnS-Cu show that this effect is associated with the photoconductivity of zinc sulphide grains, being accompanied by the increase in electrical conductivity of specimens. It seems that this effect can be applied in a new type of the UV-radiation detector, based on the measurements of capacity changes.

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Фотодиэлектрический детектор для измерения интенсивности UV излучения

Построен новый детектор для измерения интенсивности UV излучения, принцип действия которого основан на использовании фотодиэлектрического эффекта. Детектор представляет собой плоский конденсатор, емкость которого возрастает под влиянием UV излучения. Представлены световые характеристики детектора.