

Investigation of electroluminophores for their practical application in optical fibre sensor technology

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In this paper, the results of the experimental investigation of electroluminescent phenomena are presented. The electroluminescent effect is observed in some composite semiconductors, among others – ZnS, doped by Mn and Cu. The concentrations of impurities in good quality electrophosphores are higher than in photoluminophores and they are within the range of 10^{-4} – 10^{-3} g/g.

The worked out electroluminophors were tested in the electric field of sinusoidally changeable intensity. The influence of electric field both on spectral characteristics and electroluminescence intensity was examined.

The final aim of the tests is elaboration of electric intensity sensors which will be applied in monitoring of operation of electromagnetic power arrangements in the future.

Keywords: optical fibre sensors, electroluminescence, electric field measurements.

1. Introduction

The main advantage of fibre optic sensors is their insensitivity to the disturbances of intensive electromagnetic fields. Fibre optic sensors do not pose the danger of fire or explosion. Fibre optic sensors as well as optical channels are made of insulators of high quality dielectric properties, without metal elements. For this reason, they may be applied in control systems of high voltage power machines. In high voltage transformers, the measurements of electric field intensity give interesting and important information about their working conditions and damage states [1–4].

The idea of a contactless method for the measurement of electric field intensity is based on the influence of electric field on optical properties of some materials. As a result of electric field influence on electroluminophores, the light emission from them is observed [5,6]. The intensity and spectrum of luminescent light are the functions of electric field intensity. Consequently, the electroluminescent phenomena may be applied to construct the electric field intensity sensor [7,8].

2. Electroluminescent effects

Electroluminescent phenomena of two groups of electroluminescent effects are classified as follows [6,8]

- intrinsic electroluminescence,
- electroluminescence by electric carrier injection.

Most of known electroluminophores are based on semiconductors of the II–VI compounds [6,9]. Electroluminophores are prepared similarly to the activated crystalline photoluminophores [7,10]. The concentration of activating materials in electroluminophores is about 10–100 times higher than in photoluminophores.

The first group of electroluminophores examined by us was based on zinc sulfide doped with copper (ZnS-Cu). To obtain good quality ZnS-Cu electroluminophores, the concentration of Cu should be within the range of 10^{-4} – 10^{-2} g/g. Not every Cu impurity builds itself in a based ZnS lattice. Some Cu atoms exist as a separate phase, e.g., sometimes Cu forms Cu_2O on the crystal surface [7,11]. We have also obtained the electroluminescent materials by mixing ZnS powder with metal powder and powders of some semiconductor impurities (e.g. Cu_2O) [6,10].

The second group of the tested electroluminophores was based on ZnS doped with Mn atoms. The ZnS-Mn phosphors are rather average electroluminophores. However, additionally activated by Cu atoms, they have good electroluminescent properties [10,12,13]. Preliminary tests showed that the electroluminophores of the best sensitivity in external electric field were observed for ZnS-Mn,Cu, where the concentrations of Mn and Cu in ZnS were: $n_{\text{Mn}} \approx 10^{-2}$ g/g and $n_{\text{Cu}} \approx 10^{-3}$ g/g, respectively.

Literature informs that the experimental relation between the intensity of electroluminescent light and electric field intensity is usually presented in the following form [5,6,9]

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$$I(E) = A_0 \exp(-bE^{-1}), \quad (1)$$

where I is the intensity of electroluminescence, E is the intensity of electric field in electroluminophore, A_0 and b are the constant values, dependent on the kind of luminophore. For the majority of electroluminophores, Eq. (1) is correct in some orders of electric field intensity.

For mixtures of powder electroluminophores with various dimension of grains the relation $I = f(E)$ may be a more complicated function. The relation usually appears in the following form [10,14]

$$I(E) = B_0 E^n \exp(-aE^{-1/2}), \quad (2)$$

where B_0 , a , n are the constant values, dependent on the kind of electroluminophore.

2.1. Remarks on electroluminescence

Theoretical analysis of electroluminescence was carried out, among others, by Destriau [14], Henderson [15], and Lehmann [16]. For electroluminescent excitations, appropriate conditions must be satisfied. Electrons from donor levels or from electron traps must be transported to the conduction band. In external electric field, some electrons have obtained energy and their kinetic energy E_k increases faster than it is lost as the result of collisions with phonons. Some electrons must possess the energy which is needed for the excitation of luminescent centres. Let E denote the electric field intensity, e is the electron charge, λ is the average distance between two thermal dispersions for an electron and L is the geometrical dimension of an electroluminescent cell in the direction of the electric field vector. The maximum energy value W of electrons in external electric field which can be used for atom ionisation inside the electroluminescent cell is

$$W = eU = eEL. \quad (3)$$

The energy may be entirely applied for electroluminescent centres excitation when the average thermal distance of electrons λ is bigger than the thickness of luminophore L [17]

$$\lambda \geq L. \quad (4)$$

If the part of electrons in conduction band, which meet the condition of Eq. (4), is marked as α then, according to the Boltzmann's statistics, the component α is [18]

$$\alpha \approx \exp\left(-\frac{L}{\lambda}\right). \quad (5)$$

Intensity of the electroluminescent light emission $I(E)$ depends also on the electron concentration $n(E)$ in the con-

ducting band, the probability p of an electron collision with the luminescent centre and the probability η of quantum energy emission resulting from this collision [17,18]. Luminescent intensity is proportional to the product of all these probabilities

$$I(E) \approx n(E)\alpha(E)p\eta. \quad (6)$$

In Eq. (6), the expression $\alpha(E)$ is the most important function of an electric field [18]. For most of electroluminophores (in this group for ZnS luminophores, too) other functions can be omitted. Then, intensity of the electroluminescence $I(E)$, resulting from electric field excitation appears in the form

$$I \approx \exp\left(-\frac{b}{E}\right). \quad (7)$$

When an electroluminophore is placed in the direct electric field E , the light emission has a nature of a short glitter impulse which can be explained by the dielectric polarisation effect in phosphor [16].

The second of electroluminescent effects, i.e., electroluminescence by electric charges injection, is observed if phosphor is in electric contact with a metal electrode which the voltage is connected to or if a luminophore is used in the p-n junction [15]. Such a situation may appear when luminophore on an electric electrode is evaporated. Using an injection electrode or p-n junction with reverse voltage polarisation, charge carriers going through potential barriers are accelerated to the energy sufficiently high for their optical excitations. Next, electrons may join atoms and luminescent centres and they may excite luminescent centres, too [17]. For electric polarisation of the p-n junction in the conducting direction, electrons from n-region go over to the p-region and recombine at recombination centres or they recombine with holes from the valence band [17,19]. Such recombination does not require acceleration of high electrons. The basic features of this recombination are:

- light emission when the direct current flows across the electroluminescent cell,
- proportionality of luminescent intensity to electric current intensity.

It was shown in Refs. 5, 20, and 21 that in thin layers of ZnS-Mn and ZnS-CdS,Mn phosphors the strong amplification of electroluminescent signal may be observed. These effects result from a simultaneous application of an electric field and illumination of luminescent crystal and they are defined as photoelectroluminescence. Photoelectroluminescent effects were observed both for direct electric voltage and for alternating electric voltage, if phosphor was illuminated by ultraviolet light or by X radiation [21]. For ZnS-Mn, we observed the amplification of the orange part of the light spectrum from Mn atoms, although the rest of the light spectrum from the basic ZnS material was muffled [20]. The photoelectroluminescent effect can be very in-

tense for some electroluminesces. The intensity of light emission after photoelectric excitation can be even 10 times bigger than after excitation by an electric field only [22]. Unfortunately, it is technically difficult to produce photoelectroluminescent materials with stable and reproducible optical properties.

3. Experiment

3.1. Electroluminescent cell with optic fibre light transmission

As the result of our preliminary tests, certain electroluminesces have been chosen for thorough investigation and for their future application in an electric field intensity sensor.

The first group of electroluminesces examined by us was based on zinc sulfide doped with copper (ZnS-Cu). The second group of electroluminesces was based on ZnS doped with Mn and Cu atoms (ZnS-Mn,Cu).

For the tests, electroluminesces have been prepared in the form of electroluminescent cells [5,23]. The construction of the electroluminescent cell is presented in Fig. 1.

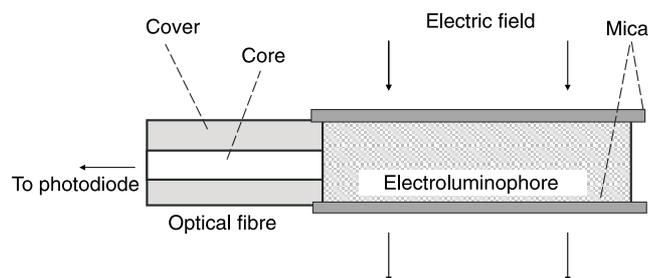


Fig. 1. Measuring electroluminescent cell.

The electroluminescent cells were performed in the form of thin tablets with a diameter of a few mm. The electroluminescent powder was mixed with epidian glue and this mixture was placed between two plates of a mica insulator with optical fibre inside. After hardening, to investigate the electric and optical properties of phosphors, the cells in electrical condensers were tested.

We used optical fibres elaborated at the Laboratory of Optical Fibre Technology, Faculty of Chemistry at Marie Curie-Skłodowska University in Lublin, Poland. The measuring cells had various geometrical dimensions and thickness for different optical fibres applied. For the preliminary examination two different optical fibres were used. The first fibre had the total diameter of 400 μm , and 200 μm of the optic core diameter and 0.26 of the numerical aperture N.A. The second fibre had dimensions 400/600 μm and N.A. = 0.24. The possibility of applying plastic fibres of 500- μm diameter was tested, too.

One observed that the cells, where the thicker optical fibre (core diameter of 400 μm) had been applied, were more sensitive. Their characteristics $I = f(E)$ were more linear and the threshold of sensitivity corresponds to the smaller value of the electric field intensity.

3.2. Experimental set-up

The experimental set-up for investigation of the optical properties of electroluminesces is presented in Fig. 2.

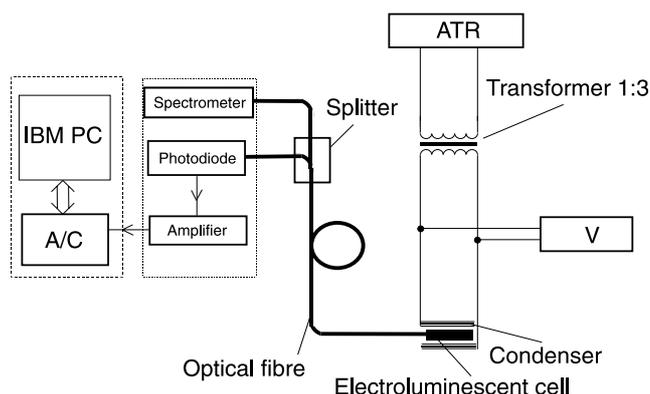


Fig. 2. Experimental set-up for investigation of electroluminescent materials.

The alternating electric voltage of 50 Hz frequency was generated by means of the autotransformer. Electric field of high intensity was formed in a capacitor, where the electroluminescent cells were placed. From the luminescent cell, the electroluminescent light was led to the photodetector by means of optical fibre. Next, the electric signal after amplification in the A/C converter was analysed. In the set-up the A/D converter of 1600 DAS type (Keithley Metrabyte LTD) has been applied. In the measuring system, the fibre optic splitter was used. This solution additionally allowed us to investigate the same electroluminescent signal by a spectrometer (spectrometer type 14.1 WOCAD, Poland).

4. Experimental results

4.1. Brightness waves

The term "brightness waves" signifies periodical changes of electroluminescent emission light caused by alternating electric field which exists inside the luminophore [6,18]. The frequency of brightness waves is two times bigger than frequency of electric field. The time shape of brightness waves depends on luminophore type (Fig. 3).

For ZnS-Mn,Cu, the shape of brightness waves had approximately sinusoidal character, but for ZnS-Cu the shape was changed. As a rule, brightness waves are out of phase to electric field excitation. A shift angle de-

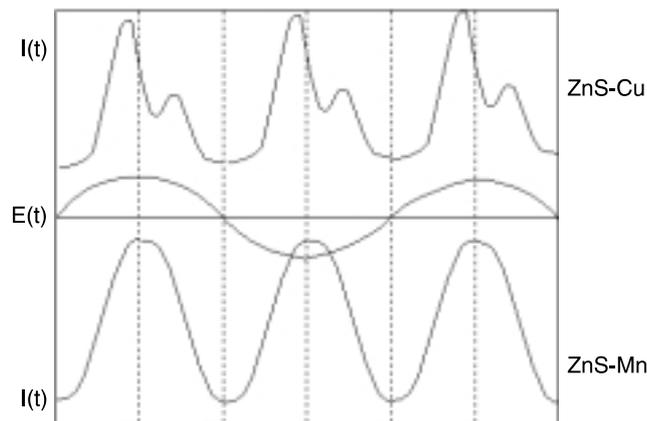


Fig. 3. Brightness waves in ZnS-Cu and ZnS-Mn,Cu electroluminophores for their excitation by sinusoidal electric field.

depends on the electric permittivity of luminophores, their electrical resistivity and frequency of electric field [17,19].

4.2. Spectral investigation of electroluminophores

In Fig. 4 the spectrum of electroluminescent signal obtained for ZnS-Cu is presented. In the cell, the optical fibre with 400- μm core diameter was used. Electroluminescent signal is in the spectrum range 540–650 nm.

Several electroluminescent cells, based on ZnS for various concentration of Cu and Mn+Cu dopants were elaborated and they were examined to obtain the best electroluminescent materials. Various electroluminophores as well as various optical fibres, applied in electroluminescent cell were tested. As mentioned above, the best sensitivity possessed the cells of a core diameter 400 μm of a quartz optical and just these cells were mainly examined.

Figure 5 presents the spectrum characteristics of emission light of ZnS-Cu electroluminophore with Cu concentrations $n_{Cu} = 5 \times 10^{-3}$ g/g for various values of electric field intensity.

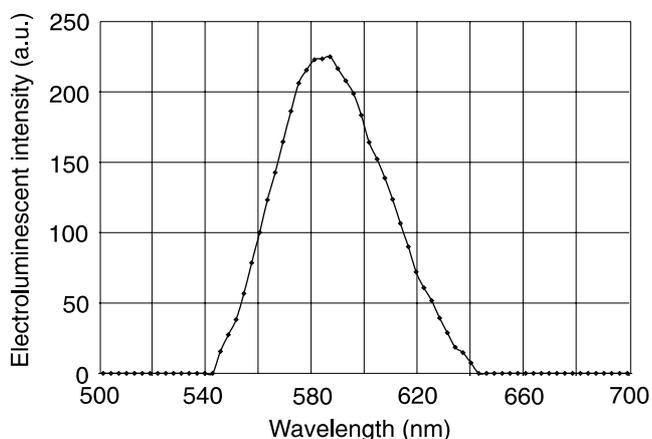


Fig. 4. Electroluminescent spectrum of ZnS-Cu for $E \approx 2 \times 10^6$ V/m.

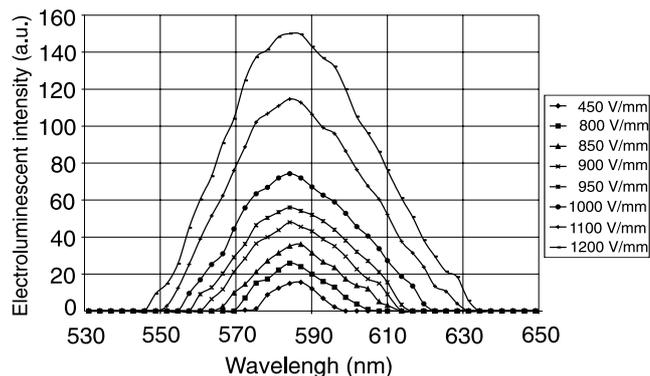


Fig. 5. Spectra of electroluminescence for various electric field intensity, ZnS-Cu, $n_{Cu} \approx 5 \times 10^{-3}$ g/g.

On the basis of these characteristics one may notice that intensity of electric field strongly influences the intensity of emission light. For ~ 500 V/mm, the electric field intensity, light emission, detected by applying spectrometer, is in the range 580–600 nm while for $E \approx 1200$ V/mm – in 540–640 nm.

In the second case, the maximum light intensity is even ten times bigger. In the range of 0–400 V/mm of electric field intensity, the electroluminescence is small and difficult to be accurately determined.

Figure 6 presents the characteristic of maximum values of electroluminescent intensity (determined on the basis of spectrum characteristics shown in Fig. 5) as the function of electric field intensity. In Fig. 4, 5, and 6, the intensities of electro-luminescence are presented in arbitrary units.

The set-up, presented in Fig. 2, additionally enabled the investigation of electroluminescent signals by means of a photodiode as an electroluminescent light detector. The high sensitivity photodiode FLM 3B was used. In Fig. 7, the relations between the intensity of electric field E and the intensity of emitted light $I = f(E)$ for three various electroluminophores are presented. Intensity of emitted light is given in arbitrary units.

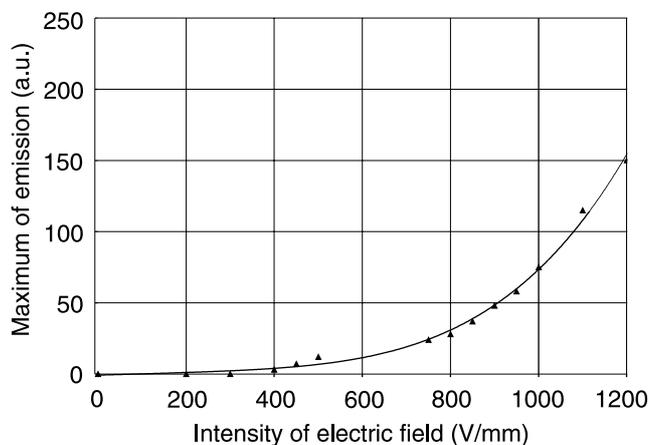


Fig. 6. Maximum of intensity of electroluminescent emission as a function of electric field intensity, ZnS-Cu, $n_{Cu} \approx 5 \times 10^{-3}$ g/g.

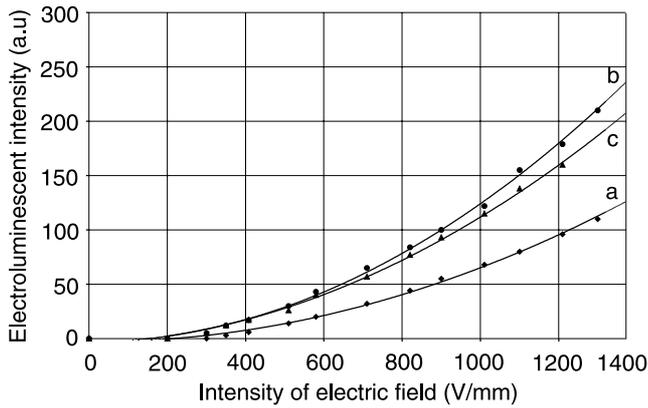


Fig. 7. Intensity of electroluminescence as a function of electric field intensity: (a) ZnS-Cu, $n_{Cu} \approx 5 \times 10^{-3}$ g/g, (b) ZnS-Mn,Cu, $n_{Mn} \approx 1 \times 10^{-2}$ g/g, $n_{Cu} \approx 1 \times 10^{-3}$ g/g, (c) ZnS-Mn,Cu, $n_{Mn} \approx 1 \times 10^{-2}$ g/g, $n_{Cu} \approx 2 \times 10^{-3}$ g/g.

The characteristics presented in Figs. 6 and 7 show that the accuracy of the determination of electroluminescent intensity strongly depends on intensity of electric field. For electric field intensity to some hundreds V/mm, the accuracy is of a single percent order. For electric field intensity of above 1000 V/mm, the presented measuring system makes possible to obtain the results of an accuracy of the order of 1%. For the higher electric field intensity, the accuracy may be even better.

Figure 8 presents the same relations but in the coordinate system $\ln(I/I_0) = f(1/E)$. It can be admitted that the experimental relations of the intensity of electroluminescent light on the intensity of electric field are in good agreement with the relation theoretically predicted and described by Eq. (1).

5. Final remarks

The aim of the presented investigations was to explain the possibility of applications of electroluminescent effects for construction of optical fibre electric field intensity sensors.

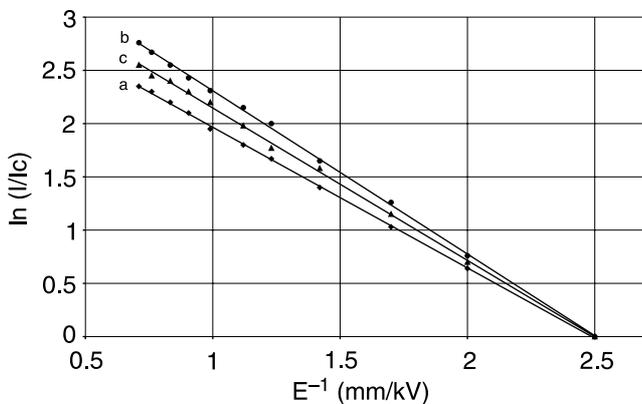


Fig. 8. The relations $\ln(I/I_0) = f(1/E)$ for: (a) ZnS-Cu, $n_{Cu} \approx 5 \times 10^{-3}$ g/g, (b) ZnS-Mn,Cu, $n_{Mn} \approx 1 \times 10^{-2}$ g/g, $n_{Cu} \approx 1 \times 10^{-3}$ g/g, (c) ZnS-Mn,Cu, $n_{Mn} \approx 1 \times 10^{-2}$ g/g, $n_{Cu} \approx 2 \times 10^{-3}$ g/g.

For this purpose, optical properties of semiconductors of II–VI group were examined. The fibre optic electric field intensity sensors, which will be elaborated on the basis of the examinations presented here, belong to the group of intensity sensors [6]. For this reason, very important problem is to assure good and stable coupling between the optical fibre and electroluminescent, as well as between the optical fibre and a photodetector. Adequate coupling between them may minimise the losses of electroluminescent light. In the optical track of the set-up, selfoc lens and optical fibre with a great numerical aperture were used. It could be observed on the basis of theoretical analysis, that the relation between intensity of electroluminescent emission light and the electric field intensity is of an exponential character Eq. (1).

This dependence was confirmed during experimental tests. It could be noticed from the exponential results that sensitivity of our system is much higher for the higher electric field intensity. For this reason, the electroluminescent sensors are aimed, first of all, at the measurements of high electric field intensity. For weak electric field, the obtained results are of a great uncertainty. The fibre optic electric intensity sensors elaborated on the basis of the presented investigations are of small dimensions. The optical parts of sensors, e.g., the electroluminescent cell and optical fibre channel are made of non-metallic elements of a high resistance. For this reason, the luminescent fibre optic sensors are likely to be used in high voltage electric arrangements [9]. Having small geometrical dimensions, the sensors could be used in inaccessible places inside electric machines.

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