

# **Blue luminescence of ZnS-Sn luminophores\***

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In this paper the experimental results of certain luminescence properties of tin-activated ZnS are presented. It was found that tin, which enhances luminescence, does not introduce its own luminescence centres into the blue-green emission range. Thermoluminescence curves show that Sn occupies the ZnS electron traps.

## **Introduction**

The characteristic orange and red photoluminescent emission of Pb- and Sn-activated ZnS was first described in papers [1-4]. MITA and SUGIBUCHI [4] presented a model of the red emission centre in ZnS-Ge, based on measurements of excitation, emission, and absorption spectra, and the results of studies on EPR in ZnS luminophores activated by elements of the IV B group. The data presented by these authors [4] indicate that tin (concentration  $10^{-2}$ ) in ZnS forms the level of the red emission centre with a maximum near 1.72 eV. UEHARA [5] studied the structure of luminescence centres in ZbS and  $\text{Ca}_3(\text{PO}_4)_2$  activated by the elements III B and IV B of the periodic system. Analyzing the emission, reflection spectra and thermoluminescence curves Uehara suggested (from the aspect of the theory of molecular orbitals) an energy structure of the luminescence centres formed by the  $\text{Ge}^{2+}$  and  $\text{Sn}^{2+}$  ions in the  $\text{Ca}_3(\text{PO}_4)_2$  and In in the ZnS. As it was shown in studies [6-8] tin intensifies the blue and green luminescence in ZnS and ZnS-Cu. The intensification of the luminescence emission is considerable and the values of the intensification coefficient depend on the concentration of tin in ZnS [6, 7]. It seems to be of a great importance from practical viewpoint to get the information which would confirm or reject the hypothesis concerning the luminescence centres of tin in ZnS.

In the investigations presented here an attempt was made to study the basic photoluminescent properties of Sn-doped ZnS and to compare them with those of self-activated ZnS luminophores obtained under the same conditions with the same host material.

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## Results of measurements

The luminescence measurements, i.e. thermoluminescence, emission spectra and temperature quenching curves were made on powdered phosphors obtained by a similar method to that described in paper [6]. The tin concentration in ZnS was  $5 \times 10^{-4}$  g/g. The photoluminescence emission spectra at a temperature of liquid nitrogen were prepared by means of a monochromator DMR-4 and a photomultiplier EMI 9558 QB. The samples were excited by UV-radiation from a mercury lamp (313 nm, 365 nm). To obtain the thermoluminescence measurements the sample was heated in an apparatus at a constant speed of  $0.3^\circ/\text{s}$  at temperatures ranging from 83 to 473 K. Figure 1 shows two thermoluminescence curves (standardized to height with respect to stationary emission) for a tin-doped luminophore (solid line) and for self-activated ZnS (dotted line). The samples were excited by the same wavelength of UV-radiation (the radiation intensity and excitation time were identical in both cases). Both sulphides gave an intensive blue thermoluminescence in a comparatively wide range of temperatures and their main thermoluminescence emission maxima were slightly shifted (133–138 K). As it can be seen from fig. 1 the introduction of tin

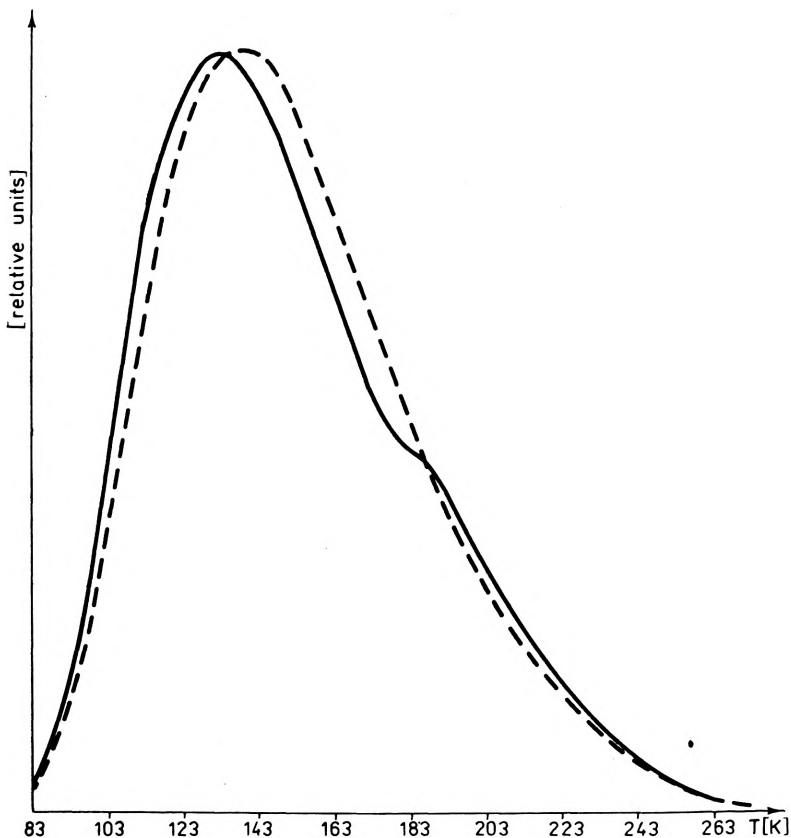


Fig. 1. Thermoluminescence of SA ZnS (dotted line) and tin-activated ZnS (solid line)

into ZnS causes a certain deformation of the thermoluminescence curve, another distinct maximum is formed in the region of 188 K and the main thermoluminescence maximum is shifted towards the lower temperature with respect to that of ZnS. The positions of the thermoluminescence maxima for ZnS-Sn are in fair agreement with those noted for this type of luminophores by UEHARA [5].

The thermoluminescence curves of both samples are not elementary and it may be assumed that these luminophores contain at least a few groups of electron traps of relatively wide energy bands. The contributions of the various electron trap groups to the thermoluminescent emission are changing.

It may be assumed that in the energy structure of ZnS tin occupies the position at the electron trap level of ZnS thermic energy of about  $E_T = 0.34$  eV. This conclusion would be in agreement with the energy model suggested in paper [4] for ZnS activated by the elements of the IV B group of the periodic system.

Figure 2 shows two excitation spectra at room temperature on the ZnS-Sn (solid line) and of the self-activated ZnS (dotted line). The two phosphors are characterized by a similar location of the maxima of their luminescence efficiency. Each of them

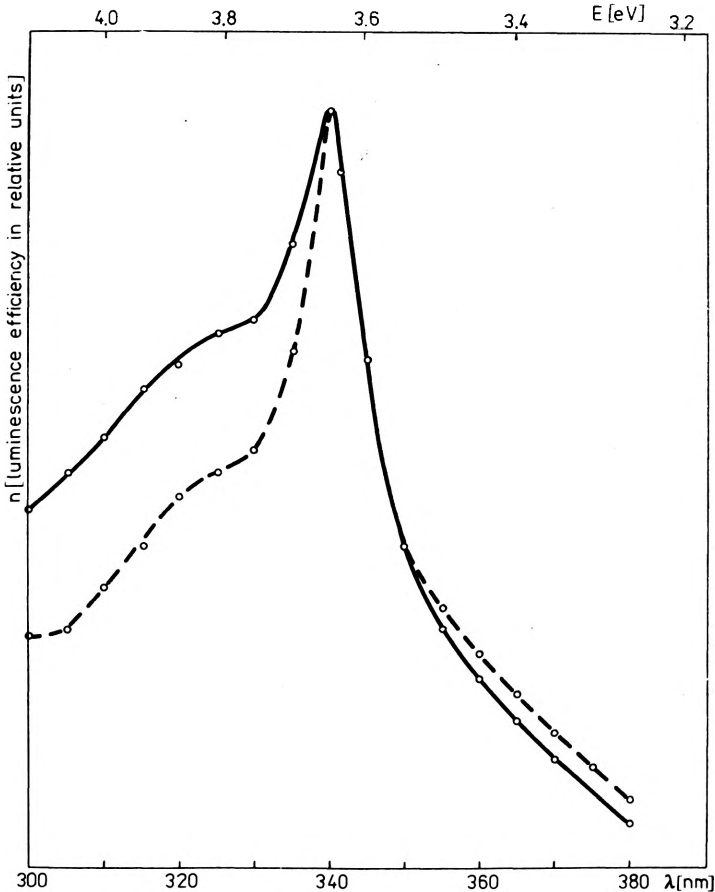


Fig. 2. Excitation spectra of ZnS-Sn (solid line) and ZnS (dotted line)

is composed of two distinct bands, the one with a higher energy (3.90 eV) may correspond to the absorption edge, and the other band (3.65 eV) may due to the characteristic absorption of the centres.

The comparison of the two curves (excitation spectra) allows to state the increase of the quantum efficiency for ZnS in the vicinity of the edge absorption. In the present investigations the SA ZnS-Sn photoluminescence spectra were resolved into single bands. This procedure of resolving continuous spectra into single bands makes it possible either to confirm or reject the hypothesis concerning the formation of luminescent emission centres in the blue-green ranges by the tin ions in the ZnS. The resolution of the continuous spectra into single bands was carried out by means of the Aencev-Fok method [9, 10]. The contours of the various spectra of zinc sulphides were obtained by excitation with different wavelengths, infrared stimulation and by making use of the phosphorescent emission of these luminophores.

In the figure 3 (the functions of the relative number of  $N$  quanta and energy  $h\nu$ )

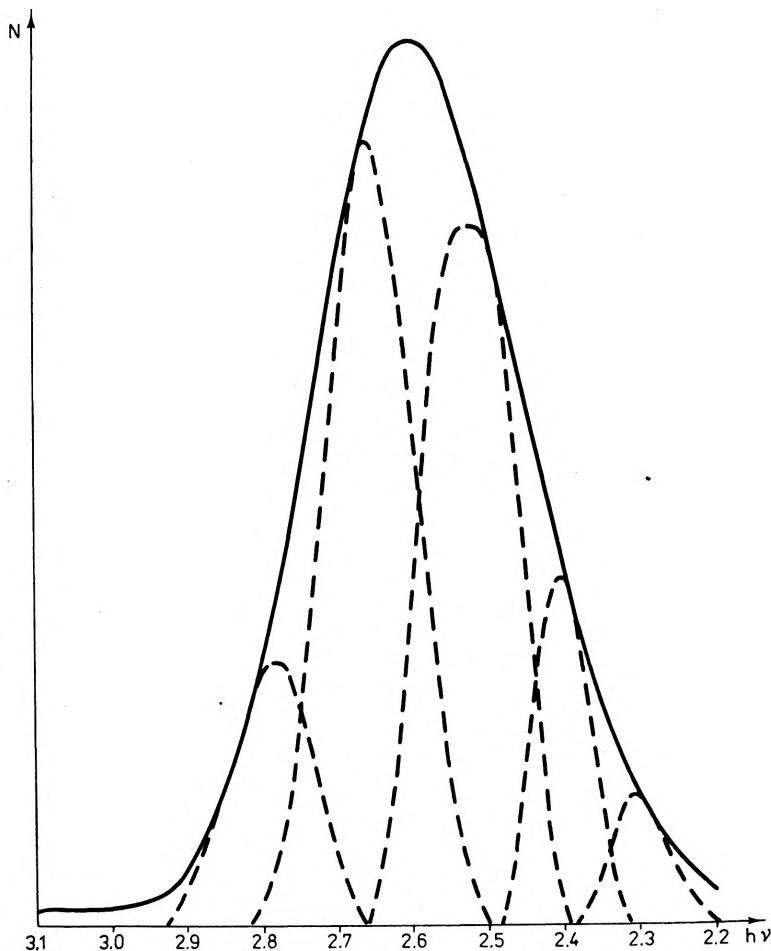


Fig. 3. ZnS-Sn Photoluminescence spectrum excited by a wavelength of 313 nm and the single emission band forming this spectrum

the ZnS-Sn photoluminescence spectrum contour and its component bands with the maxima in the region of 2.92, 2.78, 2.66, 2.50, 2.42, 2.30 eV are presented. While comparing these band positions with the ones of the self-activated zinc sulphides reported by FOK [9] and BUKKE et al. [10], it is seen that the same emission bands 2.92, 2.66, and 2.50 eV are present in both these types of luminophores in the violet-blue range. The appearance of an additional band 2.78 eV for ZnS-Sn would indicate the presence of tin luminescence centres induced by tin ions. It was, however, found that the photoluminescence spectrum of self-activated ZnS obtained from the same host material (zinc sulphide of a luminophore purity) gave emission bands identical to those emitted by a tin-doped luminophore. Figure 4 shows the contour of SA ZnS photoluminescence spectrum and the single bands into which it could be resolved. As, however, the 2.78 eV band also occurs in SA ZnS (fig. 4) thus tin is not responsible

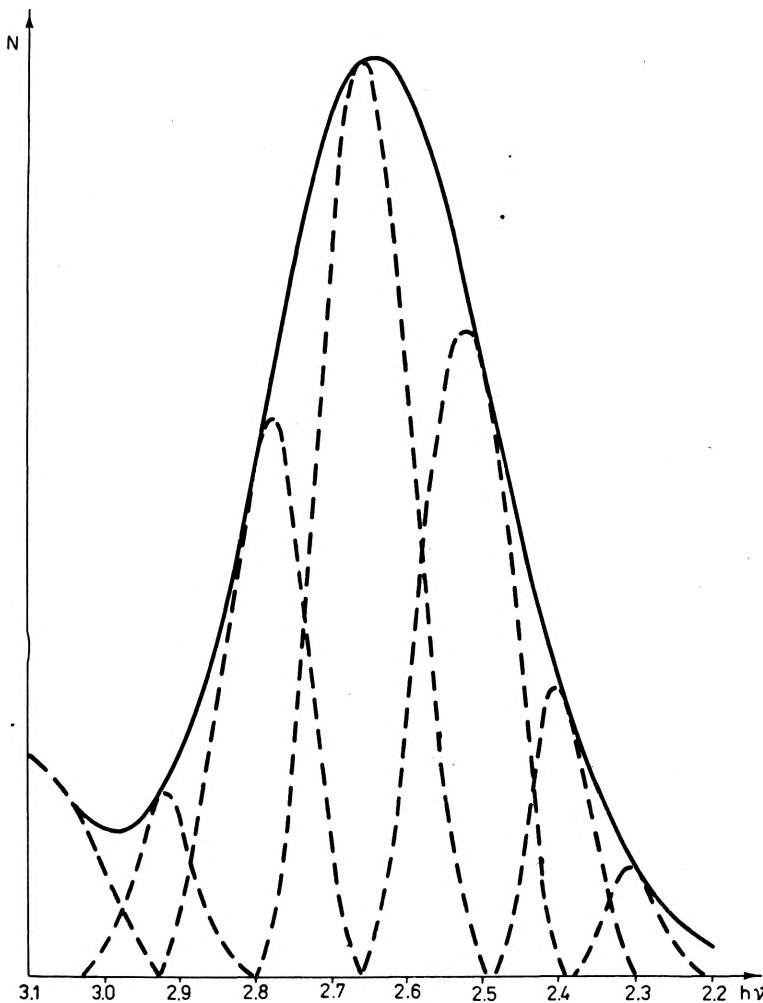


Fig. 4. SA ZnS photoluminescence spectrum excited by a wavelength of 365 nm and the single emission band of this spectrum

for its presence in the luminophore. This band 2.78 eV may be connected with either the dopant contained the zinc sulphide of luminophore purity or perhaps with the presence of the luminescence centre formed during the heat treatment of the luminophore in the atmosphere of air and sulphur.

From the results of the resolution of the ZnS and ZnS-Sn spectra into single emission bands it might be inferred that tin does not introduce its own emission bands into the blue-green range and that the intensification of the luminescence of these sulphides is not related to luminescence centres introduced by tin.

The different shapes of the ZnS-Sn luminophore photoluminescence spectra are due to the differences in the contribution of the various emission bands. Varying conditions of luminophore excitation are responsible for the different contributions of the various emission bands. Our hypothesis that tin in ZnS does not give its own bands in the blue-green emission range is substantiated by the luminescence curves illustrated in fig. 5 (the curve is standardized to one height). The process of tempe-

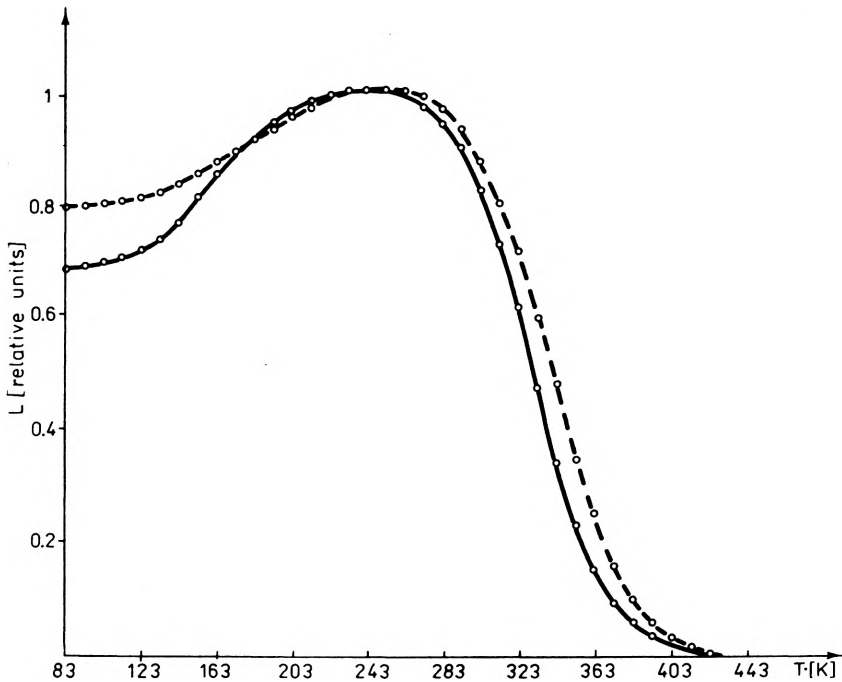


Fig. 5. Quenching temperature curve of SA ZnS (dotted line) and ZnS-Sn (solid line)

perature quenching for SA ZnS (dotted line) and ZnS-Sn (solid line) begins in the region of 253 K and is similar for both luminophores. These curves in the temperature ranges of 253 K and 383 K can be described by the following equation:

$$\eta = \frac{1}{1 + C e^{-E/kT}},$$

where  $C$  — constant,  $E$  — thermic energy of the centre activation.

## Conclusions

From the results of experiments on certain luminescence properties of tin-activated ZnS presented in this paper the following conclusions may be drawn:

— tin does not introduce its own emission bands into the blue-green range of luminescence,

— tin, as a dopant, occupies the position of the electron trap level in ZnS and increases the concentration of this type of trap in ZnS-Sn.

The debayograms prepared [8] for ZnS and ZnS-Sn are identical for the both structures. From the comparison of the ion radii ( $Zn^{2+} = 0.74 \text{ \AA}$ ,  $Sn^{2+} = 1.12 \text{ \AA}$ ,  $Sn^{4+} = 0.71 \text{ \AA}$ ) it can be suspected that the tin ion  $Sn^{4+}$  incorporated in the ZnS lattice occupies the defect which was left by the zinc ion forming the level of the electron trap (thermic energy  $E_T = 0.34 \text{ eV}$ ) in ZnS.

It can be supposed that the tin ions incorporated in the ZnS lattice occupy the defects left by the zinc ions and that, compensating for the negative electric charge in the crystals, they facilitate the formation of centres characteristic of self-activated ZnS luminophores. Tin ions incorporated in the ZnS crystal lattice compensate the negative electric charge in the crystal and are conducive to creation of centres characteristic of autoactivated ZnS luminophores.

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## Голубая люминесценция сульфида цинка с примесью олова

В работе приведены опытные результаты некоторых люминесцентных свойств сульфида цинка, активированного оловом. Выявлено, что олово, вызывая усиление люминесценции сульфида цинка не вводит собственных центров люминесценции в области голубовато-зелёной эмиссии. Кривые температурного высвечивания показывают, что олово в сульфиде цинка занимает положение электронной ловушки.