ELECTROLUMINESCENCE SPECTRA OF (Zn, Cd)S – Cu PHOSPHORS AT 77°K

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The electroluminescence spectra of (Zn, Cd)S–Cu phosphors at room temperature are known [1-3]. We measured the electroluminescence spectra of these phosphors at 77°K and compared them with the spectra recorded at room temperature.

(Zn, Cd)S phosphors activated with copper (0.05 wt. % of the host) were prepared by roasting at 800°C by the method described in [4]. The apparatus for the spectral measurements incorporated a UM-2 universal monochromator, a ZG-10 audio generator, a DRSh-250 mercury vapor lamp, a FEU-29 or FEU-22 photomultiplier, and a mirror galvanometer. The apparatus was calibrated against a standard source—a SI6-40 measuring lamp with a known spectral energy distribution. For all the measurements we used a demountable cell containing the phosphor mixed in castor oil.

Phase analysis of the powders was effected by x-ray structural analysis. The x-ray diagrams were recorded on a URS-50I diffractometer using CuKα emission. The ratio of the amounts of the wurtzite and sphalerite modifications in the phosphors was determined from the ratio of the intensity of the (100) wurtzite line to the total intensity of the superimposed (002) wurtzite and (111) sphalerite lines. In the case of the purely cubic modification this ratio is zero, and for the purely hexagonal structure it is 1.4.

As Fig. 1 indicates, the phosphor with composition ZnS–Cu had a cubic structure. Phosphors with a CdS content greater than 20 wt. % had a hexagonal lattice. Compositions containing 5 and 10 wt. % CdS consisted of a mixture of crystallites of the cubic and hexagonal modification with a predominance of the cubic modification. This change in the structure of the phosphors was reflected in the investigated electroluminescence spectra.

Figure 2 shows the normalized (to maximum intensity) electroluminescence spectra, measured at 77°K and room temperature, of a series of phosphors containing 0 to 50 wt. % CdS. The spectra were excited by alternating fields of frequency 500 Hz, 5kHz, and 20 kHz (voltage 100-200 V). Plots of the maximum (λ_max) of the electroluminescence spectrum against the CdS content of the phosphors are shown in Fig. 3.

The electroluminescence spectra of (Zn, Cd)S–Cu phosphors show two bands, distinctly resolved at 77°K and superimposed on one another at room temperature. These bands were observed previously in the photoluminescence spectra [5-7]. Compositions with a cubic structure or consisting largely of cubic crystallites are characterized by the greater intensity of the longwave component in the electroluminescence spectrum.

The room-temperature low-frequency electroluminescence spectra (excitation frequency 500 Hz) of compositions containing ≤10 wt. % CdS consist mainly of the longwave band. The region of transition from the cubic to hexagonal structure of the phosphors is characterized by a pronounced shift of λ_max of the low-frequency electroluminescence towards the values of the shortwave band (Fig. 3, curve 1). A similar anomaly at low frequencies was observed in [2]. The room-temperature electroluminescence spectra of...
Fig. 2. Electroluminescence spectra of (Zn, Cd)S–Cu phosphors at: a) 77°C (excitation frequency 500 Hz (1), 5 kHz (2), 20 kHz (3)); b) room temperature [excitation frequency 500 Hz (4), 5 kHz (5), and 20 kHz (6)]. The figures indicate the percentage weight CdS content of the phosphors.

Fig. 3. Wavelength of maximum of electroluminescence spectrum as function of composition of (Zn, Cd)S–Cu phosphors at room temperature (1, 2) [excitation frequency 500 Hz (1), 5 kHz (2)] and 77°C (3) (excitation frequency 500 kHz, 5 kHz, 20 kHz, legend as in Fig. 2) in comparison with $\lambda_{\text{max}}$ of shortwave photoluminescence band at 77°C (7).

Phosphors with a hexagonal structure consist mainly of the shortwave band. In the case of phosphors with a high content of cubic crystals the longwave component is still intense up to an excitation frequency of 5 kHz. The shortwave band becomes predominant in the electroluminescence spectra of these phosphors at 20 kHz. For hexagonal phosphors an increase in the electroluminescence excitation frequency at room temperature from 500 Hz to 20 kHz leads to a ~10 nm shift of $\lambda_{\text{max}}$ of the electroluminescence spectra towards the shortwave side.

The intensity of the shortwave band in the electroluminescence spectra of (Zn, Cd)S–Cu phosphors at 77°C, in contrast to the spectra at room temperature, is greater than the intensity of the longwave band, irrespective of the excitation frequency. An increase in the frequency of the exciting field from 500 Hz to 20 kHz causes, as at room temperature, a reduction of the longwave component in the electroluminescence spectra. This is manifested very distinctly in the electroluminescence spectra of phosphors with a predominance of cubic crystallites, where the longwave band in the electroluminescence spectra at 77°C excited by a field of frequency 500 Hz is intense, but becomes appreciably less intense at 5 kHz and 20 kHz.

Low-temperature measurements of the electroluminescence spectra of (Zn, Cd)S–Cu phosphors show that the positions of the maxima of the shortwave component of the electroluminescence spectra of any of the compositions at 77°C (Fig. 3, curve 3) are practically independent of the excitation frequency. The difference in the maxima of the electroluminescence spectra at 77°C and at room temperature excited by a frequency of 20 kHz is 13 nm on the average.

A comparison of the electroluminescence spectra with the corresponding photoluminescence spectra showed that the values $\lambda_{\text{max}}$ of the electroluminescence at 77°C coincide with the values of $\lambda_{\text{max}}$ of the shortwave photoluminescence band at 77°C. A similar fact has been reported for Zn(S, Se)–Cu, I phosphors [8] and for (Zn, Cd)S–Cu phosphors containing ≥ 20 mol. % CdS at room temperature [3].

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