

Luminescent properties of ceramics based on polymer ZnCdS:Cu,Cl

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The photoluminescence properties of ceramics based on ZnCdS:Cu,Cl powder were studied as a function of the process parameters (pressing pressure and annealing temperature) used during their preparation. It was shown that the intensity and position of the photoluminescence peaks depend on both the annealing temperature and the pressing pressure. An alternative model for the emission centers was proposed. Based on the obtained results, it can be assumed that ceramics based on ZnCdS:Cu,Cl phosphor can be used as temperature sensors.

Keywords: photoluminescence, ceramics, zinc, cadmium, sulfur.

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Introduction

Luminophores of chalcogenides of transition metals from group A^2B^6 are of interest as working media of optoelectronic devices, whose properties depend on the dimensions and imperfection of the structures [1]. Such luminophores also include triple compounds ZnCdS:Cu,Cl. There are many areas, where these compounds may be used. Compound ZnCdS:Cu,Cl, has high light intensity up to 140 cd/m² and converts electron energy 25 keV into visible light, which makes it promising for application in the professional information imaging devices, in screens of electron-optical converters (night-vision device), as amplifiers in microscopy etc. [2]. Recently a new application of ZnCdS:Cu,Cl emerged, in particular, as nanoparticles or quantum dots to label stamps, banknotes, to maintain secrecy of documents and to make infrared light diodes [3].

Currently most papers are dedicated to using the fact of temperature impact at the luminescence of the nanoparticles from ZnCdS:Cu,Cl as materials for thermometers. In these papers it was found that when the sample containing ZnCdS nanoparticles is heated, simultaneously the spectral shift and reduction in luminescence intensity were observed. Temperature dependence of the wavelength exposed to maximum radiation from temperature is linear [4]. Using the value of the luminescence maximum spectral shift, it is possible to determine the ambient temperature [5–7]. Luminescence of nanoparticles is mostly related to surface defects of their crystalline lattice [8]. Previously in paper [9] we provided a model that allows for existence of energy barriers on the surface of luminophore grains, which arise as a result of electron transition from the volume to the surface levels of adsorbed particles. These barriers significantly impact the formation of the effective capture cross section for the charge carriers in the trap centers.

The aim of this paper is to study the luminescence of ceramics based on powders Zn_{0.97}Cd_{0.03}S:Cu,Cl depending

on the technological parameters of its preparation (pressure of powder compaction and temperature of subsequent annealing).

Experimental method and procedure

The source material for ceramics was powder of grade K-93B with the following composition: Zn_{0.97}Cd_{0.03}S:Cu,Cl having blue-green glow. The size of the powder grains is approximately 1 μm. Ceramics was produced by the method of uniaxial cold compacting [10]. Ceramics was sintered from the raw product produced by uniaxial cold compacting of powder Zn_{0.97}Cd_{0.03}S:Cu,Cl in a high pressure machine of anvil type with a hole „Toroid“ at 10 MPa and 20 MPa, with its subsequent annealing on air for 2 h at 400 and 800 °C. Samples of ceramics had the disc shape with diameter of 16 mm and thickness of 3 mm.

The luminescence spectra were studied in a spectral computing complex, the main element of which is an automated monochromator MDR-23. The sample was excited with an ultraviolet laser KLM-360-40 with wavelength of 360 nm. Radiation was recorded by a photoelectronic multiplier Hamamatsu, the spectral range of the instrument sensitivity is within 230–970 nm. To measure the luminescence spectra from nitric temperatures with subsequent heating, the sample was fixed on a holder with the built-in electric oven of low capacity and was placed into a transparent cryostat made of quartz glass. The sample temperature was measured with a copper-konstantan thermocouple.

Results and discussion

Fig. 1, *a* shows photoluminescence spectra of powders Zn_{0.97}Cd_{0.03}S:Cu,Cl at room ($T = 293$ K) and nitric ($T = 77$ K) temperatures. As you can see from the figure, photoluminescence spectra have a complex structure. Two

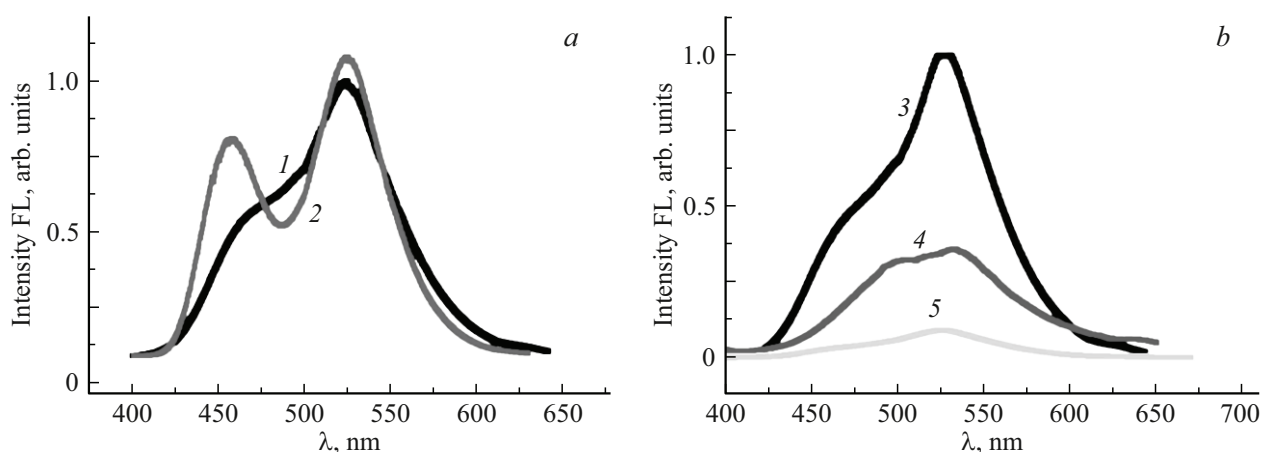


Figure 1. Photoluminescence spectrum of powder ZnCdS:Cu,Cl (a) 1 — at room ($T = 293$ K), 2 — nitric ($T = 77$ K) temperatures. (b) 3 — powder prior to treatment, 4 — after annealing 400°C , 5 — after annealing 800°C .

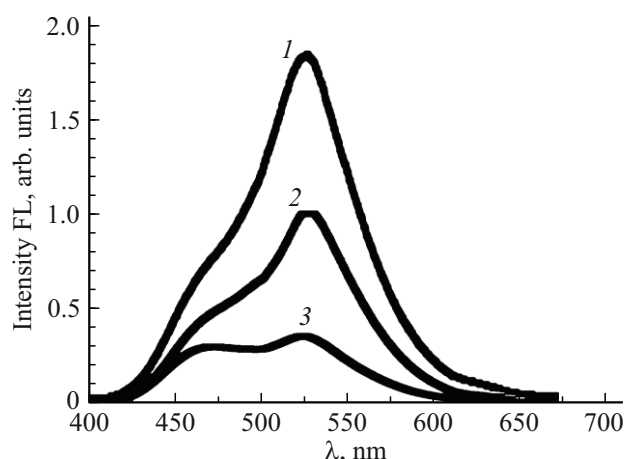


Figure 2. Photoluminescence spectrum of ceramics based on ZnCdS:Cu,Cl: 1 — source powder, 2 — ceramics annealed at 400°C , 3 — ceramics annealed at 800°C .

maxima are observed at room temperature, a more pronounced one with wavelength $\lambda_m = 530$ nm (green band), and with wavelength $\lambda_m = 460$ nm (blue band). As the sample temperature decreases down to $T = 77$ K, a minor increase in radiation intensity is observed, and this growth is more significant in the area of the band with $\lambda_m = 460$ nm.

Thermal treatment of powders $\text{Zn}_{0.97}\text{Cd}_{0.03}\text{S}:\text{Cu,Cl}$ on air causes substantial decrease in intensity of photoluminescence in the entire observed range of radiation (Fig. 1 b).

Most authors [9–12] conclude that „blue“ PL band in the area of wavelengths 450–480 nm is related to the impurity of copper atoms. Copper atoms in an interstitial position of the crystalline lattice ZnS play a donor role with the level below the bottom of the conductivity band (C-band) at 0.15 eV, substituting zinc atoms — acceptor centers with level of 0.95 eV above the valence band (V-band) ceiling. Acceptors in the $\text{Cu}_{\text{Zn}}^{+}$ state may participate in

direct band-impurity transitions, where recombination with a free electron from the C-band on them causes radiation of photons with energy $h\nu \approx 2.71$ eV, and also in formation of donor-acceptor pairs (DAP). The role of donors in pairs ($\text{Cu}_{\text{Zn}}^{+}-D_i^{0*}$) may be played by interstitial copper atoms, which captured the electron after generation of charge carriers as a result of excitation of $\text{Zn}_{0.97}\text{Cd}_{0.03}\text{S}:\text{Cu,Cl}$ with light having wavelength of 360 nm. PL bands in the „green“ (500–550 nm) area of the spectrum are related to the self-activated luminescence and bind it to internal defects of the ZnS crystalline lattice. In particular, let us consider the complex in the form of $[(D^{+}-V_{\text{Zn}}^{2-})^{-}-V_{\text{S}}^{2+}]^{+}$. Defects in the complex in the form of vacancies in zinc sublattices — V_{Zn}^{2-} and sulfur sublattices — V_{S}^{2+} are related to two-level centers and may remain in various charge states (V_{S}^{2+} , V_{S}^{+} , V_{S}^0 and V_{Zn}^{2-} , V_{Zn}^{-} , V_{Zn}^0), promoting formation of a complex energy spectrum of levels in the band gap. The acceptor in the considered complex is associate $(D^{+}-V_{\text{Zn}}^{2-})$, and fine impurities not controlled in ZnS may act as a donor. Capture of inequilibrium charge carriers generated by excitation of the luminophore with light $h\nu \geq E_g$, at the levels of zinc and sulfur vacancies converts the complexes to the excited state $[(D^{+}-V_{\text{Zn}}^{2-})^0-V_{\text{S}}^{0*}]$. Luminescent radiation $\lambda_m \approx 530$ nm is the result of the interimpurity electron transition from the level of the sulfur vacancy in inequilibrium conditions in the charge state to the acceptor level (recombination center).

Compaction and thermal treatment of powder $\text{Zn}_{0.97}\text{Cd}_{0.03}\text{S}:\text{Cu,Cl}$ in process of ceramics manufacturing causes decrease of luminescence intensity compared to the source powders, and the position of the maxima of the bands as such does not change. Fig. 2. shows the ceramics photoluminescence spectra at different temperatures of its annealing (400°C , 800°C).

Figure 3 shows the results of the studies on dependence of the luminescence intensity of ceramic powders compacted at pressures of 10 MPa and 20 MPa with subsequent annealing at 400°C .

Decrease of PL intensity in the entire spectral range during thermal treatment on air at 400°C for ceramics $\text{Zn}_{0.97}\text{Cd}_{0.03}\text{S}:\text{Cu},\text{Cl}$ is likely related to two processes — partial decomposition of complexes $(\text{Cu}_{\text{Zn}}^+ - D_i^{0*})$ and $[(D^+ - V_{\text{Zn}})^0 - V_{\text{S}}^{0+}]^{0+}$, and oxidation of the powder grain surface.

We studied the spectral dependence of luminescence intensity of powders $\text{Zn}_{0.97}\text{Cd}_{0.03}\text{S}:\text{Cu},\text{Cl}$ on temperature in the interval from -80°C to 80°C , shown in Fig. 4. In the temperature range from -80 to 80°C the blue band of radiation from $\lambda = 460\text{ nm}$ experiences a spectral shift to the low energy area of the spectrum, contrary to the green band $\lambda = 525\text{ nm}$. The shift value is approximately 0.0006 eV per degree. Dependence of spectral position of blue band maximum of powders $\text{Zn}_{0.97}\text{Cd}_{0.03}\text{S}:\text{Cu},\text{Cl}$ of radiation on sample temperature is linear (Fig. 5) and corresponds to model ideas on the donor-acceptor nature of the radiation centers. This result suggests potential use of powders as temperature sensors.

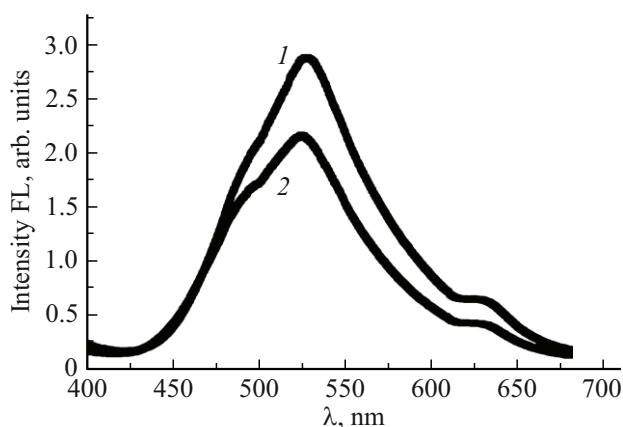


Figure 3. Photoluminescence spectrum of ceramics based on $\text{ZnCdS}:\text{Cu},\text{Cl}$: 1 — pressure of 10 MPa, 2 — pressure of 20 MPa.

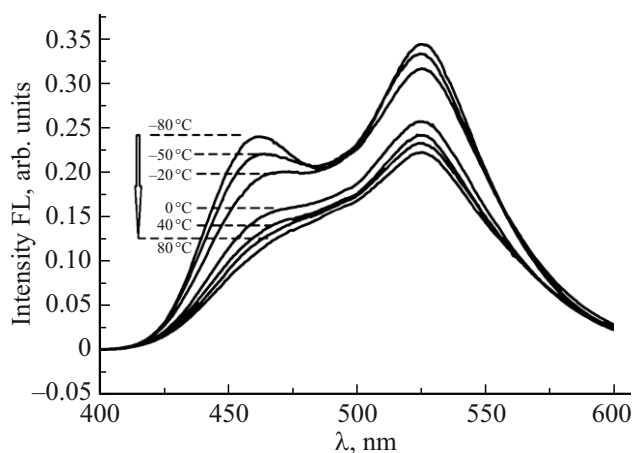


Figure 4. Photoluminescence spectrum of powders $\text{ZnCdS}:\text{Cu},\text{Cl}$ depending on heating temperature from -80°C to 80°C .

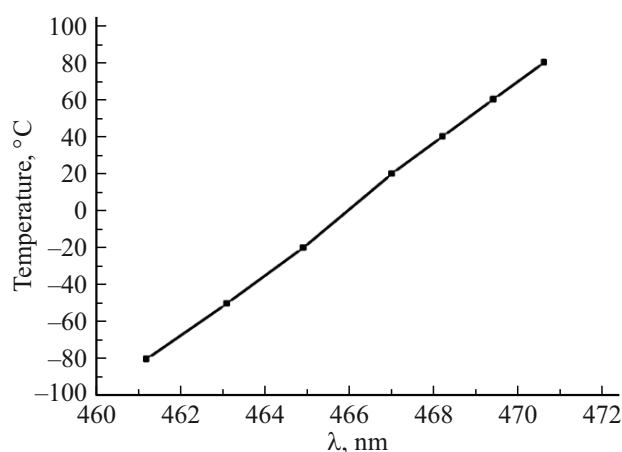


Figure 5. Spectral shift of PL band maximum $\lambda = 460\text{ nm}$ within temperatures -80 – 80°C .

Conclusion

Photoluminescence (PL) of ceramics based on powder $\text{Zn}_{0.97}\text{Cd}_{0.03}\text{S}:\text{Cu},\text{Cl}$ at room ($T = 293\text{ K}$) and nitric ($T = 77\text{ K}$) temperatures, identically to the PL spectrum of the powder as such and consists of two wide overlapping radiation bands with maxima at $\lambda_{m1} = 460\text{ nm}$ (blue band) and $\lambda_{m2} = 530\text{ nm}$ (green band), for which the point defect associations are responsible $(\text{Cu}_{\text{Zn}}^+ - D_i^{0*})$ and $[(D^+ - V_{\text{Zn}})^0 - V_{\text{S}}^{0+}]^{0*}$, accordingly. Decomposition of complexes under thermal treatment of the powder and ceramics on air and the process of sample surface oxidation is accompanied with the decrease of PL intensity in the entire spectral range. The observed spectral shift of the maximum of „blue“ PL band of ceramics with temperature change within -80 – 80°C may be used in design of temperature sensors.

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Conflict of interest

The authors declare no conflict of interest.

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