

LUMINESCENT PROPERTIES OF ZnO POWDERS SYNTHESIZED BY THE ISOVALENT SUBSTITUTION METHOD

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Abstract

Zinc oxide powders have been prepared by the isovalent substitution method by means of high-temperature annealing of a zinc sulfide powder synthesized by a chemical method. Investigation of photoluminescence (PL) spectra in dependence on annealing temperature varied from 870 to 1050°C has made it possible to find the temperature range of 920–950°C for the most active isovalent substitution of oxygen atoms for sulfur atoms and the formation of a ZnO·S phase. X-ray diffraction analysis has revealed that the powder with crystal lattice parameters $a_o = 0.3249$ nm and $c_o = 0.5206$ nm and the ratio of $c_o/a_o = 1.60$, which are characteristic of zinc oxide crystals, is synthesized at the maximum annealing temperature. It has been found that the maximum of a structureless PL band in the spectrum for the ZnO powder at room temperature is localized at 500 nm. It has been supposed that the band is caused by “free electron–acceptor” radiative transitions, where the acceptor level is 0.95 eV above the valence band edge.

1. Introduction

Zinc oxide is an important functional material used in many fields of technology. It is a direct-band-gap semiconductor with a wide band gap of 3.3–3.4 eV at room temperature and solely hexagonal crystal lattice (wurtzite structure) with parameters $a_o = 0.325$ nm and $c_o = 0.521$ nm [1]. Being an optically-transparent wide-band-gap semiconductor, zinc oxide is used for the construction of highly efficient light-emitting devices operating in blue and ultraviolet (UV) spectral ranges, solar elements, transparent conducting electrodes, thin-film transistors, sensor devices, UV-filters, etc. [2–5].

One of the promising techniques for synthesizing zinc oxide is the isovalent substitution method [6,7] that allows producing the materials with new properties. Investigation of the luminescent properties of powdered zinc oxide synthesized by the isovalent substitution method from zinc sulfide is discussed in the present paper.

2. Samples and experimental technique

A zinc sulfide powder obtained by chemical deposition from a water solution of zinc salt and thiourea [8] was used as a source material. Zinc oxide was synthesized by isothermal

annealing of the zinc sulfide powder at temperatures between 850°C and 1100°C in air for 2 h. During annealing, oxygen atoms substitute for sulfur atoms to form zinc oxide [9].

The samples used for investigation of luminescent properties were 5-mm-thick powdered zinc oxide layers deposited on glass substrates. PL spectra registered at room temperature in a range of 350–700 nm were excited by laser radiation at a wavelength of 337 nm and analyzed using an MDR-23 monochromator and a FEU-51 photomultiplier. The spectra were registered using a standard system based on synchronized detection.

3. Experimental results and discussion

PL spectra for the samples synthesized at various annealing temperatures of the ZnS powder are shown in Fig. 1. For the annealing temperature of 870°C, the main maximum of the PL band is localized at 445 nm ($h\nu = 2.79$ eV). The less-intensive PL band is localized at 465 nm ($h\nu = 2.67$ eV). As the annealing temperature increases to 920°C, the PL spectrum is slightly shifted to long wavelengths. The band at 465 nm has the highest intensity; a new band appears in the long-wave decay of the main PL band at 540 nm ($h\nu = 2.30$ eV). The band full width at half maximum (FWHM) decreases. A gradual increase in the annealing temperature of the initial ZnS powder to 1050°C causes a shift of the main PL band towards long wavelengths (Fig. 1, inset, Table 1).

Table 1. The PL band maximum position at various annealing temperatures of initial ZnS sample

$T_{\text{anneal}}, ^\circ\text{C}$	$\lambda_{\text{max}}, \text{nm}$	$h\nu_{\text{max}}, \text{eV}$
870	445	2.79
920	465	2.67
950	485	2.56
1050	500	2.48

The intensity of the PL band at 540 nm increases with increasing annealing temperature of the powder and manifests itself as an inflection in the long-wave decay of the main PL band at annealing temperatures of 950°C and 1050°C. As a result, the FWHM increases (Fig. 1); this fact is apparently attributed to increasing portion of zinc oxide in ZnS powders annealed at these temperatures.

The shift of the main PL band for the studied ZnS powders towards long

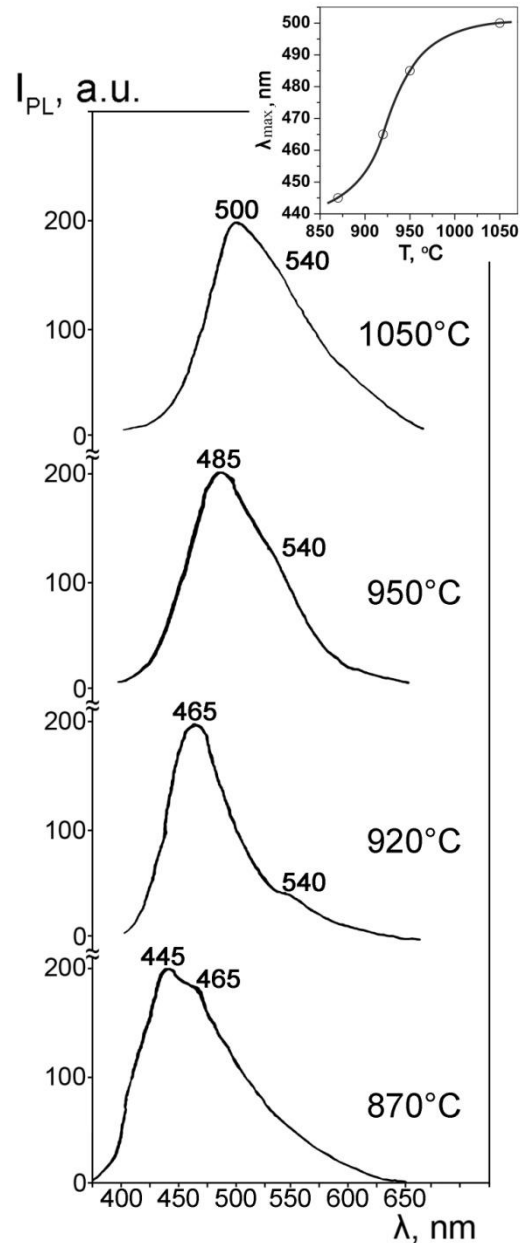


Fig.1. PL spectra of zinc sulfide powders air-annealed at various temperatures. $T = 300$ K, $\lambda_{\text{exc}} = 337$ nm. Inset: the PL band maximum position versus annealing temperature of the ZnS powder.

wavelengths with increasing annealing temperature is non-uniform (Fig. 1, inset, Table 2). The maximum rate of the PL band shift—0.67 nm/°C—is found for an annealing temperature range of 920–950°C. It can be assumed that the most intensive process of isovalent substitution of oxygen for sulfur atoms takes place in this temperature range. The subsequent increase in the annealing temperature from 950 to 1050°C leads to a rapid decrease in the PL band shift rate (Fig. 1, inset).

According to the authors of [10], the introduction of oxygen into ZnS leads to the formation of a ZnS·O substitutional solid solution; oxygen is present in zinc sulfide mainly as a ZnS·O solid solution and ZnO·S phase inclusions. It can be assumed that, for an annealing temperature of 1050°C, the ZnO·S phase portion almost completely determines the composition of the annealed powder, although a portion of the ZnS·O solid solution is still present. It is known that distribution of ZnO over the ZnS matrix leads to a decrease in the ZnS·O_s crystal lattice parameters because the ionic radius for oxygen (1.28 Å) is lower than that for sulfur (1.78 Å) [11]. Taking into account the parameters of the hexagonal ZnS structure $a_o = 0.3826$ nm and $c_o = 0.6262$ nm [11], a decrease in the lattice parameters of the ZnS powder air-annealed at 1050°C to $a_o = 0.3249$ nm and $c_o = 0.5206$ nm ($c_o/a_o = 1.602$), which were obtained from X-ray diffraction analysis using a DRON-3 diffractometer (Fig. 2), indicates the preferential formation of the ZnO·S phase in the ZnS matrix. The closeness of the obtained lattice parameters to the respective values for ZnO suggests that the synthesized powder largely represents zinc oxide, which is characterized, as it is known, by the ratio of $c_o/a_o = 1.60$ [11].

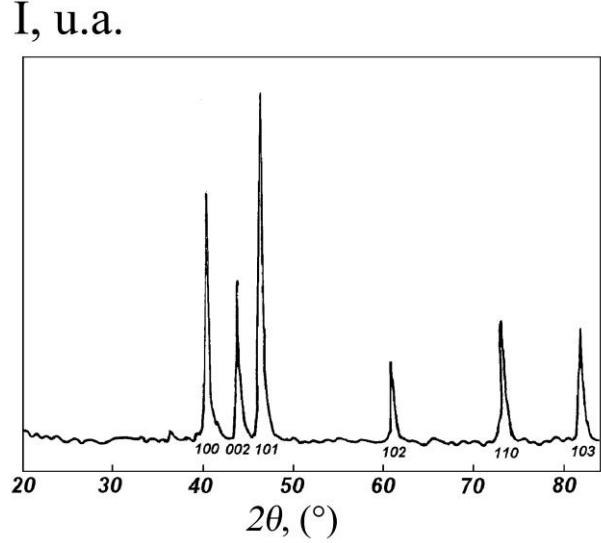


Fig. 2. X-ray diffraction pattern for the ZnS powder annealed at $T_{\text{anneal}} = 1050$ °C.

Table 2. The rate of temperature shift of the main PL band, $\frac{\Delta\lambda_{\text{max}}}{\Delta T_{\text{anneal}}}$, for various annealing temperature ranges for the initial ZnS powder

Temperature range, °C	ΔT_{anneal} , °C	$\Delta\lambda_{\text{max}}$, nm	$\frac{\Delta\lambda_{\text{max}}}{\Delta T_{\text{anneal}}}$, $\frac{\text{nm}}{^\circ\text{C}}$
870–920	50	20	0.40
920–950	30	20	0.67
950–1050	100	15	0.15

Further, during the high-temperature (1050°C) annealing of the ZnS powder in air, the PL maximum is localized at 500 nm (Fig. 1, inset), i.e., in the green spectral range, which is specific

for zinc oxide [2]. Thus, the results of X-ray diffraction analysis are in agreement with the PL data.

Despite the extensive discussions in the literature (see, for instance [2]), the nature of the green PL band localized at 500 nm in the spectra of ZnO samples is not clearly defined. In earlier papers [12, 13], the PL band in the green spectral range was attributed to copper impurity in ZnO. The specific feature of this band is the presence of a fine phonon structure. In later papers [14, 15], it was argued that V_O oxygen vacancies are responsible for the green PL band at 500 nm. However, similar to the band in Fig. 1, this band had no fine phonon structure. The authors of [16, 17] attributed the structureless green PL band in the spectra of ZnO samples to V_{Zn} zinc vacancies.

To explain the nature of the structureless band of green PL in ZnO, the following electron transitions were proposed: (1) “ V_O donor–valence band” transition, where the V_O donor level was placed ~ 0.7 eV below the conduction band [18]; (2) “ V_O donor– V_{Zn} acceptor” transition within the donor–acceptor pair model [17]; and (3) “conduction band– V_{Zn} acceptor” transition [16]. The authors of [2] note that the first two types of electron transitions are hardly probable. Taking into account the third “free-to-bond” recombination mechanism, acceptor level energy E_A can be estimated as follows:

$$E_A = E_g - h\nu_{\max} + kT,$$

where E_g is the band gap energy, k is the Boltzmann constant. $E_g = 3.4$ eV for ZnO at room temperature, $h\nu_{\max} = 2.48$ eV, and $k = 8.6 \cdot 10^{-5}$ eV/K; consequently, $E_A = 0.95$ eV.

Evolution of PL spectra of ZnS·O with increasing annealing temperature (Fig. 1) demonstrates the formation of a ZnO·S phase in the ZnS matrix. At minimum annealing temperature (870°C), the concentration of oxygen substituting sulfur atoms is rather low and the PL maximum is localized at 445 nm (Fig. 1); this position agrees well with the position of the PL maximum for ZnS samples with a low oxygen concentration (0.3–0.4 mol %) [11]. As the annealing temperature increases, the PL spectrum of the investigated powders is shifted towards long wavelengths; this finding can be reasonably attributed to increasing oxygen concentration in the powders and the formation of a ZnO·S phase. Finally, at the maximum annealing temperature (1050°C), the PL maximum is localized at 500 nm; this finding is in good agreement with the data for ZnS samples grown from the melt with an addition of more than 0.5 mol % of zinc oxide [11]. Simultaneously, as noted in [11], the number of defects in ZnS samples considerably increases and a zinc oxide phase is formed.

4. Conclusions

The isovalent substitution method for synthesizing a ZnO powder from powdered zinc sulfide obtained by chemical deposition from a water solution of zinc salt and thiourea has been discussed. Isovalent substitution of oxygen for sulfur was achieved during the isothermal annealing of a ZnS powder in air.

Examination of the PL spectra of ZnS powders annealed at various temperatures has shown that the local O_S defects and the ZnS·O substitutional solid solution are formed at relatively low annealing temperatures (about 870–920°C). At higher annealing temperatures (about 920–950°C), the ZnO·S phase is actively formed. At the annealing temperature of 1050°C, the structureless PL band in the spectra of the studied powder is localized at 500 nm; this position is characteristic of PL spectra of ZnO samples. The X-ray diffraction analysis of this powder

gives the ratio between the crystal lattice parameters $c/a_o = 1.60$, which is also characteristic of the ZnO hexagonal crystal lattice.

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