INFLUENCE OF HEAT TREATMENT ON PHOTOLUMINESCENCE SPECTRA IN ZnS:Mn CRYSTALS WITH HEXAGONAL STRUCTURE

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It has been investigated the influence of heat treatment with the following temperins on the integral photoluminescence spectra and on the individual bands of this spectra. It has been showed the correlation between the changes of intensity of photoluminescence individual bands and real structure of crystal, controlled with the help of EPR method. The basic changes of photoluminescence and structural properties have threshold nature. They begin to show up at temperature of annealing T > 650^{0}C. The maximum intensity of integral photoluminescence spectrum was observed in the region of phase transition crystal structure of zinc sulphide.

1. Introduction

Obtaining zinc sulfide crystals having a wurtzite (2H) structure stable at high temperatures (T > 1100°C) with using the method of growing from a melt was previously considered to be very difficult [1]. Moreover, this technique cannot grow ZnS crystals with a purely cubic sphalerite (3C) organization, which in turn is stable at low temperatures. Therefore basically, by this method crystals with packaging defects with structure of microtwins sphalerite are obtained; in rare cases, one of them is a 6H polytype. This imposes specified restrictions on a number of possible practical applications of such crystals. The microtwins structure is the result of a natural self-organization, which occurs during the cooling of the grown crystals as a result of the motion of partial dislocations. It was possible to complete the structural transition 2H-3C in microtwins crystals as a result of deformation recrystallization caused by the motion of partial dislocations [2]. It was found that the doping of ZnS crystals with impurity of aluminum impedes the solid-state phase transition 2H-3C, since aluminum admixture provides effective braking of moving dislocations. In the presence of ~ 0.1 wt. % aluminum impurity in the crystal, the high-temperature nonequilibrium structure 2H stabilizes at room temperature [3]. Besides of deformational recrystallization, the 2H-3C phase transition can be accomplished by thermal annealing with following quenching. As paramagnetic probes for controlling the structure of crystals, Mn^{2+} ions, which are also the centers of photoluminescence (PL) in zinc sulfide, are traditionally used.

In this work we study the behavior of the integrated PL spectrum and its constituent individual bands, conditioned by Mn^{2+} ions, during thermal annealing followed by quenching in ZnS:Mn crystals with an artificially stabilized 2H structure with the help of impurity of aluminum. These data are compared with the results of studying changes in the crystal structure of the same crystals, obtained in the work [4] using the EPR method.

2. Experimental results and their discussion

According to the results of studies of the EPR spectra [4], thermal annealing, followed by quenching, of crystals at different temperatures, makes it possible to obtain samples with different ratios of structural components.

The annealing of crystals was carried out for 30 minutes in a vacuum quartz ampoule, while the quenching was carried out in distilled water at the temperature of 25°C. The changes of the relative volumes of the crystal occupied by the hexagonal phase (V_{2H}), cubic phase (V_{3C}) and areas of stacking faults (V_{SF}) depending on the temperature of preliminary
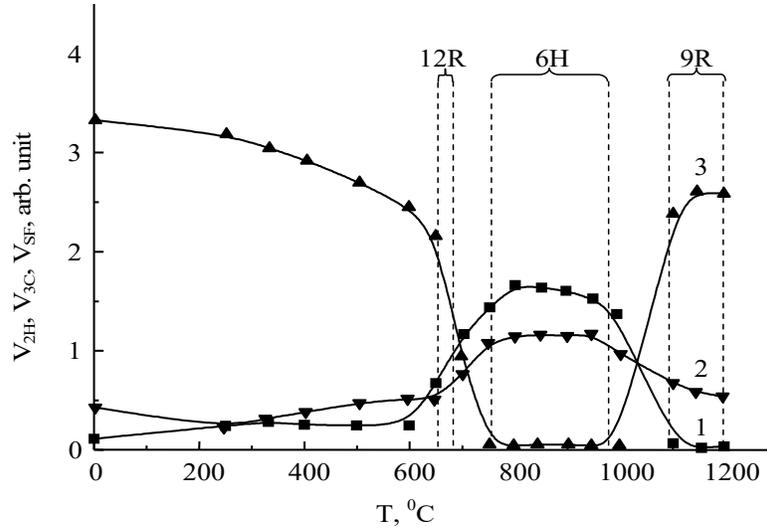
heating were established (Fig. 1).

Fig. 1. Ratio dependence of V_{3C} (1), V_{SF} (2) and V_{2H} (3) volumes in ZnS crystals on the temperature of preliminary heating [4].

EPR studies have shown that there may be only four types of nonequivalent centers of Mn^{2+} ions [3] in zinc sulfide crystals, regardless of their type structure. There are AN-type nodes in areas of sphalerite (3C). There are nodes of the AS and PN-type in the areas of stacking fault (ST) and nodes of the PS-type [3] in crystals with a hexagonal structure (2H). It is necessary to take into account that the volumes occupied by stacking faults, as well as cubic and hexagonal phases, are proportional to the number of AS–PN, AN, and PN type nodes respectively. The concentration of paramagnetic centers was determined in the area under the absorption curve of the corresponding lines in the EPR spectra. The 12R, 6H, 9R polytypes indicated in Fig. 1 were found by the ratios V_{SF}, V_{3C} and V_{2H}. There are insignificant changes in the ratio of the V_{SF}, V_{3C}, and V_{2H} volumes in the temperature range T = 25-600°C. The transition of 2H-3C is observed in the temperature range T = 650-800°C. In this case, an almost complete disappearance of the hexagonal phase occurs and the volumes of the cubic phase and stacking faults reach their maximum values. The volumes of the cubic phase and stacking faults retain their values before the temperature of the beginning of the phase transition (T = 1024°C). The structure of the crystals returns to its original state after the phase transition of 3C-2H.

Figure 2 shows the integrated PL spectra of ZnS:Mn crystals with the initial structure of 2H, depending on the annealing temperature. The PL was excited by the light with a wavelength of λ = 440 nm which corresponds to the fundamental absorption band of Mn^{2+} ions. It can be seen that the intensity of the integrated PL spectrum with the initial hexagonal structure is several times less than the intensity of the integrated PL spectrum after annealing at T = 1000°C. The crystal lattice is rearranged from sphalerite to wurtzite in this temperature range. In this case, a large number of stacking faults are recorded in the crystals, which possibly leads to an increase in the probability of radiative transitions. Along with the change in the integral intensity of the PL spectra, the position of the maximum of the integratedspectrum changes towards higher energies. The broadening of the integrated PL spectra was not observed.
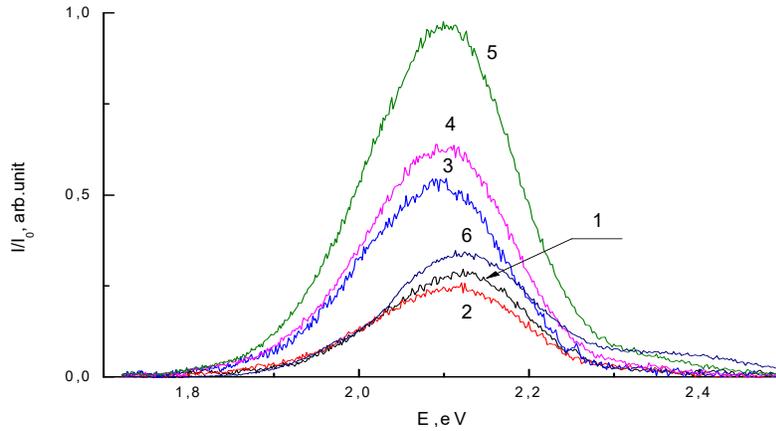
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Fig. 2. Changes in the intensity of the PL spectra depending on the annealing temperature:
1 — the PL spectrum of the initial crystal; the PL spectra of crystals after annealing
at temperatures of 700°C (2), 800°C (3), 900°C (4), 1000°C (5), 1100°C (6), respectively.

In order to receive more information on the behavior of individual bands in the PL spectrum, the experimental data were smoothed by the Tikhonov method [5]. The traditional approach to identifying individual bands in the PL spectra is based on the Alentsev-Fock method. It contains obtaining a set of PL spectra at different conditions of excitation of crystals. The analysis of the obtained PL spectra makes it possible to identify individual bands and obtain an estimate of their intensity, the position of the emission maxima (λ_{max}) and the magnitude of half-widths ($\Delta\lambda$) [5]. We will use the parameters of elementary PL bands in ZnS:Mn crystals obtained in works [5, 6] to analyze our spectra: λ_{max} = 530 nm, $\Delta\lambda$ = 32 nm; λ_{max} = 557, $\Delta\lambda$ = 25 nm; λ_{max} = 578 nm, $\Delta\lambda$ = 32 nm; λ_{max} = 600 nm, $\Delta\lambda$ = 44 nm; λ_{max} = 616 nm, $\Delta\lambda$ = 28 nm and λ_{max} = 637 nm, $\Delta\lambda$ = 37 nm. The decomposition of the obtained PL spectra into individual bands showed that band with λ_{max} = 616 nm was not appeared in our PL spectra. The dependence behavior at the intensity of individual bands on the annealing temperature of crystals is shown in Fig. 3.
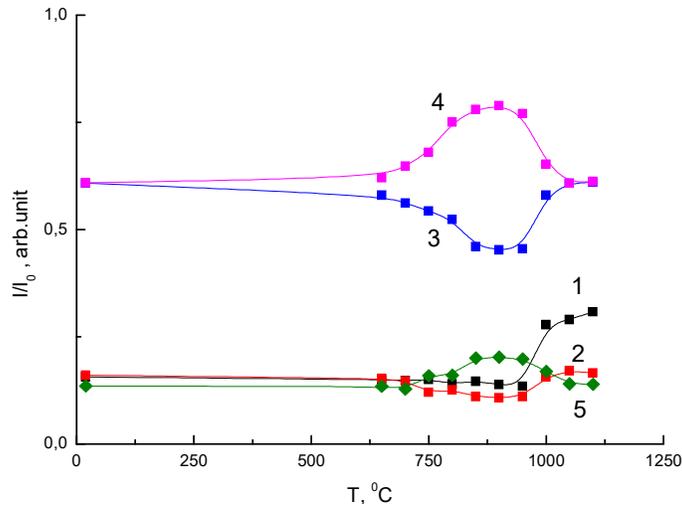

Fig.3. The change in the intensity of the elementary PL bands in ZnS:Mn crystals
with the initial structure of 2H from the annealing temperature: λ_{max} = 530 nm (1),
λ_{max} = 557 nm (2), λ_{max} = 578 nm (3); λ_{max} = 600 nm (4); λ_{max} = 637 nm (5).

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3. Conclusions

Comparing the obtained data (Fig. 3) with the results of the change in the crystal structure during such processing of samples (Fig. 1), we can draw the following conclusions. Individual bands with $\lambda_{max} = 557$nm and $\lambda_{max} = 578$ nm vary in intensity PL synchronously with the change in the hexagonal structure of the crystal. The intensities of elementary bands with $\lambda_{max} = 600$ nm and $\lambda_{max} = 637$ nm correlate with changes in the volumes of the cubic crystal phase and stacking faults.

The intensity of the elementary PL band with $\lambda_{max} = 530$ nm does not correlate with changes in the V_{SF}, V_{3C}, and V_{2H} volumes. This indicates that this band is not related to the crystal structure and is due to point defects. Consequently, the intensity of this PL band should depend on the concentration of such defects. We have shown that this band disappears when the samples are slowly cooled after annealing in sulfur vapor. This allows us to associate this elementary emission band with isolated sulfur vacancies. The number of such vacancies should enlarge with an increase in the annealing temperature of the samples. It determines the increase in the intensity of this PL band as the annealing temperature increases (Fig. 3). The above is consistent with the data of the work [7], where this emission band was also associated with isolated sulfur vacancies. It was also established that the maximum intensity of the integral PL spectrum is observed during the transition of 6H – 9R crystal structure at T = 1000°C.

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