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PHOTOLUMINESCENCE OF $ZnAl_2S_4$ IN A VISIBLE SPECTRAL REGION

The crystals of the spinel α -phase and wurtzite W-phase of $ZnAl_2S_4$ have been studied by using optical techniques, and exhibited broad green and blue PL emissions, respectively. The green emission from the α -phase is believed to originate from the DA-pair recombination, whereas the blue emission from the W-phase has been attributed to the radiative recombination of electrons, trapped by a deep donor centre, with free holes.

1. INTRODUCTION

The novel defective ternary compound $ZnAl_2S_4$ is attracting much interest due to its high photoconductivity and a promising for visible LED applications energy band gap corresponding to the UV spectral region. Since $ZnAl_2S_4$ is the defective compound it crystallizes in several crystal structures depending on the conditions of the material preparation, such as the temperature of synthesis of the compound and the Al/Zn ratio (HILLS and Ref. therein). In the low temperature region (800-900°C) $ZnAl_2S_4$ exists in two structures, i.e. a defect spinel α -phase and a wurtzite-type W-phase, while at higher temperatures (1050-1100°C) an orthorhombic β -phase and a rhombohedral γ -phase coexist together with the W-phase.

Although the structural properties of $ZnAl_2S_4$ are fairly well established, and there have been a few reports on optical absorption and Raman scattering investigations (HAEUSELER et.al; KULIKOVA et.al) in this compound, no photoluminescence (PL) study of $ZnAl_2S_4$ has been reported so far. Moreover, $ZnAl_2S_4$ has been found to be involved in a strong blue emission in heavily Zn-doped $CuAlS_2$ (AKSENOV et.al).

In the present paper we report the results on the growth and optical studies of the $ZnAl_2S_4$ compound. The results of the optical absorption, PL, PL excitation (PLE), as well as the time-resolved PL studies of the W- $ZnAl_2S_4$ single crystals are reported together with those of the PL studies of the α - $ZnAl_2S_4$ polycrystals.

2. CRYSTAL GROWTH & EXPERIMENTAL

α - $ZnAl_2S_4$ compound has been prepared by heating either the constituent elements (1250°C for several hours) or fine powders of ZnS, Al and S (600°C for one day + 900°C for one more day) in a BN crucible placed in a sealed quartz ampoule. The optimal atomic ratio of

Al_2S_3 vs ZnS for obtaining the "pure" α -phase of ZnAl_2S_4 has been found as $\text{Al}_2\text{S}_3:\text{ZnS} = 55:45$.

Single crystals of the W-phase of ZnAl_2S_4 have been grown by the CVT technique using iodine as a transport agent from the powder of the α - ZnAl_2S_4 . CVT was carried out for 7 days with the temperatures of the charge zone and growth zone being 780°C and 700°C , respectively. The resulting single crystals were found to be transparent with no colouration, as well as highly insulating, which precluded any studies of their electrical properties.

The crystal structures were evaluated by a powder X-ray diffraction. Continuous wave (CW) PL spectra were taken at 70-300 K using a 325 nm line of a He-Cd laser as an excitation source, a 25cm monochromator, and a photomultiplier. Time-resolved PL spectra (TRS) were measured using a 337 nm line of a N_2 pulse laser and a boxcar integrator. PLE spectra were taken by using a Xe-lamp combined with a 25cm monochromator as an excitation source, the emitted light being dispersed again by another 25cm monochromator and detected by the photomultiplier.

3. RESULTS AND DISCUSSION

3.1. α - ZnAl_2S_4

The typical PL spectra of the α - ZnAl_2S_4 polycrystals are shown in Fig. 1 for various temperatures. It can be seen that, while at low temperature the sample exhibits a strong and broad green emission peaked at 540 nm, the spectra taken at RT are dominated by a weak red emission consisting of two bands peaked at 790 and 850 nm.

The thermal quenching experiments for the green emission reveal the energy level with an activation energy of $E_G = 115 \pm 10$ meV. Since the value of E_G is much smaller than the energy difference between the band gap of α - ZnAl_2S_4 $E_g = 3.5$ eV (HAEUSELER et.al) and the spectral position of the green emission peak E_p ($E_g - E_p = 1.2$ eV $\gg E_G = 0.11$ eV), we believe that the green emission arises from the donor-acceptor pair recombination.

Since the PL excitation spectrum for the green emission is peaked at about 3.6 eV, we believe that the green emission is excited by indirect band-to-band optical absorption. As for the red emissions, the PLE spectrum of those has been found to peak at ~ 3.9 eV. Since the spectral position of this peak corresponds neither to

indirect (3.5 eV) or direct (4.4 eV) band gap energy of α - ZnAl_2S_4 , we assume that the excitation of the red emissions takes place via a direct excitation of the defect centre.

3.2. W- ZnAl_2S_4

The dependence of the absorption coefficient α on the photon energy $h\nu$ for the single crystals of W- ZnAl_2S_4 has been found to follow the relation $\alpha(h\nu) = (A/h\nu)(h\nu - E_g)^{1/2}$. This result indicates that the fundamental edge of W- ZnAl_2S_4 is due to direct allowed transitions between nearly parabolic bands. The band gap energy of the compound under consideration has been estimated from the absorption spectra as 3.7 eV at RT.

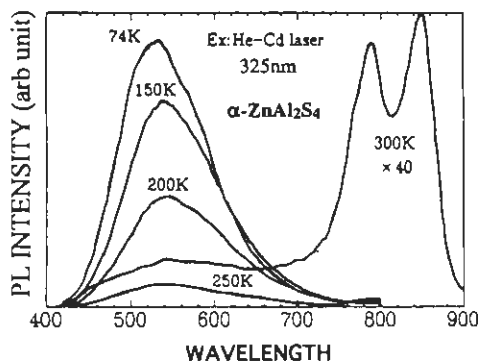


Fig. 1. CW PL spectra of α - ZnAl_2S_4 at various temperatures.

CW PL spectra of the crystals have been found to exhibit a strong blue emission under the UV excitation, which is shown in Fig. 2. The emission peak shifts with temperature from 450 nm at 70 K to about 470 nm at RT, the temperature quenching curve of the blue emission revealing the activation energy of $E_g \sim 120$ meV (Fig. 2, inset). The TRS of the W-ZnAl₂S₄ crystals are shown in Fig. 3. It can be seen that, while no shift of the blue emission peaked at 450 nm with the time lapse after excitation was observed at 70 K, the same emission measured at RT showed a shift of its peak position from 450 to 470 nm, the later being the position of the peak of this emission in the RT CW PL spectra.

These results imply that 1) the blue luminescence does not originate from the DA-pair recombination, and 2) at RT the emission is composed of two emissions, peaked at 450 and 470 nm, with the energy transfer from the former to the later emission taking place as the time lapse after excitation increases.

The PLE spectra for the blue luminescence are shown in Fig. 4. Two PL bands, peaked at 460 nm (H-band) and 480 nm (L-band), are clearly seen, each of the bands having its own excitation spectrum, peaked at 340 nm (H') and 360 nm (L') for the H- and L-emissions, respectively.

We interpreted the above results in the framework of a configuration coordinate model (Fig. 5) which considers the blue emission as originating from radiative transitions from a deep donor centre to the valence band, split in two subbands (A and B) by the effect of the non-cubic crystal field combined with the spin-orbit interaction. The excited state I corresponds to a free electron (f.e.) in the conduction band (CB) and a free hole (f.h.) in the valence band (VB), whereas the excited state II corresponds to the case when the electron is localized on the deep donor centre, whereas the hole is free. The important point of the proposed configuration coordinate model is that, at $Q=0$, the energy lines of the excited state I cross those of the excited state II. Assuming, from the energy difference between the observed spectral positions of the H- and L-emissions and their excitation bands, that the VB splitting is ~ 0.2 eV, our results can be explained as follows.

At low temperature, the absorption of a photon with $h\nu \sim 3.6$ eV (H'-exc.) by the crystal results in the f.e. in the CB and the f.h. in the VB at $Q=0$, which corresponds to the photoabsorption transition from the ground state of the system to the excited state BI. The following process is the

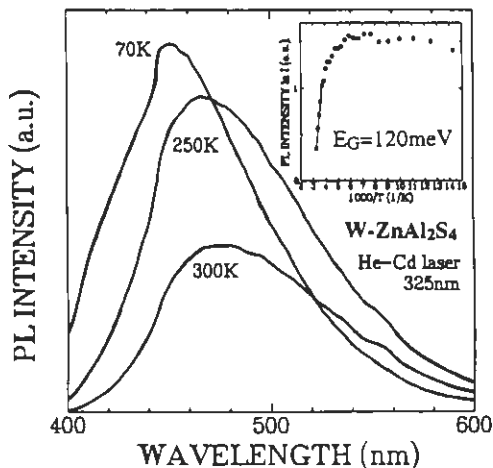


Fig. 2. PL spectra of W-ZnAl₂S₄ with thermal quenching curve for the emission (inset).

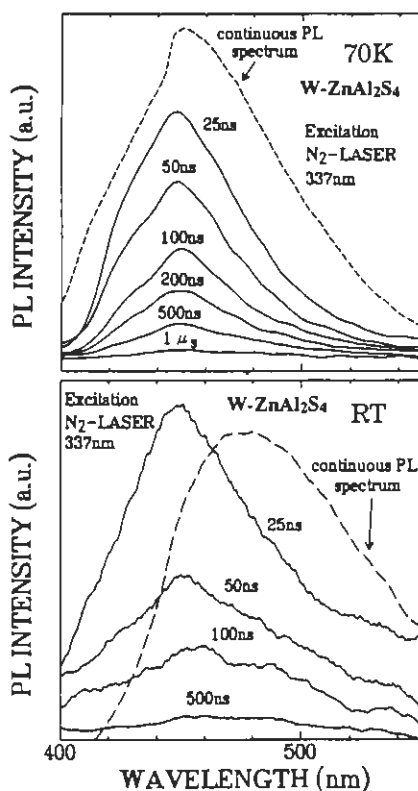


Fig. 3. TRS PL spectra of W-ZnAl₂S₄.

trapping of the f.e. by the deep donor centre with the subsequent lattice relaxation around this centre ($\Delta Q \neq 0$), the system being converted from the excited state BI to BII. The recombination of this electron with the f.h. in the VB results in the H-emission peaked at 460 nm. The absorption of photon with $h\nu \sim 3.4$ eV (L'-exc.) results in the formation of the excited state AI, with its subsequent relaxation to the state AII and the recombination resulting in the L-emission peaked at 480 nm. We, hence, experimentally observe two emission bands, spectrally separated by ~ 0.2 eV, each of which having its own excitation spectrum. Since we observe two separate emission bands, we believe that the intra-VB scattering time for the f.h. is longer compared with that required for the deep centre to trap the f.e., which is proved by an absence of any shift of the H-emission with the time lapse at low temperature (Fig. 3.a).

Upon increase in the temperature, the interaction of holes with vibrational modes is enhanced, and, therefore, the greater number of holes will have enough energy to overcome the potential barrier between the BII and AI states, which results in the thermal quenching of the H-emission with the activation energy of E_B (Fig. 2). Moreover, since the holes which have already overcome the potential barrier between the BII and AI states will subsequently relax to the bottom of the AII state, we observe the shift of the blue emission from 450 to 470 nm upon increase of the temperature.

The RT TRS (Fig. 3.b) also support the above considerations. Since a finite time is required for f.h. to accumulate enough energy via interaction with the vibrational modes to overcome the potential barrier between the BII and AI states, the longer the time lapse after excitation, the greater number of holes will be able to transfer to the AI and, subsequently, AII state. The resultant emission, hence, is expected to experience the shift from the spectral position of the H-emission to that of the L-emission as the time lapse after excitation increases, which has been observed experimentally.

We, therefore, believe that the configuration coordinate model proposed qualitatively explains all the essential features of the blue emissions from the $W-ZnAl_2S_4$.

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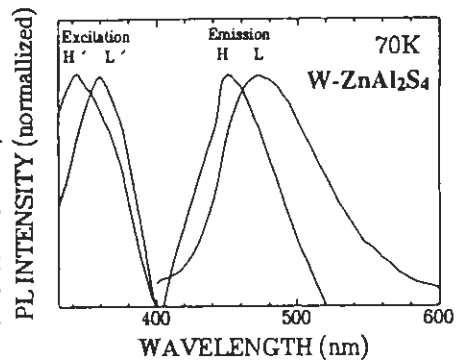


Fig. 4. PLE spectra of the blue emissions.

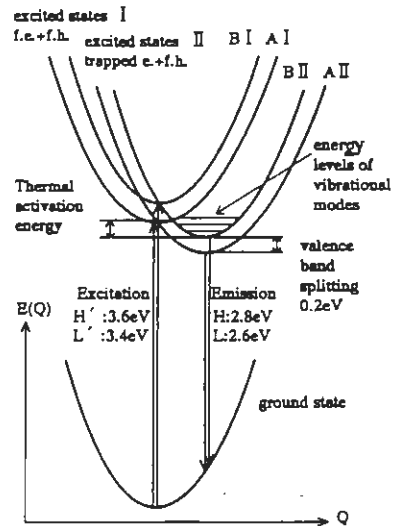


Fig. 5. Configuration coordinate model for the H- and L-emissions, where Q is the lattice distortion coordinate appropriate to the Jahn-Teller relaxation of a deep centre.