

Visible Photoluminescence in Undoped and Zn-doped CuAlS₂

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Photoluminescence (PL) properties of undoped and Zn-doped CuAlS₂ crystals have been studied. The Zn-doped crystals have been found to exhibit several strong emissions in the green-to-violet spectral region, the dominant emission being determined by the concentration of Zn-dopant. On the basis of the detailed PL studies we have determined the activation energies of the donor-like Zn_{Cu}- and the acceptor-like V_{Cu}-defects, the last result being confirmed by the ESR experiments.

KEYWORDS: CuAlS₂ ternary compound, Zn-doping, visible photoluminescence, defect energy level

CuAlS₂ ternary semiconductor is the widest band gap member of A¹B³C₂-type compounds which crystallizes in the tetragonal chalcopyrite structure. With the observation of very efficient blue and green emissions from Zn-doped CuAlS₂ having been recently reported,¹⁾ this compound is expected to be a possible candidate for blue-to-ultraviolet light emitting device application.

In the present paper we report the results of the PL investigations of the undoped, as well as Zn-doped CuAlS₂ crystals.

Single crystals were grown by the CVT technique from the polycrystalline CuAlS₂ compound, which was prepared by the direct melting of the constituent elements in a BN crucible.²⁾ The resulting crystals, used for Zn-doping, were typically bulk-shaped with dimensions of about 6×3×1.5 mm³, the colouration of the crystals being transparent green due to the charge-transfer transitions in residual transition atom (TA) impurities.³⁾

Zn-doping was carried out by 1) adding of the Zn-dopant into the starting composition of constituent elements prior to the synthesis of the CuAlS₂, the analyzed concentration of Zn in the CVT-grown crystals being found to be equal to the nominal one (0.1–0.5 mol%), or 2) by annealing of the undoped crystals at T_a=500–900°C for 20–120 h in the presence of Zn, the Zn-metal being placed in one end of the ampoule and the crystals to be doped being placed in the other end. In the latter case the analysed concentration of Zn has been found to depend on the amount of Zn added into the ampoule, on the annealing temperature T_a, as well as on the duration of annealing. It has also been found that the increase of the annealing temperature above 600°C results in the formation of a multiphase structure in the bulk of the Zn-doped samples, this structure consisting of the original CuAlS₂ phase, as well admixtures of CuAl, ZnS, and a spinel ZnAl₂S₄ phases, the relative concentrations of these phases being dependent on the annealing conditions, as well as on the distance from the original surface of the samples.⁴⁾ The formation of the multiphase structure is believed to be caused by the decomposition of the original chalcopyrite phase due to alloying of Zn with CuAlS₂ at high annealing temperatures.

The chemical composition of the samples has been determined by the inductively coupled plasma emission spectroscopy, as well as by the electron microprobe analysis. Steady-state PL was studied in the temperature range 4.2–520 K and was excited by the 325 nm line of a He–Cd laser, with the samples being put into an Oxford Instruments continuous-flow cryostat. Time-resolved PL was studied at 2 K and was excited by the 308 nm line of an excimer laser with a pulse width of 20 ns.

The typical PL spectrum of undoped CuAlS₂ crystals has been found to exhibit several emissions in different spectral regions (Fig. 1), i.e.

- 1) a series of sharp lines in the UV spectral region (346–357 nm) caused by the recombination of free and bound excitons (Ex),⁵⁾
- 2) several weak free-to-bound (FB) transitions in the violet spectral region (370–384 nm), presumably related to the native defects,⁶⁾
- 3) a series of intense emissions in the purple spectral region (406–423 nm), supposedly originated from the donor-acceptor (DA) pair recombination,⁵⁾ and
- 4) a broad orange band peaked at 590–620 nm originated from DA-pair recombination involving deep levels.⁷⁾

Although the intensities of these emissions vary from sample to sample, in most of the CVT-grown CuAlS₂

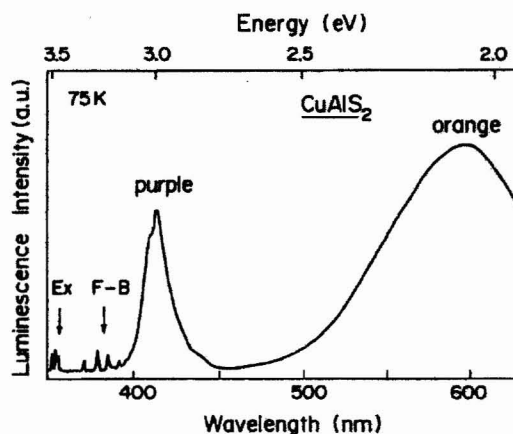


Fig. 1. The typical PL spectrum of undoped CuAlS₂ crystals.

crystals the orange emission dominates the spectra, and, therefore, the orange-coloured emission from the crystals is usually observed under photo- or electron beam-excitation.

Doping of the crystals with Zn causes drastic changes in the PL spectra, i.e. quenching of the orange emission band together with the appearance of several strong emissions in the green-to-UV spectral region.

The spectra of the samples with relatively low Zn concentration (0.1–2.0 mol%) are shown in Fig. 2 and exhibit a violet V-emission peaked at 390 nm under steady-state excitation (a), as well as two (FB) transitions under the high-intensity pulsed excitation (b). Contrary to the FB-transitions, the V-emission exhibits an obvious peak shift towards lower energies with the time lapse after excitation, which gives the ground to consider this emission as originating from the DA-pair recombination. On the basis of the general expression for the emission energy for a DA pair, and taking into account the spectral position of the low-energy base of the last time-resolved spectrum,⁸⁾ as well as that of the free exciton emission (3.55 eV at 10 K),⁵⁾ the sum of the activation energies of the donors and acceptors, involved in the V-emission, has been estimated as being $E_D + E_A = 0.5 \pm 0.03$ eV.

The temperature dependence of the intensity of the V-emission reveals a defect level with the activation energy of 180 ± 10 meV, which has been assigned to copper vacancies V_{Cu} . The above assignment is supported by 1) the results of the compositional analysis, showing the Cu-deficiency of the crystals and, therefore, implying the high concentration of the V_{Cu} -defects, and 2) by the

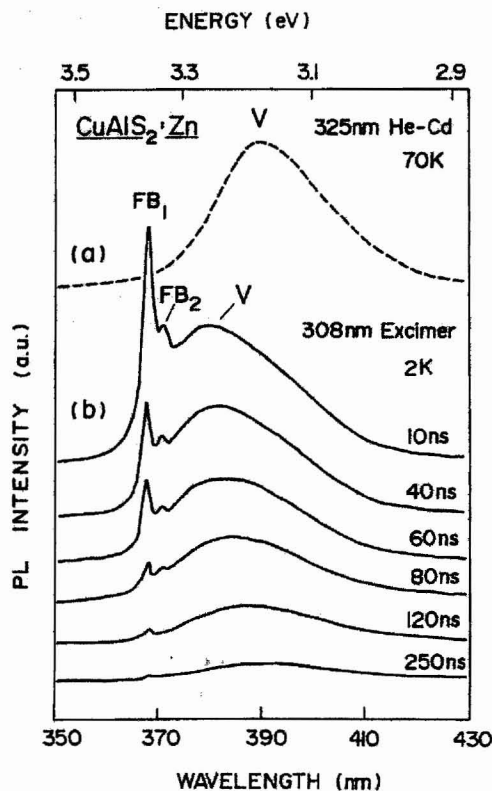


Fig. 2. Steady-state (a) and time-resolved (b) PL spectra of the Zn-doped $CuAlS_2$ crystals, with the concentration of Zn being 0.1 mol%.

results of the optically excited ESR studies of the $CuAlS_2$ crystals, showing the appearance of a sharp isotropic signal at $g=2.019$,⁹⁾ which was attributed to a hole trapped on V_{Cu} , with the activation energy, found from the thermal quenching of the ESR signal ($E_A=190$ meV), being equal within the experimental error to that found from the thermal quenching of the V-emission.

Taking into account the above results the V-emission has been attributed to the radiative recombination of an electron bound on a Zn_{Cu} -donor ($E_D=320$ meV) and a hole bound on the V_{Cu} -acceptor ($E_A=180$ meV).

The heavily Zn-doped samples (concentration of Zn being higher than 2 mol%) have been found to exhibit the multiphase structure, discussed above, this structure emitting very bright blue (B) and green (G) emission peaked at 445 and 520 nm, respectively (Fig. 3). The visible emission exhibit a remarkable feature, i.e. an increase in intensities of the emissions with the increase of the temperature in some temperature region, caused by the redistribution of carriers between several defect levels. Due to this phenomenon the B- and G-emission are very bright even at RT, and the G-emission is visually observed up to 500 K (the upper temperature limit of our cryostat).

Taking into account that the energy separation between the spectral position of the free exciton emission and that of the B- and G-emissions is much larger than the corresponding activation energies for these emissions deduced from the thermal quenching curves (0.35 eV and 0.7 eV for the B- and G-emissions, respectively),⁴⁾ the visible emission have been tentatively attributed to the DA-pair recombination, involving deep Zn-introduced defects. It is impossible at the present stage to ascertain definitely the nature of the centers, responsible for the visible emissions.

The results obtained suggest that the $CuAlS_2$ compound may be considered as a perspective material for blue and green LED realization.

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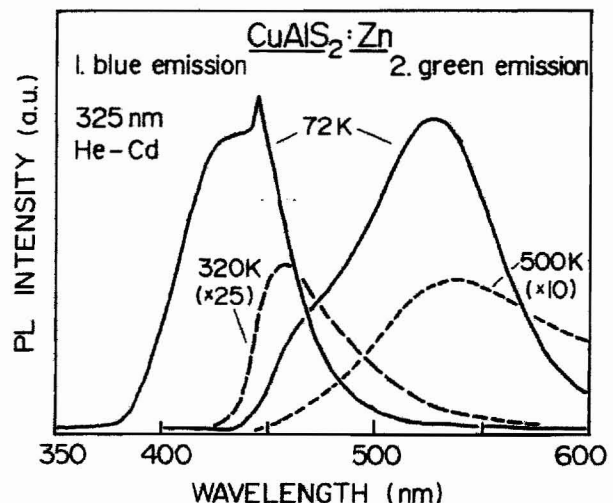


Fig. 3. PL spectra of the heavily Zn-doped samples (Zn concentration being higher than 2 mol%): 1) blue emission from the bulk of the samples, 2) green emission from the surface of the samples.

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