

Visible photoluminescence of Zn-doped CuAlS₂

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The observation of a very intense blue and green photoluminescence from low-resistivity CuAlS₂ crystals, grown by chemical vapor transport and subsequently doped with Zn, is reported. The emission is strong even at room temperature, the color of emission being dependent on Zn-doping conditions. Results obtained suggest that the CuAlS₂ compound can be considered as a perspective material for blue and green light-emitting device realization.

Ternary compounds of the $A^1B^3C_2^6$ type have been attracting much interest, mainly due to their promising luminescent and nonlinear optical properties. The CuAlS₂ compound is the widest band-gap member of ternaries, which is considered to be a perspective material for visible light-emitting device application. The CuAlS₂ has been found to have a wide direct band gap of 3.5 eV,¹ comparatively low melting temperature of 1245 °C,² and low-resistivity crystals of this compound have been obtained.³

The typical luminescence spectrum of the CuAlS₂ crystals at low temperatures is shown in Fig. 1 and exhibits a series of sharp lines in the spectral region 346–357 nm caused by free- and bound-exciton recombination,⁴ several free-to-bound transitions in the spectral region 370–384 nm,³ an intense purple emission band at 410 nm caused by donor-acceptor (DA) pair recombination,⁵ as well as a broad orange emission band originating from DA recombination, involving deep levels.⁶ In most of the CuAlS₂ crystals, the orange emission band dominates both the photoluminescence (PL) and the cathodoluminescence spectra, and therefore, the orange-colored emission from the crystals is usually observed under photo- or electron-beam excitation.

In the present letter, we report the observation of a very bright blue and green photoluminescence from the CuAlS₂ crystals doped with Zn.

Single crystals were grown by the chemical vapor transport technique from the polycrystalline CuAlS₂ compound, which was prepared by the direct melting of the constituent elements in a BN crucible.⁷ The resulting crystals, which typically had been platelike with dimensions of 20×10×0.5 mm³, were then annealed in evacuated and sealed quartz ampoules in the presence of Zn-Zn metal in the amount of 100 mg being placed in one end of the ampoule and the CuAlS₂ crystals being placed into another end of the ampoule. Thermal treatments were carried out for 50 h at different temperatures in the range 700–900 °C, with the sulphur or a powder of CuAlS₂ being added or not added into the ampoule. PL was studied in the temperature range 72–520 K, and was excited by the 325-nm line of a He-Cd laser (10 mW), with the samples being put into an Oxford Instruments continuous-flow cryostat.

The PL spectra of the crystals, annealed at 700 °C in the presence of Zn and sulphur (*S* pressure being ~5 atm), are shown in Fig. 2. The spectrum taken at 72 K exhibits four broad bands *V*, *P*, *B*, and *G*₂ peaked at 380, 410, 445, and 520 nm, respectively, as well as a sharper

band at 374 nm, superposed on the high-energy edge of the *V* emission. The *P* band and the band at 374 nm have been previously observed in undoped CuAlS₂, and are supposed to be originating from DA and free-to-bound transitions, respectively.^{3,5} At the same time the *V*, *B*, and *G*₂ emissions have been observed for the first time and only in Zn-doped crystals. Therefore, these emissions are believed to be caused by transitions involving Zn-originated defects in the crystal lattice. Since the *V* band is the strongest one in the spectra, taken at both 72 K and room temperature (RT), the color of emission in this case is violet, and the emission is observed at temperatures up to 290 K, although at RT the violet emission is very weak.

The thermal quenching curves for the *V* emission reveal the existence of two energy levels with the activation energies of $E_{A1} = 50 (\pm 10)$ meV and $E_{A2} = 180 (\pm 10)$ meV involved in this emission. Hence, the *V* emission is supposed to be caused by DA pair recombination. The emission energy for a donor-acceptor pair at a distance *r* is, in the first approximation

$$h\nu = E_g - (E_D + E_A) + e^2/r,$$

where E_g is the band-gap energy, E_D and E_A are the activation energies of donors and acceptors involved in the emission, and the last term takes into account the electrostatic interaction between electron and hole, bound on the donor and acceptor, respectively.

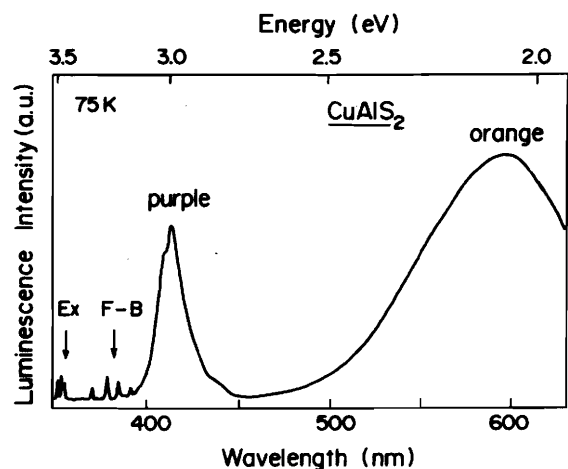


FIG. 1. The typical PL spectrum of as-grown CuAlS₂ crystals exhibiting exciton emission (*Ex*), free-to-bound transitions (*F-B*), as well as purple and orange bands caused by DA pair recombination.

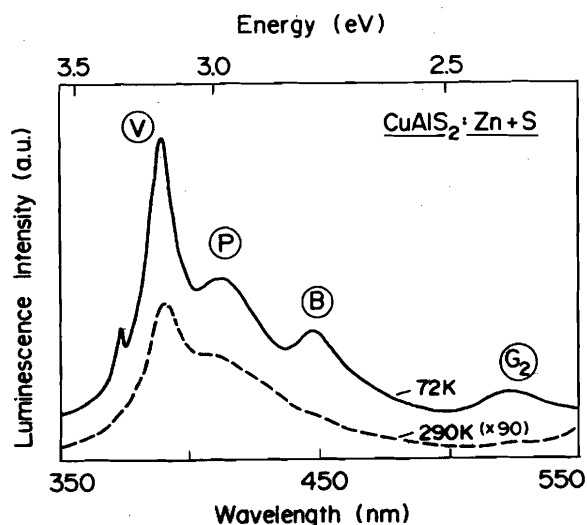


FIG. 2. PL spectra of CuAlS_2 crystals annealed at 700°C in the presence of Zn, plus sulphur being added into the ampoule in the amount corresponding to the S pressure of about 5 atm.

The energy separation between the spectral positions of the free-exciton emission at 3.550 eV ⁴ and the V emission at 3.26 eV is 290 meV . Taking into account this value and the value of electrostatic term $e^2/r \sim 30\text{ meV}$,⁸ as well as the sum of the activation energies found from the thermal quenching measurements $E_{A1} + E_{A2} = 230 (\pm 20)\text{ meV}$, it is concluded that some other (the deepest) level (except for the two levels, deduced from the thermal quenching curves) must also be involved in the V emission. Therefore, the V emission originates from transitions between several energy levels of Zn-introduced and native defects.

The annealing of the crystals at 800°C in the presence of Zn, plus CuAlS_2 powder being added into the ampoule, greatly strengthens the green emission (Fig. 3). In this case, the green emission dominates the spectra and consists

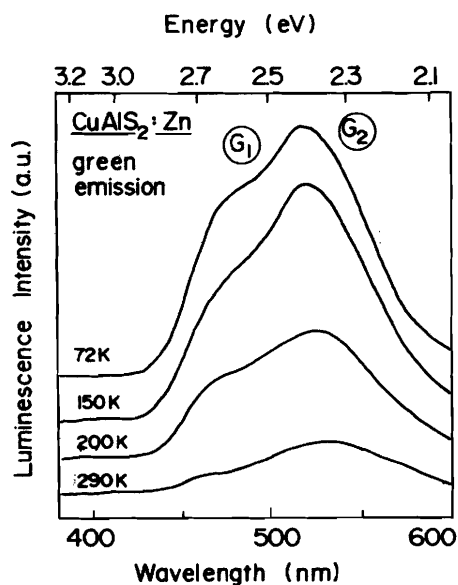


FIG. 3. PL spectra of CuAlS_2 crystals annealed at 800°C in the presence of Zn and CuAlS_2 powder.

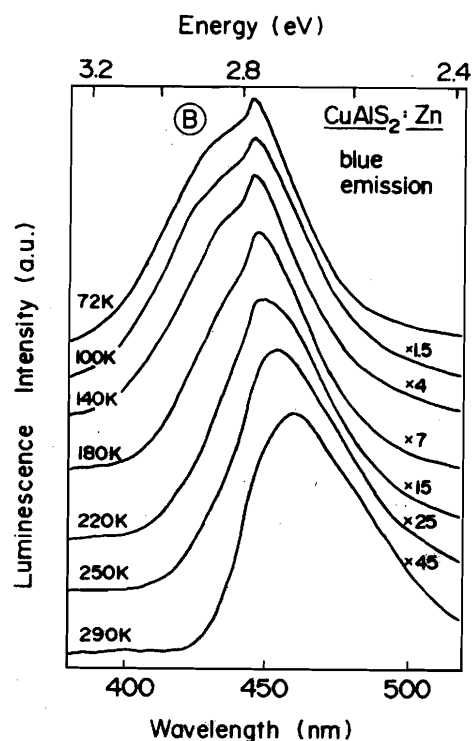


FIG. 4. PL spectra of CuAlS_2 crystals annealed at 900°C in the presence of Zn and CuAlS_2 powder.

of two bands, i.e., a G_1 band at 480 nm and the previously observed G_2 band. The resulting green-colored emission from the crystal is very bright, even at RT and is observable up to $T = 250^\circ\text{C}$.

Rising of the annealing temperature up to 900°C causes drastic changes in the spectra, the luminescence in this case being dominated by the very strong B -emission band shown in Fig. 4. The unusual line shape of the B emission at low temperatures suggests that this emission also consists of several bands originated from transitions between several energy levels and introduced into the band of the CuAlS_2 by Zn-originated and native defects. The activation energies of two shallow levels involved in the B emission, are found from the thermal quenching curve to be $E_{A3} = 24 (\pm 5)\text{ meV}$ and $E_{A4} = 90 (\pm 10)\text{ meV}$. The resulting blue emission is very bright, even at RT, and as in the case of the green emission, is observed up to $T = 250^\circ\text{C}$.

The observed effect of Zn doping on the properties of the CuAlS_2 , i.e., the observation of the intense emission bands in the visible spectral region, as well as the obtaining of the crystals with high conductivity and low carriers mobilities,³ may be tentatively explained under an assumption that the concentration of the Zn-introduced defects in the crystal lattice of the CuAlS_2 is high enough to form the impurity band in the band gap of the host compound due to the overlapping of the wave functions of the electrons trapped on Zn-introduced deep levels.

In conclusion, we have shown in this letter that the CuAlS_2 crystals doped with Zn emit strong violet, blue, and green luminescence, the color of emission being dependent on the conditions of Zn doping. Therefore, the

CuAlS₂ compound can well be considered as a perspective material for the fabrication of a homojunction or CuAlS₂/ZnS-heterojunction blue and green light-emitting device.

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