Reversible Creation and Annihilation of a Violet Fluorescence Band in Doped ZnS Crystals *

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(Z. Naturforsch. **30 a**, 1205–1206 [1975] ;
received August 18, 1975)

Annealing of doped (Cu, Ag, Au) ZnS crystals at 1200 °C and subsequent quenching or slow cooling, respectively, create or annihilate a violet fluorescence band, reversibly. The experimental results indicate that the emission must be due to isolated native defects in the ZnS lattice.

The SAL-emission of ZnS, as termed in literature, is located in the spectral region between 380 and 420 nm. The models concerning the nature of the emission centers of this luminescence are up to now still very contradictory. The previous experimental results indicate that the emission is due to two different centers, because of the different energy positions of the observed fluorescence maxima. Rothschild[1] and Uchida[2] have reported upon an emission band with the peak between 380 and 400 nm. The SAL-emission, as has been described by Samelson and Lempicki[3], shows a maximum at 415 nm. Rothschild[1] has reported low energy SAL-emission bands, too, which are observed in (Zn, Cd)S mixed crystals doped with the chemical defects Cl, Al, Ga, In. The SAL_v-emission, as has been described by Gill and Rothschild[4], shows a maximum at 430 nm.

In the course of investigations on the influence of high temperature annealing on the luminescence of ZnS crystals doped with Cu, Ag, and Au we observed an emission band with maximum at 415 nm. By altering the cooling rate we were able to create and annihilate this band, reversibly. ZnS crystals doped with Al did not show this effect.

The used experimental set-up has been described elsewhere[5]. The crystals investigated in this study were obtained from Eagle Pitcher-Company. The phosphors studied were: ZnS/Cu, ZnS/Ag, ZnS/Au, and ZnS/Al with defect concentrations of $1 \cdot 10^{-4}$ g X/g ZnS (X = Cu, Ag, Au, Al). The foreign atom concentrations noted are those given by the producer. The experimental procedure was as follows:

1) Recording of the fluorescence spectra of the as-grown crystals under excitation with UV-light of 320, 340, 360, and 400 nm wavelength at the temperature of liquid air (LAT) and at room temperature (RT).
2) Annealing of the crystals at 1200 °C for an hour, quenching to RT, recording of the emission spectra as in 1).
3) Annealing at 1200 °C, cooling to RT with a rate of about 6 to 7°/min, recording the luminescence spectra as in 1).
4) Anew treatment as in 2).

The crystals were annealed in evacuated Suprasil ampoules.

The fluorescence spectra of ZnS crystals doped with Cu and Au are shown in Fig. 1 and 2, respectively. The annealed and afterwards quenched crystals exhibit, besides a number of lower energy luminescence bands, an emission with a maximum at 415 nm; if excited with UV-light between 340 and 360 nm at low temperatures (spectrum 2 in Fig. 1 and 2). If we take the spectra from crystals at RT or excite with lower or higher energy light, no violet band is emitted from the samples. The same holds for ZnS/Ag crystals. A slow cooling rate after annealing at 1200 °C destroys the centers of the violet fluorescence band in doped ZnS crystals (spectrum 3 in the figures). However, after a second annealing and quenching the 415 nm emission band can be observed again (spectrum 4 in Fig. 1 and 2). This behaviour demonstrates that the creation and annihilation of this luminescence band is reversible.

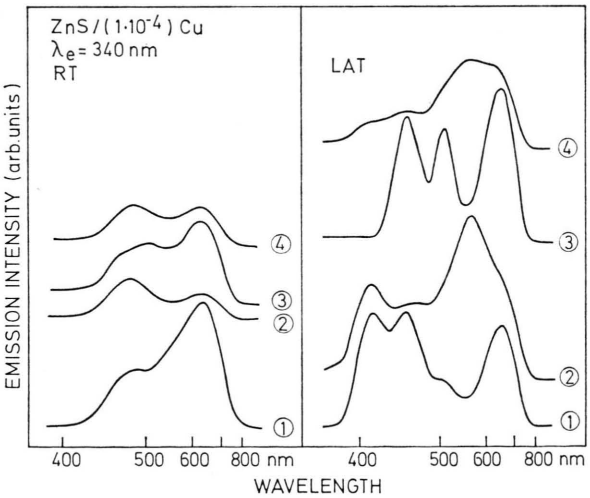

Fig. 1. Fluorescence spectra of ZnS/Cu at RT and LAT under excitation with 340 nm UV-light. 1. as-grown crystal; 2. annealed in an evacuated ampoule for an hour at 1200 °C, quenched; 3. annealed in an evacuated ampoule at 1200 °C, slowly cooled; 4. anewly treated as in 2.

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* Dedicated to Prof. Dr. K. Neumann on occasion of his 70th birthday.

** Part of thesis, Giessen 1974 (D 26).

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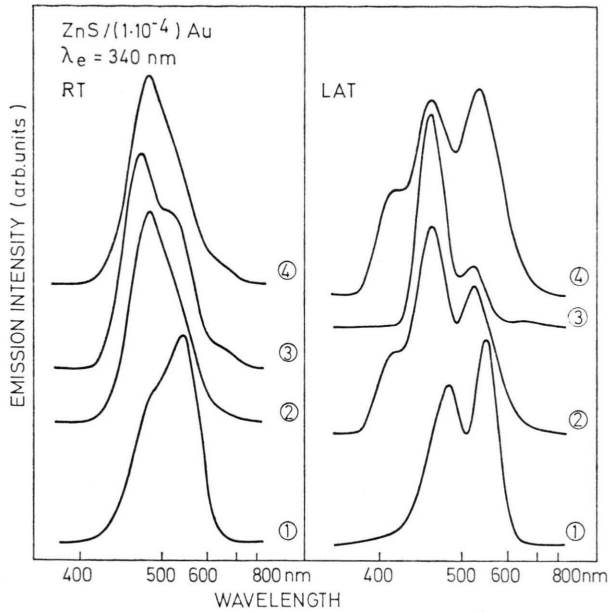

Fig. 2. Fluorescence spectra of ZnS/Au at RT and LAT under excitation with 340 nm UV-light. 1. as-grown crystal; 2. annealed in an evacuated ampoule for an hour at 1200 °C, quenched; 3. annealed in an evacuated ampoule at 1200 °C, slowly cooled; 4. anewly treated as in 2.

In ZnS/Al the same procedure does not lead to any detectable effect. About the observed spectral changes of the other emission bands of these phosphors we shall report in the near future.

The described violet photoluminescence differs from the commonly observed blue fluorescence of activated ZnS, which has been the subject of numerous studies. Above all, the energy of the emission maximum of the violet band is too large. Moreover, the investigated impurity doped ZnS crystals show additional luminescence bands in the blue spectral region. The violet emission is similar to the luminescence reported by Samelson and Lempicki[3].

In summary the main features of the violet fluorescence band are as follows:

1) The band is induced in Cu, Ag, and Au doped ZnS crystals by annealing at 1200 °C and subsequent quenching to RT.
2) The energy position of the emission maximum is independent of the chemical nature of the activator.
3) After annealing at 1200 °C the reversible creation and annihilation of the emission depend on the cooling rate, only.
4) It is impossible to produce the violet band in ZnS/Al by any heat treatment.

A participation of Al and Cl in the electronic processes which give rise to the emission of the 415 nm band must be excluded on account of the experimental results and the specified impurity concentrations. Since the violet fluorescence only exists in quenched activated ZnS crystals, we presume that associated defect centers are not involved in the luminescence process. The independence of the energy position of the emission peak on the chemical nature of the defects indicates that Cu, Ag, and Au stimulate the center formation, only. The foreign atoms should not be part of the luminescence centers. Due to the reported experimental results of this study, we expect that the centers of the violet emission band are isolated native defects of the ZnS lattice.

We have to thank Dipl.-Phys. W. Schwedes for helpful assistance and the Deutsche Forschungsgemeinschaft for support.

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[1] S. Rothschild, J. Electrochem. Soc. **110**, 28 [1963].

[2] I. Uchida, J. Phys. Soc. Japan **19**, 670 [1964].

[3] H. Samelson and A. Lempicki, Phys. Rev. **125**, 901 [1962].

[4] W. van Gool, Philips Res. Rept. Suppl. **3**, 1 [1961].

[5] R. Grasser, G. Roth, and A. Scharmann, Z. Physik **249**, 91 [1971].