

Luminescent properties of plastically deformed ZnS-Cu(Al) crystals

J. MOCHNIAK, S. WAGA, J. MALINOWSKI, M. KIWUS

Institute of Physics, Pedagogical Academy, Opole, Poland.

The photoluminescence spectra, the polarization diagrams and the glow curves of the previously plastically deformed ZnS-Cu(Al) crystals are presented. The transformation of the G-Cu \rightarrow B-Cu luminescence centres as well as the decreasing number of the G-Cu centres parallel to the optical axis of the crystals have been observed.

1. Introduction

It is known [1] that apart from point defects in the synthetic ZnS crystals there occur also nonperiodic changes in the sequence of the close packed layers. Moreover, the ZnS crystals are, in fact, systems of different polytypes, hardly distinguishable one from another. It seems that these faults are due to similar values of Madelung's constant [2] (1.638 for cubic 3C structure and 1.641 for hexagonal 2H structure), and of enthalpy (-48.5 kcal/mole and -45.3 kcal/mole), respectively. For both the structures the first and the second coordination spheres composed of only one type of atoms situated at the same lattice distances are identical, whereas the third and the further coordination spheres are different. The dopant, as another atom differing in size and charge from the host lattice atom, disturbs the existing thermodynamic equilibrium of the crystal, the migration of such dopants towards the surface of the growing crystal increases their concentration which, in turn, generates the formation of growth faults. In the case described, it can be expected that the concentration of the dopants will increase in the vicinity of the stacking faults. The increase of the concentration of copper as activator on the (111) plane in ZnS has been reported, for example, in [3]. Zinc sulphide crystals obtained by various methods differ not only by their structure (amount of the hexagonal and cubic phases), but also by the concentration of point defects and random dopants. These defects play the role of the luminescence centres, often exhibiting the properties of the acceptor pair. The distribution of these centres in ZnS-Cu(Al) crystals is not isotropic [4-6, 9, 10].

A remarkable tendency of ZnS crystals to various polytypic modifications, as well as a distinct anisotropy of the spatial orientation of luminescence centres, have encouraged us to undertake the studies on the luminescence of the previously plastically deformed ZnS crystals.

It seems that the plastic deformation of crystal, understood as a motion of dislocations and a displacement of the atomic layers by several interatomic distances, should cause the change in the orientation of the luminescence centres, partial dissociation of the donor-acceptor pairs, disappearance of some luminescence centres and the change of the concentration of the electron traps.

2. Experimental results and discussion

The experimental results of luminescence studies of ZnS-Cu(Al) crystals presented below have been obtained with the help of a standard equipment. The spectral and polarization measurements were made at room temperature using an Hg 365 nm line excitation. The glow curves have been recorded during the crystal heating at a constant rate of 0.3 K/s.

ZnS-Cu(Al) crystals grown from the vapour phase, with the concentration of Cu and Al being of about 10^{-5} g/g ZnS, have been used for investigations. The plastic deformation of the crystal has been realized in the device constructed specially for this purpose which enabled a continuous increase of the stress and the measurements of the deformation degree.

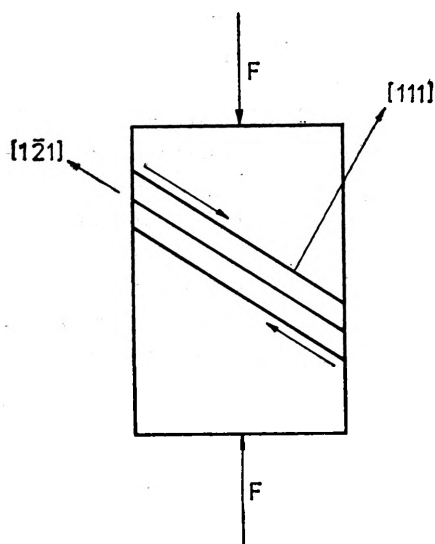


Fig. 1. Orientation of the crystal with respect to the stress direction (F)

The crystal has been ground and polished in form of a cuboid, so as to deflect the optical axis from the stress direction by 45° (Fig. 1). Such an orientation of the crystal facilitates its deformation [7] because the closely packed planes (111) are generally the displacement ones.

The effect of a stable plastic deformation can be easier achieved after the crystal is heated up to about 500 K. Before this deformation the photoluminescence spectra, the polarization diagrams, and the integral and coloured thermo-

luminescence have been investigated. The consecutive stages of the plastic deformation and the stress distribution inside the crystal located between the polarizer and the analyser have been observed on the screen using polarized light. After the deformation the crystal has been cooled to room temperature and all the above mentioned luminescence measurements were repeated again.

2.1. Photoluminescence

The luminescence spectra of the nondeformed and deformed ZnS-Cu(Al) crystals are shown in Fig. 2. The deformation degree was equal to about 10%. The intensity of the photoluminescence emission (as a relative number of the quanta N) of the crystal was measured for two positions of the analyser: parallel — $I_{\parallel}(0^\circ)$, and perpendicular — $I_{\perp}(0^\circ)$ to the optical axis of the crystal.

It has been found that at room temperature the dominating intensity in the spectrum of the nondeformed crystal (dashed line) is that of the green luminescence characteristic of ZnS-Cu(Al), the concentration of Cu and Al being comparable and not very high.

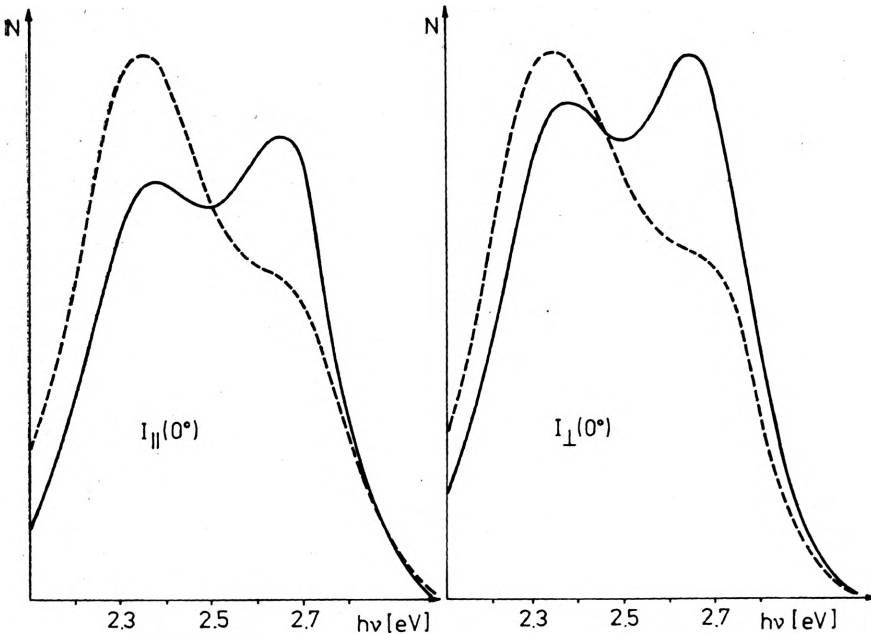


Fig. 2. Luminescence spectra of the nondeformed (dashed line) and plastically deformed (solid line) ZnS-Cu(Al) crystals

During the deformation of the crystal one observed the gradual transformation of the luminescence spectrum from the green emission to the luminescence with the prevailing blue emission.

Figure 2 shows that the shape of the luminescence spectrum of the nondeformed crystal does not depend on the direction of the oscillation of the

electric vector of the emission light. For both the parallel $I_{\parallel}(0^\circ)$ and perpendicular $I_{\perp}(0^\circ)$ components the maxima of the emission intensity occur at the same value of the energy $h\nu$.

Besides the transformation of the spectrum one observes an increasing participation of the perpendicular component $I_{\perp}(0^\circ)$ if compared to that of the parallel component $I_{\parallel}(0^\circ)$ stated after the deformation of the crystal.

The contribution of the blue emission band (2.70 eV) present in the luminescence spectrum of nondeformed crystal increases in the spectrum after deformation. Our observations indicate that the processes of the transformation of the spectrum due to the deformation of a crystal occur always, but their extent and the contributions of individual bands may be different, depending on the type of the crystal.

It is known that the G-Cu emission band in ZnS-Cu(Al) crystal originates from donor-acceptor pairs [4–6]. The substitutional copper ion is an acceptor [8], and aluminium ion is a donor. Both the defects are localized at the same sublattice instead of the zinc vacancies.

Blue emission band (B-Cu) is also related to the donor-acceptor pair but the donor level, playing also the role of the excited state of the blue centre, is situated just below the conductive band of ZnS.

The transformation of the photoluminescence spectra observed in our crystals confirms the fact that a certain number of the G-Cu luminescence centres are transformed into the B-Cu luminescence centres in consequence of the deformation of the crystal. Such an effect is probably due to dissociation of some "green" donor-acceptor pairs situated between the stacking faults along the glide planes. The liberation of the acceptors Cu_{Zn} permits the centres responsible for the blue luminescence of the crystal to increase in number.

2.2. Polarization of luminescence

From the hitherto published papers [9, 10] it is known that the luminescence of both the B-Cu and G-Cu copper emission bands is polarized perpendicularly to the optical axis of the crystal. The polarization measurements [10] have shown that the luminescence centres in ZnS-Cu(Al) crystals have axial symmetry and that they can be oriented along the directions joining the nodes of two different sublattices or the nodes of the same sublattice of a ZnS crystal. In papers [9, 10] it has been shown that in the investigated crystal an orientation-limited degeneration of the luminescence centres occurs distinctly at the directions perpendicular to its optical axis.

The azimuthal polarization dependences $P(\varphi)$ and $P_n(\varphi)$ of the B-Cu and G-Cu luminescence, obtained during polarized and unpolarized excitation of the crystal have been shown in Fig. 3. The polarization diagrams of nondeformed crystal are represented by the dashed line. The polarization diagrams of the green luminescence (Fig. 3) give the evidence to increasing polarization degree of the G-Cu luminescence of deformed crystal. These increased polariza-

tions $P(\varphi)$ and $P_n(\varphi)$ are probably due to the decreasing numbers of the green centres (parallel to the optical axis of the crystal) and to the centres depolarizing the luminescence, the transition directions of which are oriented perpendicularly to the c -axis.

Hence, in the emission spectrum of deformed crystal we observe the spectrum transformation from the green to the blue luminescence and the increased degree of the green luminescence polarization. The state of the polarization of the blue B-Cu luminescence behaves in a somewhat different way.

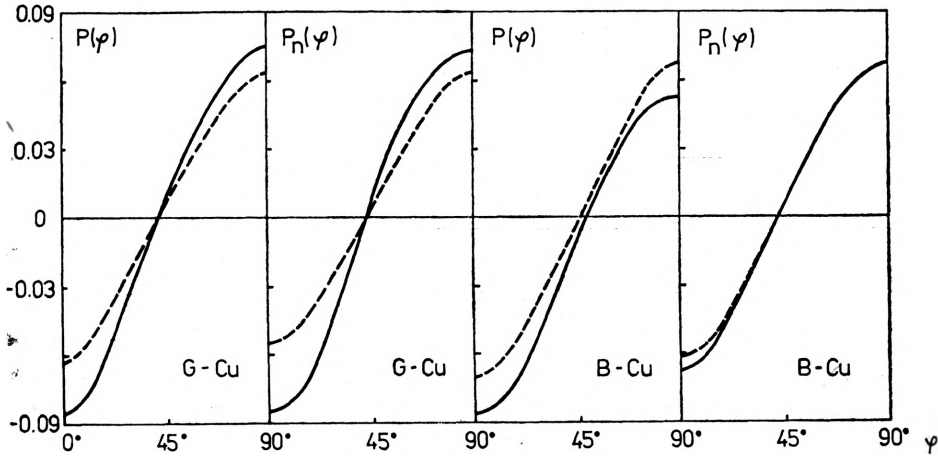


Fig. 3. Azimuthal dependences of the polarization of the B-Cu and G-Cu luminescence of ZnS-Cu(Al) crystal excited by polarized — $P(\varphi)$, and unpolarized — $P_n(\varphi)$ UV radiation. Dashed line represents the polarization diagrams of nondeformed crystal

The polarization diagrams of the blue luminescence of the deformed crystal are more asymmetric than those of the non deformed one. It may be supposed that the increase in the number of the blue centres in the deformed crystal, as compared with that of the nondeformed crystal takes place mainly at the planes perpendicular to the optical axis of the crystal. The increases of absolute values of polarization $P(\varphi)$ and $P_n(\varphi)$ for $\varphi = 0^\circ$ are, most probably, due to the increasing number of the centres, the transition momenta of which are perpendicular to the c -axis.

The optical birefringence of the crystal affects undoubtedly the shape of the polarization diagrams. The deformation of the crystal changes the birefringence and its influence on the values $P(\varphi)$ must be easily detectable for $\varphi = 45^\circ$.

2.3. Thermoluminescence

It can be supposed that the plastic deformation of a crystal changes not only the relative concentrations of different luminescence centres but also the concentration of the electron traps due to the dissociation of some defect centres, which in the case of the ZnS-Cu(Al) crystal might be Al_{Zn} or V_S .

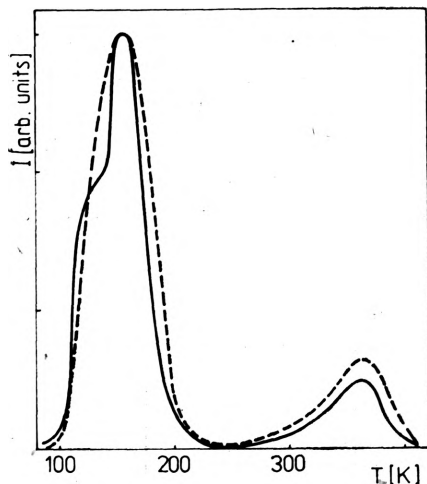


Fig. 4. Integral glow curves of the nondeformed (dashed line) and plastically deformed (solid line) ZnS-Cu(Al) crystals

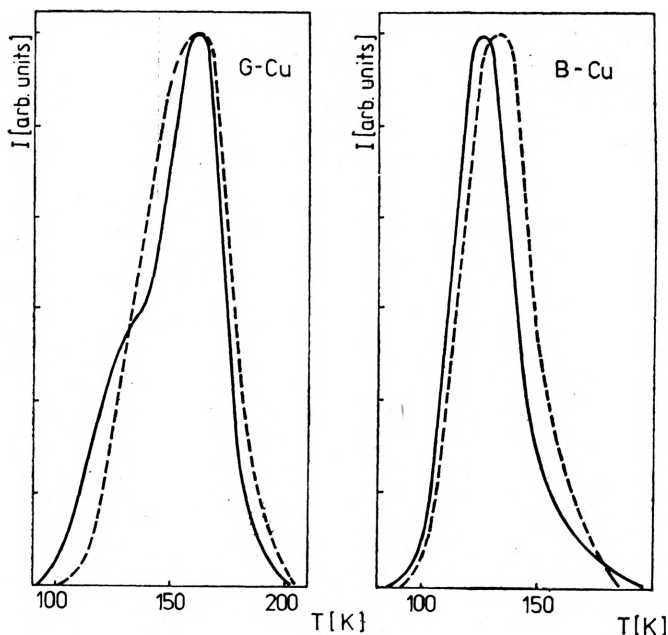


Fig. 5. Colour glow curves of the ZnS-Cu(Al) crystal before (dashed line), and after (solid line) plastic deformation

Figure 4 shows the integral glow curves recorded before (dashed line) and after plastic deformation (solid line) of the crystal. A comparison of the thermoluminescence curves presented in Fig. 4 shows that the plastic deformation of the crystal at $T^x = 364$ K ($E_g = 0.77$ eV) lowers the glow peak which belongs to the green emission centres. The glow peak at $T = 160$ K ($E_g = 0.33$ eV) belongs also to the green emission centres. The most remarkable changes in the shape of the TL glow curves due to the plastic deformation of the crystal were observed in the low temperature region.

The colour thermoluminescence curves (Fig. 5) proves that the low-temperature glow peak at about 130 K, being clearly shaped in the deformed crystal, belongs to the blue B-Cu luminescence centres.

It seems that our hypothesis concerning the dissociation of donor-acceptor pair in the deformed crystal, accompanied with the formation of new B-Cu luminescence centres as well as new shallow trap levels related to these centres, is confirmed by the carried out measurements.

The initial results of investigation of some luminescence properties of the deformed ZnS-Cu(Al) crystals, presented above, confirm the assumption that the luminescence can directly interfere with the orientation of the anisotropic luminescence centres in these crystals.

The plastic deformation of the crystals, changing their optical birefringence, affects the shape of the polarization curves and changes the anisotropy degree of the centres, as well as their concentration along equivalent crystallographic directions.

It seems that the results of our measurements confirm once more the axial symmetry of the luminescence centres formed by the donor-acceptor pairs which are able to undergo the dissociation or to change their orientation in the crystal. These effects are manifested in the transformation of the emission spectra as well as in the change of the polarization degree of luminescence and in the deformation of the shape of thermoluminescence curves due to the deformation of crystal.

Acknowledgement — This study was sponsored by the Institute of Physic of Warsaw University under contract M.R. I.5.

References

- [1] VERMA A. R., KRISHNA, *Polymorphism and Polytypism in Crystal*, J. Wiley and Sons, New York 1966.
- [2] ROT V. L., *Fizika i Khimiya Soedinenii A₂B₆*, Mir, Moscow 1970.
- [3] ARKHANGELSKII G. I., BUKKE E. E., GORBACHEVA N. E., GRIGOIREV N. N., FOK M. V., *Trudy FIAN SSSR (in Russian)* **129** (1981), 66.
- [4] GOLDBERG P. [Ed.], *Luminescence of Inorganic Solids*, Academic Press, New York, London 1966.
- [5] SHIONOYA S., ERA K., WASHIZAWA Y., *J. Phys. Soc. Jap.* **21** (1968), 1624.
- [6] SUZUKI A., SHIONOYA S., *J. Phys. Soc. Jap.* **31** (1971), 1455.
- [7] SHEKHTMAN V. S., SHMYTKO YA. I., ARISTOV V. V., ABDIKAMALOV B. A., *Fiz. Tverd. Tela* **18** (1976), 1358.
- [8] JAMES J. R., CAVENETT B. C., NICHOLAS J. E., DAVIES J. J., DUNSTON D. J., *J. Luminesc.* **12-13** (1976), 447.
- [9] SHIONOYA S., KOBAYASHI Y., KODA T., *J. Phys. Soc. Jap.* **20** (1965), 2046.
- [10] MOCHNIAK J., WAGA S., *Acta Phys. Polon.* **A53** (1978), 819.

*Received March 22, 1985
in revised form September 20, 1985*

Люминесцентные свойства пластично деформированных кристаллов ZnS-Cu(Al)

Были исследованы спектры фотолюминесценции, поляризационные диаграммы и кривые термолюминесценции пластично деформированных кристаллов ZnS-Cu(Al). Исследования показали, что после деформации кристаллов получается трансформация центров G—Cu в центры В—Cu. Было доказано, что можно определить их ориентацию в кристаллической решетке.