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THERMALLY STIMULATED LUMINESCENCE OF POLYCRYSTALS ZnS

Thermally stimulated luminescence and kinetics of signal attenuation of glow of zinc sulphide polycrystals received by method of high-temperatured synthesis are investigated. The persistence of is samples in green region of spectrum ($\lambda_{max} = 520$ *nm*) with anomalously major duration of glow is revealed. In TSL spectrum a series of strips are revealed. It is observed, that the spectrum TSL can be surveyed in approach of repeated capturing absence. The activation energies relevant to chlorine levels are calculated. It is shown, that for the indicated features for glow kinetics and TSL spectrum the impurity of chlorine is responsible.

Among semiconductors of A^2B^6 group zinc sulphide is of special interest. Zinc sulphide is wide band and direct band compound with width of energy gap 3,6 *eV* (when $T = 77$ K) — 3,7 *eV* (at room temperature). In energy gap of ZnS, there is a set of energy levels with various occurrence depths stipulated both by availability of impurities and native defects. Usually, the undoped crystals of zinc sulphide practically independent on production procedure, have conductance of *n*-type.

One of methods to produce deriving polycrystalline materials distinguished by simple technology and low energy costs, is self-spreading high-temperature synthesis (SHS) [1]. With its help it is possible to gain both stoichiometric, and doped polycrystals. The investigation of spectra for thermally stimulated luminescence (TSL) is one of methods to define the energy position trapping levels.

We have investigated ZnS(Cl) polycrystals. The measurements of TSL spectra were carried out as follows: at the temperature of fluid nitrogen the sample was lighted during 20—30 mines by laser and at the same time the defined photosum was stocked on traps. Photoexcitation was conducted in the lack of exterior padding illumination (in darkness). After the traps were essentially filled with electrons, the light source was switched off. Then the heating of sample was produced with constant velocity.

TSL curves of ZnS(Cl) polycrystals under three various heat rates ($\beta_0 = 20$ degree/mines, $\beta_0 = 10$ degree/mines, $\beta_0 = 5$ degree/mines) were obtained. The given curves are stipulated by superposition of two processes: by the kinetics of photoluminescence signal damping and thermally stimulated luminescence. Judging by the form of curves, it is possible to tell, that change of intensity and displacement of glow band maximums depend on the chosen heat rate in samples. The intensity of luminescence for ZnS(Cl) polycrystals with heat velocity of 20 degrees per one minute (0,3 degree/sec) is more, than with other velocities of heat.

To separate the kinetics process from that of TSL, we measured photoluminescence kinetics under temperature and temperature of fluid nitrogen within 1 hour after the moment when stimulating light was lockout (fig. 1). It was noticed, that the shape of curves of a relaxation did not vary during of excitation of sample with various waves lengths.

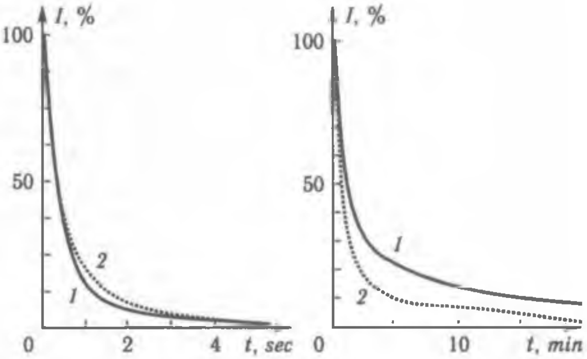

Fig. 1. Kinetics for signal attenuation of ZnS(Cl) photoluminescence for various time intervals (*a*, *b*):

1 — under ambient temperature; *2* — at the temperature of fluid nitrogen

Under measurement of relaxation curves in the course of different temperatures ($T_1 = 80$ K, $T_2 = 173$ K and $T_3 = 290$ K) it was observed, that the dependence on temperature has not practically come to light. Therefore, the curves of photoluminescence signal attenuation were measured only at temperature $T = 290$ K, but for various time intervals relevant to duration of measurement of TSL curves with various heat rates: $t_1 = 15$ *min* for $\beta_0 = 20$ degree/min, $t_2 = 30$ *min* for $\beta_0 = 10$ degree/min and t3 = 60 *min* for $\beta_0 = 5$ degree/min.

By deduction of curves of photoluminescence relaxation from the above-stated curves, the TSL spectra without contribution imported by kinetics of photoluminescence signal attenuation have been obtained. The results for various heat rates are shown in fig. 2.

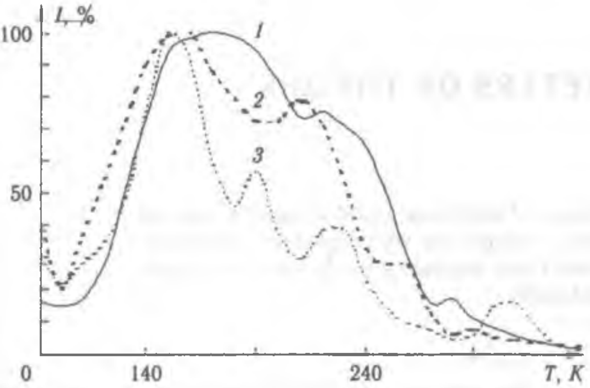

Fig. 2. TSL spectrums measured under of various heat velocities:

1 — 20 degree/min, *2* — 10 degree/min, *3* — 5 degree/min

The received dependencies represent integral curves composed for a series of partial strips of glow, stipulated by the contribution of various trap centres. On maximums for sectional individual strips of glow it is possible to define their quantity and to calculate the depth of occurrence centres of traps E_t.

As the methods to define E_t depend on a view of glow kinetics, it is necessary to determine correctly the character of glow kinetics. This question was solved taking into consideration the following criteria: character of symmetry for TSL strips, dependence T_m for reserved photosum quantity and dependence of TSL bandwidth on quantity of the reserved photosum.

As it is shown in fig. 2, TSL spectra consist of a series of glow strips, which overlap one another. So the guess on linear glow kinetics was accepted, because the spectra broadened to the leg of low temperatures, and, hence, parameters of glow T_m strip and δ did not depend on quantity n_{t_0}.

To define the quantity E_t the approximate computational methods were used.

1. The quantity E_t was calculated on the basis of relations, determining dependence, δ or E_t of half-width. When TSL is linear the formula can be obtained as followed:

$$E_t = \frac{2kT_m^2}{\delta}.$$

At the same time, calculation of quantity E_t it was required to define only two parameters TSL — T_m and δ.

2. For the case of the linear kinetics, the quantity E_t can be rather simply calculated under the availability of two radiation spectra measured under various heat rates of crystalline phosphor. Let temperature position of TSL strip maximum corresponds to T'_m under heat rate β'_0 and to T''_m — under β''_0. Taking into consideration the approaches of linear kinetics, the temperature standing of maximum is defined by the formula

$$T_m = \frac{E_t}{k} \cdot \left| \ln\left(\frac{W_0}{\beta_0} \cdot \frac{kT_m^2}{E_t} \right) \right|^{-1}.$$

The relation of quantities T'_m/T''_m allows to determine quantity E_t as follows:

$$E_t = k \cdot \left(\frac{1}{T'_m} - \frac{1}{T''_m} \right)^{-1} \cdot \ln \left| \frac{\beta''_0}{\beta'_0} \cdot \left(\frac{T'_m}{T''_m} \right)^2 \right|,$$

3. On initial stages of thermally stimulated luminescence, when the difference $T - T_0$ is such, that the reserved photosum quantity has not enough time to change considerably, the relation ships for two types of the kinetics determining TSL spectrum, irrespective by to character of kinetics, acquires the following form:

$$I(T) = A \cdot e^{-\frac{E_t}{kT}},$$

where A — stationary value, not temperature-dependent. Hence, at the initial TSL stages, the dependence $I(T)$, constructed in $\ln I \sim T^{-1}$ coordinates, is represented as direct line with E_t/k declination. To calculate E_t quantity from figure 2, the quantities T_m and δ were measured. The values T_m are also shown in table 1.

Table 1

Temperatures of maximums of TSL strip intensities *s* for three heat rates and half-width of apparent glow strips

β_0	T_{m1}, K	δ_1, K	T_{m2}, K	δ_2, K	T_{m3}, K	δ_3, K
20	168	212	219	94	276	20
10	160	260	210	52	254	24
5	150	162	190	46	224	31

The average results on E_t, particular three approximate methods are shown in table 2.

The nature of centres, responsible for traps has not already been defined. According to the printed sources [2] depth for occurrence of chlorine levels ~0,25 *eV*, that is well agreed with energy standing of one sticking levels the define by us. It is supposed, that the intrinsic defects of polycrystal and impurity of chlorine (Cl_i) are responsible for the relevant centres.

Table 2

Values E_t for each of glow strips

E_{t1}, *eV*	E_{t2}, *eV*	E_{t3}, *eV*
0,06	0,12	0,3

References

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