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IN ACTIVATED ALKALI HALIDES

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ЭЛЕМЕНТАРНЫЕ МЕХАНИЗМЫ ОБРАЗОВАНИЯ ЦЕНТРОВ ОКРАСКИ
ЭКСИТОНАМИ В АКТИВИРОВАННЫХ ПГК

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BASIC MECHANISMS OF COLOUR CENTRES PRODUCTION BY EXCITONS
IN ACTIVATED ALKALI HALIDES

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The present paper deals with some peculiarities of colour centres formation which are caused by introduction of the activator in alkali halides.

As it has been proposed by Hersh, Vitol and Pooley, the main primary reactions of defect production in alkali halides are anionic exciton decay resulting in Frenkel pair formation:

F - H and α - I centres
with high quantum efficiency - 0.5 - 0.8 [1].

It is also well known that impurities affect the stable F-centres concentration but it is not clear whether they influence the primary decay of the anion excitons or the secondary reactions of colour centre production only.

The above mentioned problem is closely connected with the basic mechanisms of colour centre production in activated alkali halides, with the spatial distribution of electron and hole centres and their recombination in photo- and thermostimulated processes.

The formation of electron and hole centres was studied under ultraviolet light irradiation conditions creating primarily a single type of the electron excitations in crystal -

the anion excitons

In such a way we hope to suppress the electron-hole processes which are dominant under X-ray or electron beam irradiation.

Another specific feature of the present investigation is the irradiation with small doses of ultraviolet light when the influence of activator is displayed at most.

The objects under investigation were crystals of KBr and KI activated with Tl^+ , In^+ , Sn^{++} in concentrations 10^{17} - 10^{18} cm^{-3} irradiated by a deuterium lamp D-400 light and grating monochromator MDP-3 with linear dispersion 1 nm.

The presence of colour centres was detected by both measuring the excitation spectra of photostimulated activator luminescence and optical stimulated spectra as well as thermoluminescence.

Production of Electron Centres

1. In all the investigated crystals with cationic activators the complex structure of excitation spectra of activator luminescence photostimulated in F-absorption band has been observed. In the spectral region from the excitation band maximum where the free excitons are produced in regular lattice, till the D-absorption band where the exciton is absorbed near the activator, at least two (or more) narrow exciton-like bands are observed (Fig. 1, curve 1). The maxima of these bands, especially for the longwave, change in crystals with different activators.

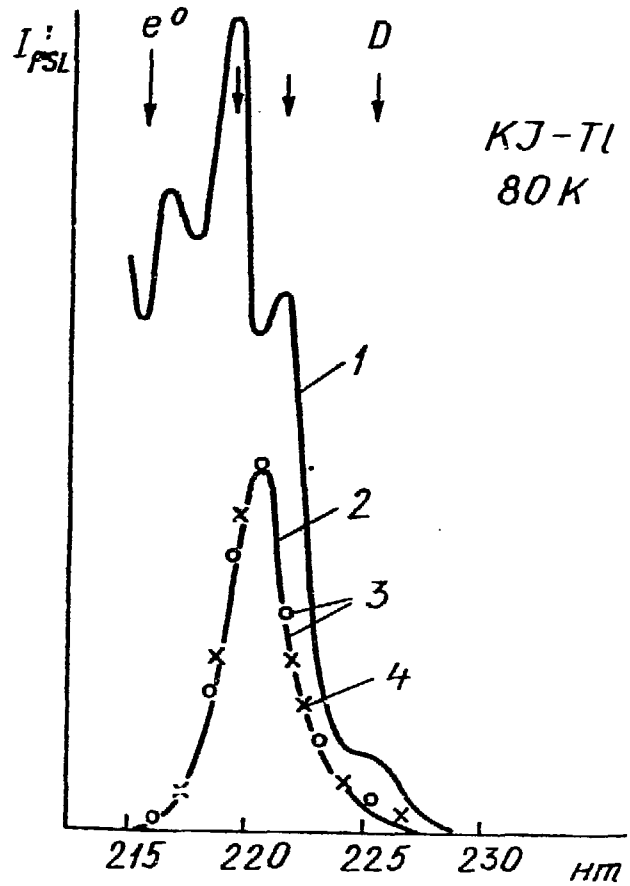
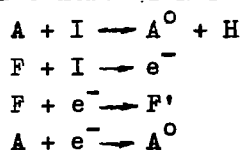


Fig. 1.

- 1 - excitation spectra of activator luminescence in F-absorption band;
 2 - excitation spectra of activator luminescence photo-stimulated in Tl^0 absorption band;
 3,4 - excitation spectra of Tl^0 and F' centres glow peaks.

It is proposed that the origin of the bands observed could be explained by exciton absorption at discrete distances from the activator, and therefore the decay of such exciton with F-centre formation takes place at the corresponding distances from the activator too.

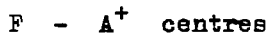
2. The formation of Tl^0 and F' charged electron centres by excitons was investigated too. In Fig.1 (curves 3,4) the excitation spectra of activator luminescence photostimulated in Tl^0 absorption band in KI-Tl at 100 K are presented. They differ from the excitation spectra of photostimulated luminescence in F-absorption band. The maximum of excitation spectra for charged electron centres is situated on the edge of the exciton absorption band and depends on the activator type^{*}. The formation efficiency of charged centres at maximum of exciton bands is approximately 10-100 times smaller. The difference of exciton spectra for F and $A^0(F')$ centres can be explained by different mechanisms of centre production. We suppose that formation of Tl^0 , In^0 , F' centres is predicted by interaction of I-centre with F and A centres



It is suggested that the exciton spectrum of the F' and Tl^0 type charged electron colour centres characterizes the direct optical absorption of the self-trapped exciton decaying near the activator which forms the pair of charged defects of \mathcal{O} and I centres.

Production of Activator Hole Centres

The formation of hole centres by excitons has been discussed below. At temperatures when H-centres are mobile and can interact with other crystal defects, the main light sum in activated alkali halides is stored on



(A^+ is activator hole centre). The quantum yield of such activator light sums stimulated with F-light is about $10^{-3} - 10^{-4}$ RT [2]. The concentration of A^+ centres is assumed to be proportional to the photostimulated activator light sum (it is correct when $n_F \gg n_{A^+}$).

The temperature dependence of Tl^{++} and In^{++} centres production in KI is presented in Fig.2 where two temperature regions are distinguished - temperature-independent formation of A^+ centres above 200 K and temperature dependent production of Tl^{++} and In^{++} centres with activation energies 0.05 and 0.07 eV, respectively.

The temperature dependent A^+ centres formation prevailing at RT should be explained by activator capture of unrelaxed holes formed in the crystal during the irradiation according to the reaction



^{*} For KI-In excitation band at 80 K maximum is 225 nm, for KI-Sn at RT - 237 nm.

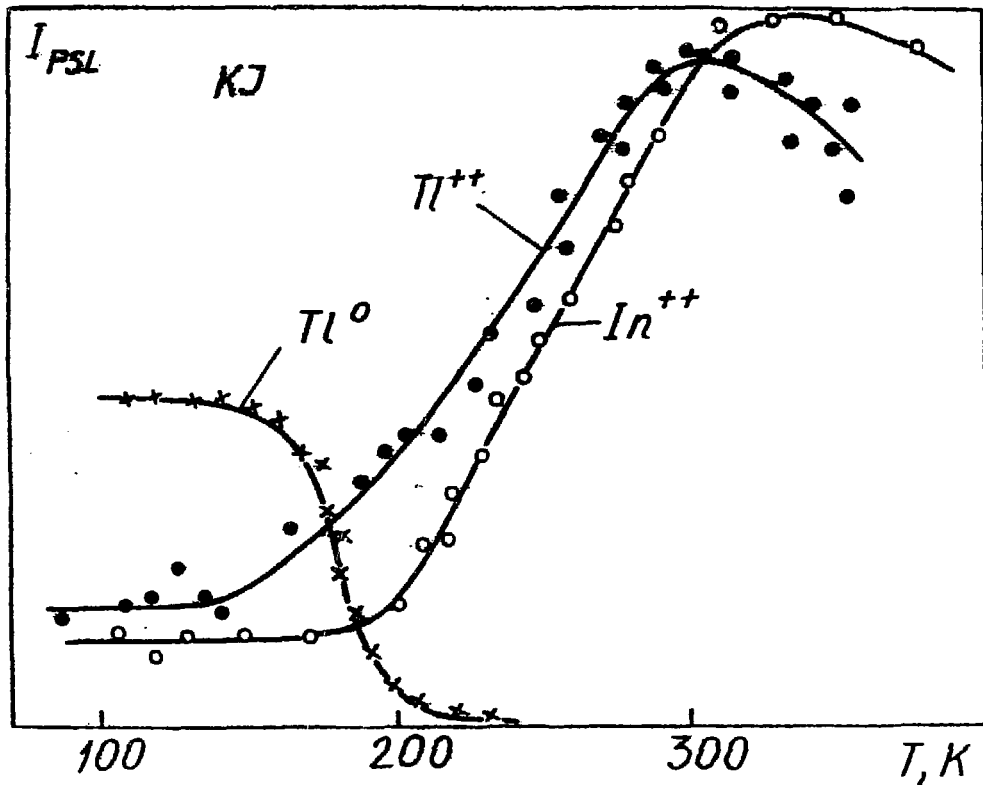


Fig. 2.

Temperature dependences of activator colour centres production by excitons in KI.

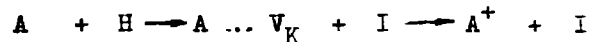
The production of α centres has been discussed before [see also 3,4].

It has been established [5] that unrelaxed holes are captured by the activator with approximately the same energy barrier $\bar{\epsilon}$. In our case the activation energy presents the sum of stable F-H centres production energy in primary exciton decay process as it has been proposed by Sonder [9] (for KI it is 0.015 eV) and the barrier for unrelaxed hole capture.

Therefore we propose that activator hole centres are formed in secondary reactions of

F, α , H, and I centres

primarily produced in exciton decay; the mutual reverse reactions determine the quantum yield of the activator light sum stored on F-A⁺ centres as well as the top concentration of A⁺ centres. The latter is known to be more than 10 % of the activator concentration. The formation of some colour centres as a result of direct interaction of excitons with vacancies and activator ions [11] is not excluded. The temperature independent formation of A⁺ centres is connected with tunnel ionization of the activator in the near pair A⁺-V_K-centres appearing after the overcharge of H-centre in the lattice distorted by the activator:



Mechanism of Photostimulated Activator Luminescence and the Spatial Distribution of Colour Centres

The spatial distribution of colour centres is generally observed in two contradictory models. According to one of them - radiation defects are produced in correlated pairs, and in terms of the other one they are formed statistically.

Let us discuss the A⁺ centres production with regard to the spatial distribution of F and A⁺ centres. There are two possibilities - first, the activator affects the primary exciton decay with F-H pair formation. If the primary decay of exciton occurs mainly near the activator ion leading to the formation of correlated F-A⁺ pairs in the same decay act (as it has been proposed in [6]), then the photostimulated activator luminescence will occur in isolated pairs too, i.e. the F centres electron recombines only with its own hole activator centre, and we observe the exponential decay of luminescence.

If the decay of exciton occurs statistically in regular lattice sites as in pure alkali halides, then the spatial distribution of F-A⁺ centres will be statistic too, and the photostimulated activator luminescence will obtain the characteristics of zone-recombination mechanism.

It is necessary to mention that the existence of stable F-A⁺ centres at the distances of same lattice constants is doubtful. Tunneling process is likely to occur in such pairs resulting in the formation of α - A centres [7].

Besides, in order to decay near the activator ion the free anion exciton produced in regular lattice site must reach the activator. For mean activator concentrations these distances are about 20-30 lattice constants. The free

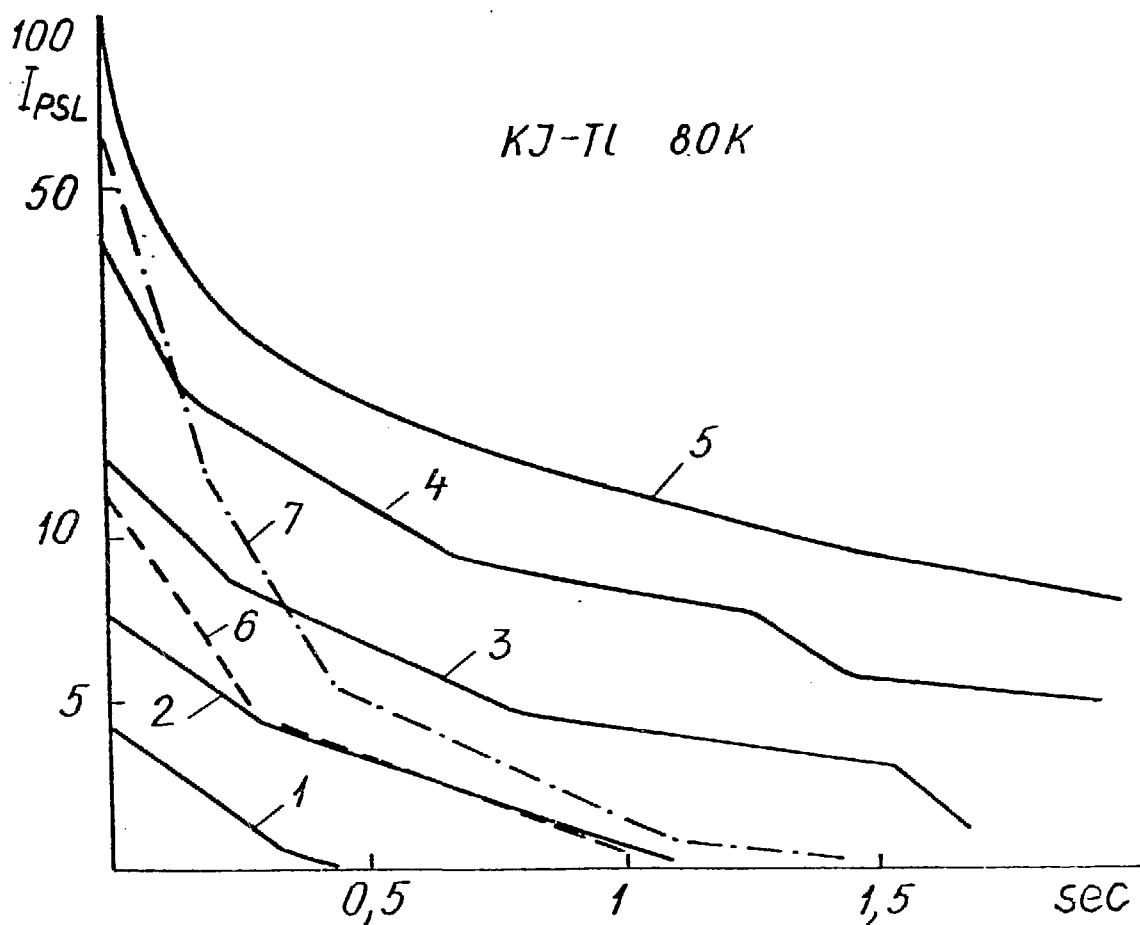


Fig. 3.

Photostimulated activator luminescence decay after excitation with various doses of light (1-5) at maximum of excitation absorption band at 80 K in KI-Tl after preirradiation of crystal (6), and after preirradiation and heating up to 200 K (7).

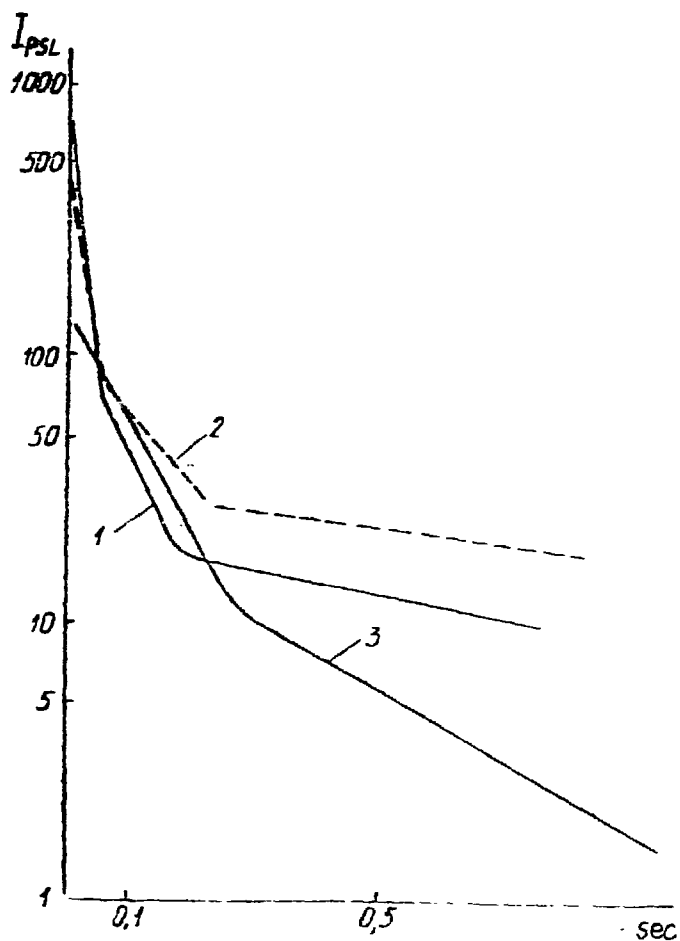


Fig. 4.

Photostimulated activator luminescence kinetics of KI-Tl (1) and KBr-In (3) crystals irradiated and stimulated by light at room temperature (RT), and stimulated by light at 100 K (curve 2 for KI-Tl; for KBr-In - below the sensitivity threshold of the measuring technique).

exciton in KBr and KI can travel within such distances only at low temperature while at RT the free anion exciton is practically motionless [8] and decays at the site of production. As seen from the experiment, all types of exciton and X-ray excitation the manifold decay of photostimulated activator luminescence is observed. For example, in Fig.3 the dose dependence of photostimulated activator luminescence decay after excitation by light at maximum exciton absorption band (at 80 K) in KI-Tl is presented. In spite of these most favourable conditions for correlated pair formation the appearance of fast as well as slow stages of luminescence decay is observed with dose rise; further they form a continuous single curve. The observed decay of photostimulated luminescence is characteristic for zone recombination luminescence mechanism among statistically distributed colour centres with display of secondary electron retraps. It can't be explained in terms of the correlated pairs model.

The photothermal zone character of photostimulated luminescence is confirmed by cooling of light sum emission at 100 K in KBr crystals irradiated at room temperature (Fig.4).

Let us resume the temperature dependence of Tl^{++} and In^{++} centres production (Fig.2). Beside the early mentioned interpretation of the dependences as being related with secondary reaction of A^+ centres creation another possibility of interpretation related with primary division of stable F and H centres should be discussed, as proposed in [9] by Sonder. We prefer the case of the secondary reactions of A^+ centre creation due to the difference of the temperature dependences from those reported by Sonder in undoped crystals (activation energy being 0.015 eV) including the case of exciton creation of colour centres. However, it may be still assumed that in KI-Tl and KI-In the above mentioned activation energy is higher than in undoped crystals if the exciton is excited optically from absorption bands localised at some distance from the activator. Then the activation energy characterizes the primary distribution of F-H centres near activator. In the above case the creation of F centre occurs at a discrete distance from the activator (but not from A^+ centre). The situation discussed is possible under X-ray and other excitation types when the exciton results from the electron and V_K centre recombination if the V_K centres preferentially localize near the activator.

Conclusions

1. In activated alkali halide crystals under the ultraviolet irradiation in anion exciton band region the complex structure of excitation spectra of activator luminescence photostimulated in F absorption band has been observed. At least two narrow exciton-like bands are detected at the tail of exciton absorption band which are interpreted in terms of exciton absorption at discrete distances from the activator, and therefore the exciton decay which results in F centre generation occurs at the corresponding distances from the activator too.

2. It is suggested that the excitation spectrum of the F' and A^0 type charged electron colour centres characterizes the direct optical absorption of the self-trapped exciton near the activator. The exciton decay forms

the pair of the charged defects of O_V and I centres while interaction of I centre with F and A centres results in creation of F' and A° centres.

3. The formation of A^+ type activator hole colour centres by H centres due to exciton decay results at least in two mechanisms. The temperature independent formation of A^+ centres is connected with tunnel ionization of activator in a close pair of A-V_K centres appearing after the overcharge of H centre in the lattice distorted by the activator. The temperature dependent A^+ centres formation prevailing at the room temperature is explained by the capture of the unrelaxed hole formed in the crystal bulk during the irradiation when H centre is captured by the anion vacancy.

4. Basing on experimental investigations of kinetics of photostimulated activator luminescence decay after excitation by light in anion absorption bands and X-rays in activated KI and KBr systems it has been concluded that anion exciton decays which leads to formation of F-H pair at regular lattice sites as in undoped crystals. The mechanism of photostimulated activator luminescence has the character of zone recombination between statistically distributed F and activator centres.

It has been concluded that the activator does not affect the primary reaction of exciton decay with F-H pair generation but only the secondary reactions of colour centre production.

R e f e r e n c e s

1. R.T.Williams, J.N.Bradford and W.L.Faust. Short-pulse optical studies of exciton relaxation and F center formation in NaCl, KCl and NaBr. - Phys. Rev.B, 1978, vol.18, No.12, pp.7038-7057.
2. G.Vāle, G.Vlasov, I.Plyavin. The absolute quantum yield of stored light sums in activated alkali halide crystals. - Izv.AN Latv.SSR.Ser.fiz.-tehn.nauk, 1978, No.5, pp.13-15.
3. G.Vāle. Production of electron colour centres by excitons in activated alkali halide crystals. - Izv.AN Latv.SSR (to be published).
4. G.Vāle. Mechanism of activator center ionization in alkali halides by excitons. - Izv.AN Latv.SSR. Ser.fiz.-tehn.nauk, 1981, No.1, pp.123-125.
5. E.Aluker, V.Flerov, S.Chernov. Influence of temperature on probability of hole localization and capture by activator in alkali halide crystals. - Solid State Phys. USSR, 1979, 21, No.12, pp.3660-3665.
6. G.Vlasov, R.Kalnins, L.Nagly et al. Some physical phenomena in activated alkali halide crystals and the possibility of optical data processing. - Avtometriya, 1980, No.1, pp.66-84.
7. Ya.Bogans, Ya.Valbis, U.Kanders et al. Tunnel luminescence in pure and activated with Tl and Ag alkali halide crystals. - Izv.AN USSR, ser.fiz., 1978, 37, pp.741-746.
8. E.Aluker, D.Lusis, S.Chernov. Electron excitations and radioluminescence of alkali halide crystals. - Riga, Zinatne, 1979, pp.134-139.
9. E.Sonder. Temperature dependence of Frenkel pair production from F-aggregate center destruction. - Phys.Rev.B, 1975, vol.12, No.4, pp.1516-1521; E.Sonder. Radiation annihilation of F-aggregate centers in KCl. - Phys.

10. G.Vāle. Kinetics of Recombination Photostimulated Luminescence and Distribution of Radiation Defects in Activated Alkali Halides. - Izv. AN Latv.SSR. Ser.fiz.-tehn.nauk, 1981, No.1, pp.46-50.
11. R.Kink, G.Liidja. Exciton-induced colour centre growth in KBr and KI crystals at 5 K. - Phys.stat.sol., 1970, vol.40, pp.379-387.