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**Manifestation of H-Centre Aggregation
in the Exciton-Induced
Thermostimulated Luminescence
of KBr:In and KBr:Tl Crystals**

By

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Introduction The primary processes of defect production, in particular, of F- and H-centres by ionizing radiation in alkali halides appear now to be understood in a considerable detail /1/. Since the H-centres become mobile at rather low temperatures (≥ 40 K in KBr), it follows that these defects might be stabilized via either (1) their capture by anion or cation impurities, or (2) H-centre aggregation leading to hole V-centre creation /2 to 5/.

Significant progress in studying the processes of the V-centre production has been made in the case of pure alkali halides as well as alkali halides doped with mono- and divalent impurities /2, 3/. As is known, there exist several types of V-centres, but V_2^- and V_3^- -centres only are thermally stable in pure alkali halides above room temperature (RT) /3/.

In this note we concentrate mainly on the production of V-centres via H-centre aggregation in KBr doped with ns^2 ions (In^+ , Tl^+). Such crystals were proposed as perspective materials for reversible optical memory for recording UV radiation images /6/.

It should be mentioned that in the case of alkali halides doped with ns^2 ions the traditional absorption spectra investigations are not efficient because of the considerable overlapping of two groups, i.e. V_2^- and V_3^- -absorption bands (with peaks at 265 and 230 nm in KBr, respectively) and ns^2 -ion absorption bands (so-called A-, B-, C-bands having peaks at RT at 300 to 310, 277, and 240 nm in KBr:In, respectively). For this reason luminescent methods were used in this note.

Experimental KBr:In and KBr:Tl crystals were prepared by means of the Stockbarger technique. The concentrations of In^+ and Tl^+ ions were 9×10^{16} and 1×10^{17} cm^{-3} , respectively. For measurements, a 400 W deuterium lamp combined with an SPM-1 monochromator was used. The thermostimulated luminescence (TSL) curves were monitored with a linear heating rate of 10 K/min displayed on the X-Y recorder. In some experiments during thermoluminescence recording the very low-

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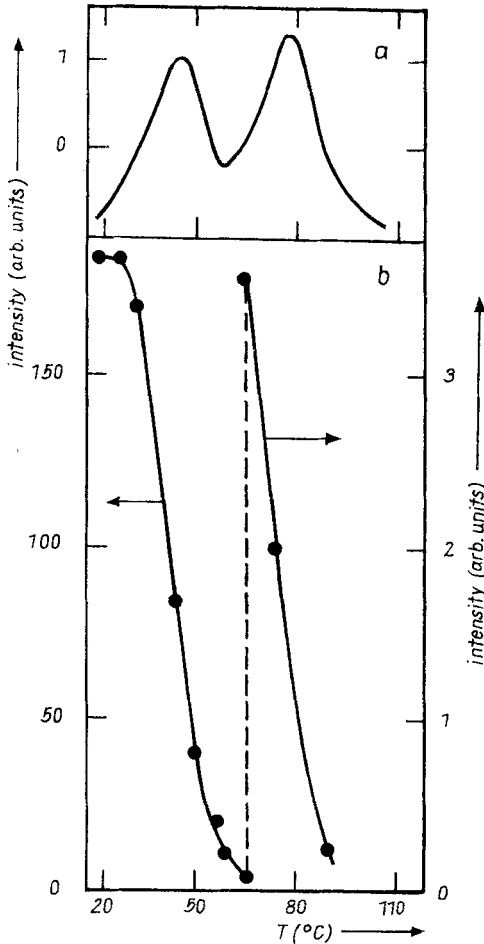


Fig. 1. a) TSL glow curve, b) PSL dependence on temperature measured in the probing regime of a KBr:In crystal irradiated in the exciton fundamental absorption band ($\lambda = 192$ nm)

intensity F-light stimulation was used with a He-Ne laser through the combination of attenuating filters. It was chosen deliberately to be so weak that its influence had no effect on the kinetics under study. Such a regime of synchronous recording of the photostimulated luminescence (PSL) and TSL, when a predominant portion of F-centres recombined via TSL is called hereafter probing.

Results and discussion Fig. 1 shows some typical results of the probing regime of synchronous monitoring of both TSL and PSL curves, namely: (a) TSL glow curve of a KBr:In crystal irradiated by UV light in the exciton fundamental absorption band ($\lambda_{\text{irrad}} = 192$ nm, dose $\approx 10^{14}$ photons/cm²) at RT,

and (b) PSL dependence on temperature T measured in the probing regime. These experimental results demonstrate that defects being associated with the peak I ($T_{\text{max}} = 45$ °C) of TSL anneal out together with the PSL defects and thus they are responsible for the PSL. These defects are $\{F, \text{In}^{2+}\}$ pairs as well as other pairs consisting of the In^{2+} ion and the F-type electron centre, as was proved by the PSL experiments /7 to 9/.

Besides TSL peak I, another peak II with $T_M = 80$ °C is also observed. The dose dependence of both TSL peaks is shown in Fig. 2. Their behaviour clearly differs: The total emitted TSL light sum in peak I is proportional to the irradiation dose, then it saturates, while the TSL peak II shows a superlinear growth with dose increase.

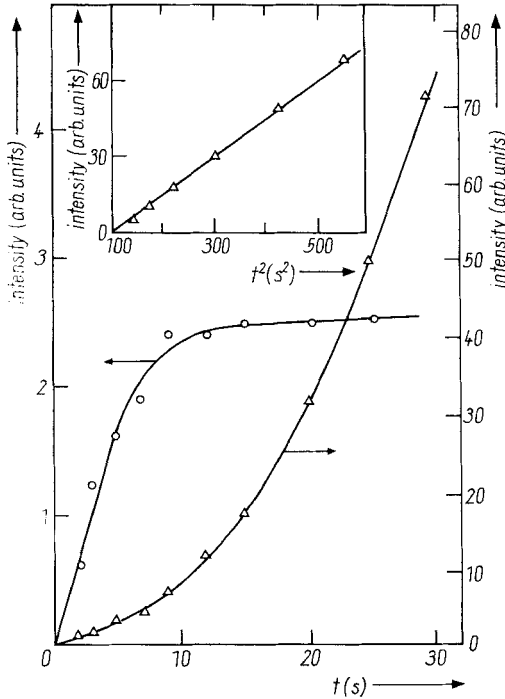


Fig. 2. TSL light sum at peak I (open circles) and peak II (triangles) as a function of irradiation time t . The insert shows the latter dependence as a function of t^2

Note that the dose dependence of TSL peak I could be explained through the exciton decay into defects in the vicinity of the A^{2+} -centre, as was proposed first by Plavina et al. /10, 11/. The observed saturation of the TSL peak I may be easily explained by In^{2+} -centre exhaustion. A more detailed analysis of processes which are responsible for the PSL and TSL in peak I will be published elsewhere /12, 13/.

In this note our main attention is paid to the TSL peak II. Its above-mentioned superlinear dependence can be straightened if total emitted TSL light sums versus t^2 coordinates (t is the irradiation time) are used (see insert in Fig. 2). This indicates that in this case the aggregation of two mobile defects occurs. As a result, more complicated halide molecules of free Br_3^- type are created according to the reaction /4/



where Br_2^- is an H-centre; Br_3^- is a molecular halogen ion localized at two anion and cation vacancies called also V_2 -centres /14, 15/. V_2 -centres are known to be the simplest interstitial aggregates which are created at RT /2 to 4, 15, 16/. Ishii and Rolfe working on KBr have found at RT that a short X-irradiation creates V_2 -centres unlike prolonged X-irradiation producing V_3 -centres (corresponding to more complicated halide aggregates /16/).

Thus, if we suppose that the exciton-produced mobile H-centres create V_2 -centres according to the reaction (1), the V_2 -centre concentration, n_{V_2} , has to be equal to the squared H-centre concentration, $n_{V_2} \sim n_H^2$, n_H is the H-centre concentration participating in V_2 -centre production. For low-dose irradiation, when the first stage of a coloration takes place, we may assume that $n_H = n_F$, where n_F 4 physica (b)

is the concentration of the stable F-centres created. Moreover, it is assumed also that n_F is proportional to the irradiation dose (or irradiation time t): $n_F(t) \sim t$. This conclusion comes immediately from an analysis of the F-centre growth kinetics. Alvarez Rivas and Levy /17/ have analyzed the F-centre growth in terms of the following phenomenological equation:

$$\alpha_F = \alpha_L t + \sum_{i=1}^n A_i (1 - \exp(-a_i t)) \quad , \quad (2)$$

where α_F is the absorption coefficient at the F-band peak and n is the number of "exponential" components in the coloring curves. Using a Taylor's series expansion, one obtains easily that the relation $n_F(t) \sim t$ is expected for low-dose irradiation whereas for V_2 -centres $n_{V_2} \sim t^2$. So, we suggest reasonably that the squared dependence of the TSL peak II with dose (irradiation time) arises due to H-centre aggregation (V_2 -centre creation).

Our TSL peak II located at ≈ 80 °C agrees well with literature data on the temperature region of the $V_2(\text{Br}_3^-)$ -centre destruction varying in the interval 350 to 370 K (80 to 100 °C) /4, 18, 19/.

For KBr:Tl crystals the results are practically the same, except that the TSL peak II although squared with dose has a slope less than in the KBr:In case. It may be explained by a considerable overlap of the C-band of Tl^+ ions ($\lambda_c(\text{Tl}^+) = 212$ nm) with the exciton band. As a result, in this case the simultaneous V_2 -centre destruction via Tl^+ -ion ionization with further recombination of the released electrons with V_2 -centres takes place /20, 21/.

It is not clear in which crystal lattice sites interaction of two H-centres takes place: As is known, there exist several plausible mechanisms for the $V_2(\text{Br}_3^-)$ -centre creation via two H-centre interaction. In particular, their interaction may occur in: (1) a regular lattice site; (2) in a site that is close to the anion vacancy, (3) near to the cation vacancy, or (4) near a divacancy /4, 5, 19/. To answer this question, further experiments are in progress.

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