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Section B

Optical production and destruction of V_2 centres in KBr–In and KBr–Tl crystals

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The ultraviolet light induced defects in KBr–In and KBr–Tl crystals were studied by means of the sensitive thermostimulated luminescence method. Glow curves reveal several peaks at 45, 80 and 125°C. We focus our attention on the 80°C peak which corresponds to the well known V_2-peak in pure KBr, arising due to annealing of V_2-centres (Br_3^- ions) with F-centres. Squared dose dependence shows that V_2-centres are produced via aggregation of two interstitial centres: $H + H \rightarrow V_2$. It is also shown that the V_2-centres may be destroyed at RT under illumination in the C-absorption band of In^+ (or Tl^+) ions accompanied by their ionization. The latter fact argues for the direct recombination of optically released electrons with V_2-centres.

1. 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 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 V-centre creation [2–5]. For these reasons room temperature (RT) ionizing irradiation of alkali halides leads to the formation of F- and different types of V-centres whose stability is essentially dependent on the irradiation dose as well as types of impurities involved [2–4].

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 now, there exist several types of V-centres, of which only V_2- and V_3-centres are thermally stable in pure alkali halides above RT [3].

The irradiated crystals can be thermally or optically bleached [4,6–11]. It is generally assumed that thermal annealing of the irradiated crystals destroys the V-centres with further formation of mobile defects (such as H-, V_K- and V_F-centres) [4,6,7]. Their further recombination with F-centres leads to thermal bleaching. The other way of the radiation defect destruction is by well known phenomenon called the "optical bleaching". It is usually done by F-light illumination, where the optical decomposition of F-centres into anion vacancies (α-centres) and free electrons (e^-) takes place. In this case, several types of the optically-induced processes can exist. They could be summarized in the following manner: i) direct electron recombination with V-centre [8]; ii) interaction between a mobile halogen vacancy (α-centre) and a V-centre [8]; iii) the phenomenon of the F-centres migration induced by light [10,11]. In the latter case, under the F-light interaction; the F-centres start migrating through the lattice, and when an F-centre gets close to a trapped interstitial (V-centre), their recombination occurs [10].

Thus, the investigation of the F-light destruction of the V-centres can lead to the ambiguous interpretation of the experimental results.

In this paper, we concentrate mainly on the V-centres created in KBr doped with ns^2 ions (In^+, Tl^+) under ultraviolet light irradiation in the fundamental exciton absorption band. These crystals are known as perspective materials for reversible optical memory for recording UV radiation image [12]. Firstly, we show that the H-centre aggregation in KBr–In and KBr–Tl crystals results in the creation of the V_2-centre known as the most simple type of V-centres at RT. Secondly, we demonstrate that the direct recombination of an electron with V_2-centre really occurs.

It should be mentioned that in the case of alkali halides doped with ns^2 ions the traditional methods of absorption spectra investigation are no longer efficient because of the considerable overlapping of two groups of bands takes place, namely 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-,

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C-bands" having peaks at RT in KBr–In at 300–310, 277 and 240 nm respectively). For this reason luminescent methods are used in this paper.

2. 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 SPM-1 monochromator was used. The thermostimulated luminescence (TSL) curves were monitored with the linear heating rate 10°C/min displayed on the X–Y recorder. In some experiments during TSL curves recording low-intensity F-light stimulation was applied with a He–Ne laser through the attenuating filter combination. It was chosen deliberately to be so weak that its influence had no effect on the kinetics under study. Such a regime of the simultaneous recording of the photostimulated luminescence (PSL) and TSL, when the main part of F-centres predominantly recombined via TSL, is called hereafter as a probing.

3. 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 KBr–In crystal irradiated at RT in the exciton fundamental absorption band ($\lambda_{irrad} = 192$ nm, dose $\sim 10^{14}$ photons/cm^2), and b) PSL dependence on temperature T measured in a probing regime. These experimental results demonstrate that defects being associated with the peak I ($T_{max} = 45$°C) of TSL anneal out together with the PSL defects and thus they are responsible for the PSL. As is proved by the PSL experiments [12–14], these defects are F, In^{2+} pairs as well as other pairs consisting of In^{2+} ion and F-type electron centre. Besides TSL peak I, another peak II with $T_M = 80$°C is also observed. Dose dependence of both TSL peaks is shown in fig. 2. Their behaviour dramatically differ. A total emitted TSL light sum in the peak I is proportional to an irradiation dose, then it saturates, while peak II shows a superlinear growth with a dose increase. The observed saturation of the TSL peak I may by easily explained by In^{2+} centre exhaustion which nearby the exciton decay into defects occurs, as was proposed first by Plavina et al. [15,16]. (The detailed analysis of the processes which are responsible for the PSL and TSL in the peak I will be published elsewhere [17,18,25]). In this paper our main attention is focused

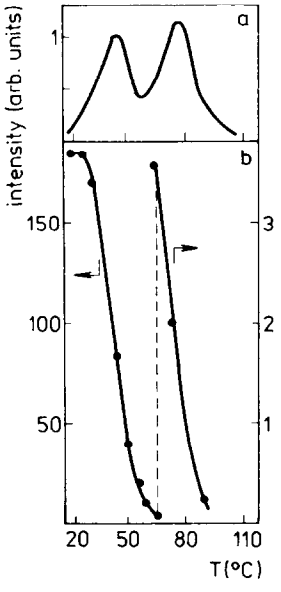

Fig. 1. (a) TSL glow curve, (b) PSL dependence on temperature measured in the probing regime of KBr–In crystal irradiated in the exciton fundamental absorption band.

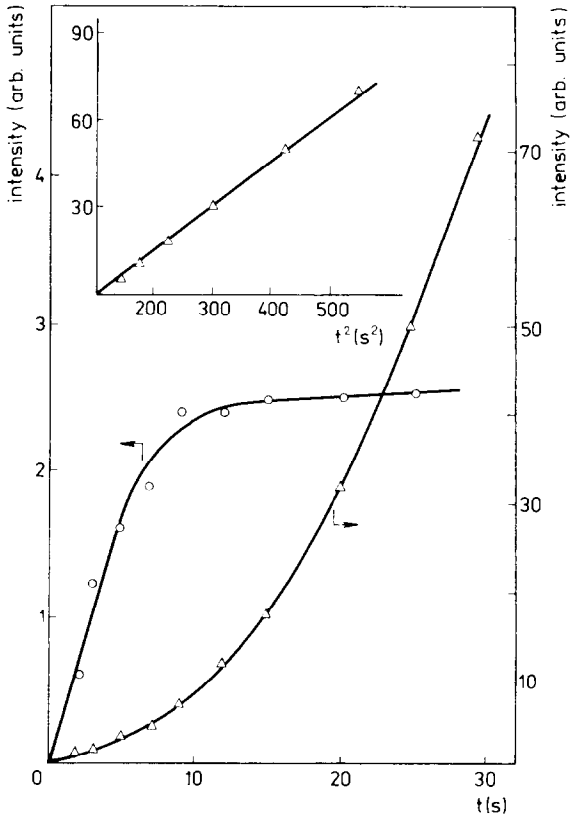

Fig. 2. TSL lightsum at the peak I (open circles) and peak II (triangles) as a function of irradiation time t. Insert shows the latter dependence as a function of t^2.

into the TSL peak II. Its above-mentioned superlinear dependence can be straightened where a total emitted TSL lightsum and t^2 coordinates (t is an irradiation time) are used (see an insert in fig. 2). This fact gives a hint that in this case the aggregation of two mobile defects occurs. As a result, more complicated halide molecules of a Br_3 -type are created according to the reaction [4]:

$$Br_2 + Br_2 \rightarrow Br_3 + Br^-, \quad (1)$$

where Br_2 is just an H-centre; Br_3^- is the molecular halogen ion localised by two anion and one cation vacancies (called also V_2 centre) [19,20]. It is known that V_2-centres are the most simple interstitial aggregates which are created at RT [2–4,15,16]. Ishii and Rolfe [21] working on KBr found that at RT the short X-irradiation creates V_2-centres whereas prolonged X-irradiation produces V_3-centres corresponding to more complicated halide aggregates.

Thus, if we suppose that the exciton-produced mobile H-centres create V_2-centres according to the reaction of eq. (1), V_2-centre concentration, n_{V_2}, has to be equal to a squared H-centre concentration, $n_{V_2} \sim n_H \times n_H$, where n_H is the H-centre concentration participating in the V_2-centre production. For low-dose irradiation, when the first coloration stage takes place, we may assume that $n_H = n_F$, where n_F is the concentration of the stable F-centres created. Moreover, it is supposed also that n_F is proportional to the irradiation dose (i.e. irradiation time t): $n_F(t) \sim t$. This conclusion comes immediately from an analysis of F-centre growth kinetics. Rivas and Levy [22] have analyzed the F-centre growth in terms of the following equation:

$$\alpha_F = \alpha_L t + \sum_i^n A_i(1 - \exp(-a_i t)), \quad (2)$$

where α_F is the absorption coefficient of the F-band peak and n is the number of "exponential" components in the coloring curves. From here using the Taylor's expansion, one easily obtains that

$$\alpha_F \approx \left(\alpha_L + \sum_i^n A_i a_i\right) t. \quad (3)$$

Therefore, for a low-dose irradiation the relation $n_F(t) \sim t$ is expected, whereas for V_2-centres we expect $n_{V_2} \sim t^2$. So, one can suggest reasonably that the squared dependence of the TSL peak II with a dose (irradiation time) arises due to H-centre aggregation (V_2 centre creation). It should be noted that our TSL peak II at ≈ 80°C agrees well with the literature data on the temperature region of V_2 (Br_3^-)-centre destruction varying between 350 and 370 K (80–100°C) [4,18,23,24].

Finally let us discuss the mechanism of direct recombination of the electrons with V_2-centres. It should

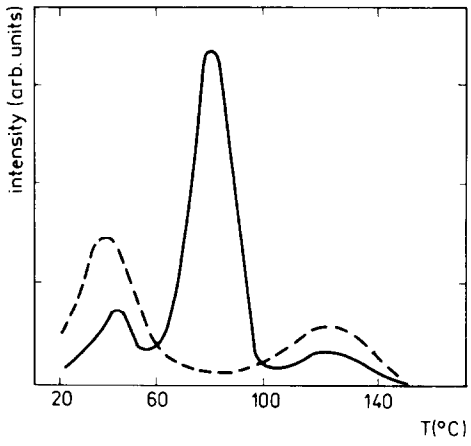

Fig. 3. TSL glow curve of KBr–In crystal irradiated in the exciton fundamental absorption band ($\lambda_{irrad} = 192$ nm) – solid curve and TSL glow curve of KBr–In crystal after two irradiations, firstly in the exciton band ($\lambda_{irrad} = 192$ nm) with the same dose as solid curve, and secondly in the C-absorption band ($\lambda_{irrad} = 240$ nm) – dashed curve.

be noted, that the above-mentioned ambiguous interpretation of the experimental results concerning the F-light destruction of the V_2-type centres is due to the fact that under F-light several kinds of moving species (such as free electrons, excited F-centres (F*) and α-centres) are created simultaneously. Therefore, in order to prove the mechanism of direct electron recombination with V_2-centres, it is necessary to find such electron sources that the free electrons would be created exclusively under their optical excitation. We suggest that the substitutional impurity ns^2-ions incorporated into lattice could serve as such sources. They indeed reveal electron delocalization observed when the crystal is excited by photons with an energy corresponding to C-absorption band of A^+ centres: $A^+ \rightarrow A^{2+} + e$. It is known that A^{2+}-centres thus created are stable and leave unaltered. If the created free electrons recombine with previously produced V_2-centres then the observed recombination seems to be the direct one (without ionic movement of some species). In fig. 3 we show the results of the following experiments, namely: 1) TSL glow curve of KBr–In irradiated in the exciton fundamental absorption band ($\lambda_{irrad} = 192$ nm) with a dose which is larger than that in fig. 1; 2) TSL glow curve of KBr–In after two subsequent irradiations, namely

(i) first irradiation in the exciton band with the same dose as in the case 1),

ii) second excitation in the C-absorption band ($\lambda_{irrad} = 240$ nm). As follows from fig. 3, an exciton irradiation produces effectively V_2-centres (TSL peak II at $T_M = 80$°C) which are also effectively destroyed by the C-band irradiation. The other conclusion could be

drawn from fig. 3 that C-band irradiation leads to the TSL peak I shift into the low-temperature side. This may be explained by the fact that spatially non-correlated F- and In^{2+}-centres are produced by C-band irradiation [14], whose thermal stability is lower then that of the F-, In^{2+}-pairs [17,25]. The new TSL peak III at $T_M = 125°C$ is due to unknown electron traps, as described in refs. [17,25].

In summary, we have shown in this paper that the $V_2(Br_3^-)$-centre creation via a two H-centre interaction is revealed in KBr–In crystal under exciton band irradiation. The results obtained for KBr–Tl are practically the same, except that the TSL peak II, although showing a square dependence on dose, has a slope smaller than that in the KBr–In case. This may be explained by a considerable overlap of the C-band of Tl^+-ions ($\lambda_C(Tl^+) = 212$ nm) with the exciton band [26]. As a result, simultaneous V_2-centre destruction via Tl^+ ion ionization, accompanied by further recombination of electrons with V_2-centres, takes place, as was shown in the second part of this paper using KBr–In crystals (where there is no overlap of the C-band of In^+-ions with the exciton band).

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