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Optical Destruction and Restoration of {F, In²⁺} Pairs in KBr–In Crystals

By

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Using photostimulated luminescence of {F, In⁺} defect pairs in KBr–In crystals, their F-light optical destruction under excitation has been investigated. It is shown that the effective absorption cross-section of F centers manifests itself in the kinetics of photostimulated luminescence of {F, In²⁺} pairs under constant F-stimulation. It is shown also that the resulting products – {v_a⁺, In⁺} pairs – may be again converted to {F, In²⁺} under C-absorption band illumination.

Методом фотостимулированной люминесценции исследовалось оптическое разрушение F-светом {F, In²⁺} пар в кристаллах KBr–In. Показано, что эффективное сечение поглощения F-центров непосредственно проявляет себя в кинетике фотостимулированной люминесценции. Показано также, что остающиеся после этого {v_a⁺, In⁺} пары могут быть превращены в {F, In²⁺} облучением в C-полосе поглощения.

1. Introduction

It is well known that an F center in ionic crystals can be associated with a variety of anionic, cationic or vacancy point defects [1 to 3]. Recently, one such type, the F center associated with an activator hole center A²⁺, in ionic crystals doped with ns² ions A⁺ (= In⁺, Tl⁺) has attracted a considerable amount of attention [4 to 9]. This is partly because of their possible practical application in optically erasable memory devices [4 to 6] and in medical radiography [7 to 9], as well as the interesting physics they bring about.

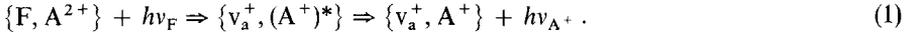
In our recent papers [10 to 12] it was shown that such {F, A²⁺} defect pairs, which are responsible for the distinctive photostimulated luminescence (PSL), are produced under exciton-band excitation. We have also shown that when the number of exciton-created photons is less than 6.0×10^{13} photons/cm², only the {F, In²⁺} pairs are formed. In order to destroy these pairs, the crystal has to be illuminated with light into the F-band. As a result, the F center electrons are excited and captured by the nearby In²⁺ centers. This electron transfer from F* to In²⁺ results in the PSL. The interesting feature of the PSL of {F, In²⁺} pairs under constant F-light stimulations is the dependence of the decay time τ of the PSL recovery on the F-light intensity I_F: $\tau = 1/\sigma I_F$ [10]. It has been suggested that one can determine the optical absorption cross-section σ of F centers in the absorption band peak [10 to 12].

The main purpose of this paper is twofold: 1. to discuss the kinetics of the PSL of {F, A²⁺} pairs; 2. to provide an additional support for our model of correlated {F, A²⁺} pairs. A preliminary study of this problem has been published in [10].

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2. Kinetics of the Photostimulated Luminescence of {F, A²⁺} Defect Pairs

A wide variety of experimental results concerning the mechanism of the PSL in A⁺ impurity doped (In⁺, Tl⁺, etc.) alkali halides suggests the existence of defect pairs, which consist of an F center spatially well correlated with a recombination center – an ionized impurity A²⁺. In these pairs the photostimulated F-center electron transfer to the A²⁺ center results in light emission, a form of intrinsic A⁺-center luminescence. This process can be written schematically as



As is known, the F-electron transfer within {F, A²⁺} pairs is sufficiently effective to suppress the F ⇒ F' conversion [13] as well as F-electron recapture by an anion vacancy v_a⁺ [6, 10, 11]. According to the experimental results on the temperature dependence of the PSL decay time, the mechanism of the electron transfer between F and A²⁺ nearby center is the *photostimulated tunneling* from an excited F center state [5, 7].

Thus, the following elementary stages of the PSL of {F, A²⁺} pairs should be taken into account: 1. An F center being initially in the ground state is excited to an excited F* center state by absorption of a photon with energy hv_F. Its probability can be written as the product 1/τ = σ_FI_F, where σ_F is the optical absorption cross-section of F center.

2. The F center electron either radiatively or nonradiatively returns with the probability 1/τ_F^{*} to its ground state or tunnels to the neighboring A²⁺ center with the probability 1/τ_{tun.}. In principle, the excited F* center also may give up its electron to the conduction band, but, in our opinion, this process in the particular case of {F, A²⁺} pairs is improbable, because the F'–F conversion [13] as well as F-electron recapture processes are suppressed [6, 10, 11].

3. The final stage of PSL is the intrinsic luminescence of the activator A⁺ ion.

The energy level diagram describing the PSL of the {F, A²⁺} pairs is plotted in Fig. 1. The simple rate equations for the number of electrons of the F centers in the ground state n_F, those in the excited state n_F^{*}, and for excited (A⁺)^{*} centers n_{(A⁺)^{*}} can be straight forwardly written as

$$\begin{aligned} \frac{dn_F}{dt} &= -\sigma_F I_F n_F + \frac{n_{F^*}}{\tau_{F^*}} , & \frac{dn_{F^*}}{dt} &= \sigma_F I_F n_F - \frac{n_{F^*}}{\tau_{F^*}} - \frac{n_{F^*}}{\tau_{tun.}} , \\ \frac{dn_{(A^+)^*}}{dt} &= \frac{n_{F^*}}{\tau_{tun.}} - \frac{n_{(A^+)^*}}{\tau_{(A^+)^*}} , \end{aligned} \tag{2}$$

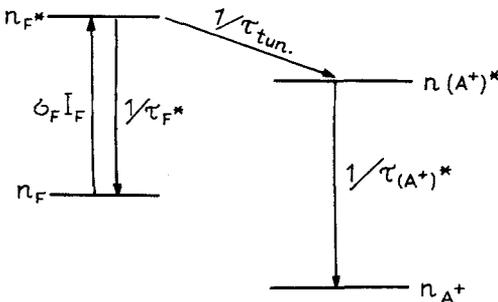


Fig. 1. Schematic diagram of the photostimulated luminescence process of the close defect pair consisting of F-center and activator

where $\tau_{(A^+)^*}$ is the lifetime of the excited state of the A⁺ ion. The initial values of n_F , n_F^* , and $n_{(A^+)^*}$ concentrations are

$$n_F(0) = N, \quad n_F^*(0) = n_{(A^+)^*}(0) = 0,$$

where N is the initial concentration of the {F, A²⁺} pairs.

In order to obtain an expression for the time development $n_{(A^+)^*}(t)$, we must solve the characteristic equation of the set (2). Proceeding in this way, we easily obtain the concentration of an excited activator center (A⁺)^{*},

$$n_{(A^+)^*}(t) = \frac{\sigma_F I_F N_F}{\tau_{\text{tun.}}(\omega_1 - \omega_2)} \left\{ \frac{\exp(-\omega_1 t)}{\omega_1 - 1/\tau_{(A^+)^*}} - \frac{\exp(-\omega_2 t)}{\omega_2 - 1/\tau_{(A^+)^*}} + \frac{(\omega_1 - \omega_2) \exp(-t/\tau_{(A^+)^*})}{(\omega_1 - 1/\tau_{(A^+)^*})(\omega_2 - 1/\tau_{(A^+)^*})} \right\}, \quad (3)$$

where

$$\begin{aligned} \omega_{1,2} &= \frac{\sigma_F I_F + 1/\tau_F^* + 1/\tau_{\text{tun.}}}{2} \pm \sqrt{\left(\frac{\sigma_F I_F + 1/\tau_F^* + 1/\tau_{\text{tun.}}}{2} \right)^2 - \frac{\sigma_F I_F}{\tau_{\text{tun.}}}} \\ &= \frac{\sigma_F I_F + 1/\tau_F^* + 1/\tau_{\text{tun.}}}{2} \left(1 \pm \sqrt{1 - \frac{4\sigma_F I_F}{\tau_{\text{tun.}}(\sigma_F I_F + 1/\tau_F^* + 1/\tau_{\text{tun.}})^2}} \right). \end{aligned}$$

For the PSL intensity we may use the following obvious expression:

$$I_{\text{PSL}}(t) = \frac{n_{(A^+)^*}(t)}{\tau_{(A^+)^*}}. \quad (4)$$

Now, in order to make suitable approximations, we consider the most typical values occurring in (3) and (4). Since a typical value of σ_F is 10^{-16} cm^2 and the experimentally used intensity $I_F \approx 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$, we find immediately that $\sigma_F I_F \approx 10^{-1} \text{ s}$. In the particular case of KBr crystals it is known that at room temperature (RT) $\tau_{(\text{In}^+)^*} = 2.6 \times 10^{-6} \text{ s}$ [9, 14] and $\tau_{(\text{Tl}^+)^*} = 3 \times 10^{-7} \text{ s}$ [15]. As is known from the experiments based on pulsed PSL [19] $\tau_{\text{tun.}} \ll \tau_{(A^+)^*}$. Finally, let us estimate the lifetime τ_F^* of an electron in the relaxed excited state of the F-center. According to Swank and Brown [16] for isolated F centers in KBr at RT $\tau_{F^*} = 1.3 \times 10^{-11} \text{ s}$. Thus, the conclusion could be drawn here that the values τ_{F^*} , $\tau_{\text{tun.}}$, and $\tau_{(A^+)^*}$ are much less than $\sigma_F I_F$. Under these conditions (4) may be simplified as

$$I_{\text{PSL}}(t) = N \sigma_F I_F \exp\left(-\frac{t}{\sigma_F I_F}\right). \quad (5)$$

Equation (5) predicts that under constant F-light stimulation the PSL of the {F, A²⁺} pairs is *exponential* in time. Its decay time depends on the F-light intensity I_F as $\tau = 1/\sigma_F I_F$. In terms of physics, (5) means that the effective absorption cross-section directly determines the PSL kinetics of {F, A²⁺} pairs. Another prediction of the present simple model is that the spectral dependence $\sigma(E)$ is a function of both the F-light intensity $I(E)$ and an appropriate $\tau(E)$,

$$\sigma(E) = \frac{1}{\tau(E) I(E)}, \quad (6)$$

where E is the energy of stimulating photons and $\tau(E)$ is the decay time of PSL under stimulation by F-photons with energy E ; i.e. $\sigma(E)$ is defined by the absorption band of the electron center.

The experimental results of the PSL kinetics of the $\{F, A^{2+}\}$ pairs are presented and discussed below.

3. Experimental

The experiments were carried out on thin ($d = 0.038$ cm) single-crystalline samples of KBr–In. The In^+ concentration was estimated to be $9 \times 10^{16} \text{ cm}^{-3}$. Irradiation of the sample was performed at room temperature with ultraviolet (UV) light from a LDD-400 lamp. The UV light passed through an SPM-1 monochromator, selecting the required spectral region. To excite the PSL, the irradiated crystal was illuminated with a He–Ne laser or a halogen lamp in combination with the ZMR-3 monochromator. The PSL was detected with a photomultiplier and its decay curves as a function of time were recorded by on ENDIM-662.01 X–Y recorder.

In order to apply the relation $\tau = 1/\sigma I_F$, it is necessary:

(i) to obtain a more uniform distribution of the exciton-produced electron centers over crystal thickness; (ii) to produce a constant stimulated F-light intensity I_F in the bulk of an irradiated crystal. An appropriate method to obtain this was described elsewhere [6, 10].

4. Results and Discussion

In order to investigate the PSL process after optical creation of anion excitons, we measured carefully the kinetics of PSL versus the dose of absorbed photons in the fundamental exciton absorption band as well as stimulation spectra, which resembles the spectral dependence of the optical absorption cross-section of the appropriate electron center, $\sigma(E)$. PSL of a KBr–In crystal can be identified as the In^+ characteristic emission (Fig. 2).

Under UV irradiation ($\lambda = 200$ nm, $I(\lambda) = 4.2 \times 10^{10}$ photons/cm² s) in the fundamental exciton absorption band of KBr–In crystals, with a dose ranging from 1.0×10^{12} to 6.0×10^{13} photons/cm², the PSL decay reveals an exponential behaviour, with decay time obeying (6). When the stimulation is performed with a He–Ne laser (whose wavelength $\lambda = 632.8$ nm falls into the F-absorption band peak of the KBr crystal) the value of σ_F defined by means of (6) turns out to be in good agreement with known σ values for F centers [10, 11, 17]. In order to ensure that this component actually corresponds to F centers, we measured the $\sigma(E)$ stimulation spectrum. It was detected after the UV irradiation ($\lambda = 200$ nm, dose 8.4×10^{12} photons/cm²) monitoring the PSL intensity at a selected stimulation wavelength from a halogen lamp. The calculated spectrum $\sigma(E)$ as a function of the stimulation energy $I(E)$ is presented in Fig. 3. This spectrum peaks at 1.97 eV with a half-width of 0.32 eV. It is similar to the earlier published F-band absorption spectra [18]. However, in our case it is slightly narrower. We ascribe this to our more precise determination of the spectrum half-width. In our opinion, this is evident because in absorption measurements the aggregate center bands are covered by the F band and they distort its shape [11, 19].

Thus, we have concluded that the PSL, appearing under F-stimulation after low dose ($D < 6 \times 10^{13}$ photons/cm²) of the exciton created photons is due to $\{F, In^{2+}\}$ close pairs. This process could be described by means of (1). It seems to be self-evident that an excited F electron recombines with a nearby A^{2+} center leaving behind an anion vacancy, v_a^+ .

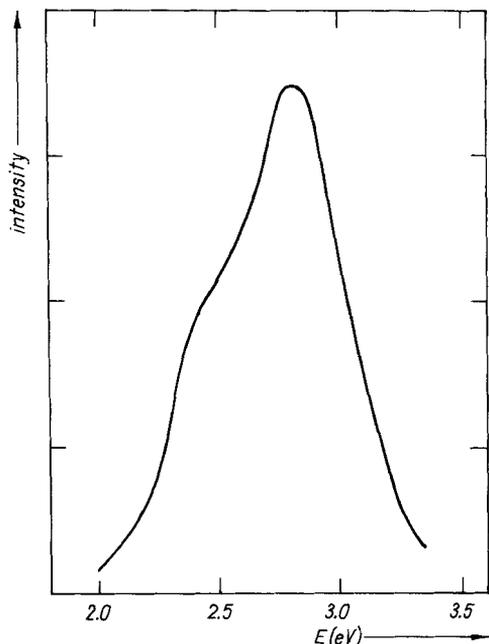


Fig. 2

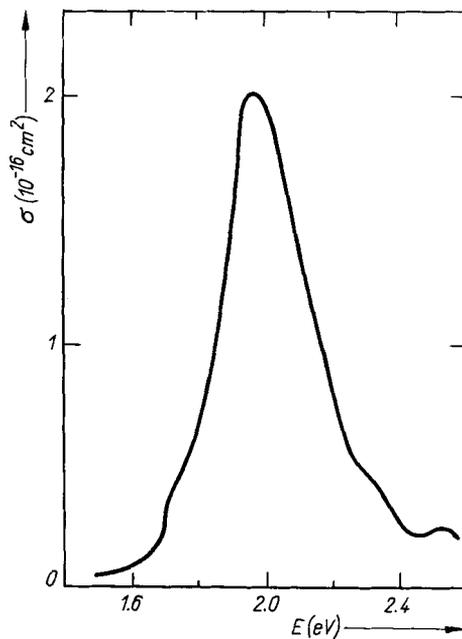


Fig. 3

Fig. 2. Photostimulated luminescence spectrum of a KBr-In crystal irradiated in the exciton band at RT

Fig. 3. Optical absorption cross-section, σ , of F-centre electrons for KBr-In plotted as a function of the stimulating light energy

The rest of this paper is devoted to prove the production of close $\{A^+, v_a^+\}$ pairs as a result of the previous UV irradiation in the exciton band followed by F-stimulation. In order to prove this, we suggested the experimental method permitting to restore $\{F, A^{2+}\}$ pairs from $\{v_a^+, A^+\}$. For this purpose the reverse electron transfer from A^+ ion to anion vacancy v_a^+ is evidently required, which is equivalent to the ionization of an A^+ ion and this may be accomplished under irradiation in the so-called C-absorption band of the In^+ ion. It is well known that such irradiation leads to the optical ionization of impurity ns^2 ions [20 to 22]. In this case, the released electrons are captured by the Schottky vacancies, thus creating F centers. Schottky vacancies are randomly distributed in the crystal as are the F and A^{2+} centers. The kinetics of F-destruction of the such randomly arranged F and A^{2+} centers differ considerably from that for $\{F, A^{2+}\}$ pairs [6, 10, 12]. For example, in such a case when KBr-In is irradiated in the C-band ($\lambda = 245$ nm), the corresponding decay time of the optical recovery of the PSL using constant F-light of the same intensity ($I_F = 9.2 \times 10^{14}$ photons/cm² s) equals $\tau_C = 50$ to 500 s depending on the prehistory of the crystal [6, 10]. In some cases, the PSL component with $\tau = 5.3$ s also appears, resulting from a closely spaced In^+ center and an anion vacancy v_a^+ . Then under optical ionization of this In^+ ion, electron capture by the Coulomb field of the nearby anion vacancy should be very effective. This process can be represented schematically as



Table 1

The increasing of the PSL intensity (I_2/I_1) after C-irradiation as a function of the intermediate irradiation dose in the exciton band

dose (photons/cm ²)	I_2/I_1
2×10^{12}	9.5
1.2×10^{13}	17.5

Thus, it is shown that the appearance of the PSL component with $\tau = 5.3$ s after C-band irradiation depends strongly on the prehistory of the crystal under investigation. In particular, the considerable growth of the PSL with $\tau = 5.3$ s under C-band irradiation is observed for crystals previously irradiated in the exciton fundamental absorption band and then illuminated by F-light.

The data of such experiment are given in Table 1. The experiment was performed on the earlier virgin non-irradiated crystal sample. The scheme of the experiment was as follows. At first, the crystal was illuminated in the C-absorption band (1st C-irradiation). The resulting PSL showed a long-time PSL decay with $\tau_c \approx 450$ s along with the PSL component ($\tau = 5.3$ s, $I_1 = 1$ arb. unit), resulting from closely spaced $\{v_a^+, In^+\}$ pairs (see (7)). Then, the crystal was irradiated in the exciton absorption band with an accumulated dose of 1.2×10^{12} photons/cm² after which F-light destruction of the $\{F, In^{2+}\}$ pairs was performed. According to (1) this manipulation led to the effective production of $\{v_a^+, In^+\}$ pairs. Then, the final stage of the experiment involved repeated irradiation in the C-band (second C-irradiation) with the same dose as in the first C-irradiation. It is supposed that in this stage the effective transformation of $\{v_a^+, In^+\}$ pairs into $\{F, In^{2+}\}$ pairs should happen. In fact, the PSL observed after the second C-irradiation showed the component $\tau = 5.3$ s with the considerably increased intensity $I_2 = 9.5$ arb. units. This result leads us to the hypothesis that such surprising difference ($I_2:I_1 = 9.5$) in creation efficiencies of $\{F, In^{2+}\}$ pairs by C-band irradiation is due to the effective production of $\{v_a^+, In^+\}$ pairs by realizing between the first and second C-irradiation both exciton band irradiation and further F-destruction. In the case of the irradiation in the exciton absorption band with a dose of 1.2×10^{13} photons/cm² we obtain $I_2:I_1 = 17.5$. Thus, without specifying the mechanism of the exciton-induced $\{F, A^{2+}\}$ centre production the conclusion nevertheless is drawn that the such pairs are really produced by the fundamental exciton absorption band irradiation.

5. Conclusions

We have studied the photostimulation process of $\{F, In^{2+}\}$ pair luminescence in a KBr-In crystal. We have shown that the effective absorption cross-section of F center manifests itself in the PSL kinetics of $\{F, In^{2+}\}$ pairs under constant F-stimulation. We have shown also that the resulting $\{v_a^+, In^{2+}\}$ pairs may be again converted to $\{F, In^{2+}\}$ pairs under C-absorption band illumination.

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