Determination of the Effective Absorption Cross-Section of F-Centres in KBr–In by Photostimulated Luminescence

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Using photostimulated luminescence of F, In^{2+} defect pairs in KBr–In are proposed to be a very sensitive method for the determination of the effective absorption cross-section of F-centres. It is shown that the effective absorption cross-section of F-centres equals to 2.0×10^{-16} cm^2. Some criteria for the applicability of this method are analysed.

На основе явления фотостимулированной люминесценции в парах F, In^{2+} разработана методика определения эффективного сечения поглощения F-центров в KBr–In, которое составляет 2.0×10^{-16} cm^2. Анализируются также некоторые критерии применимости данной методики.

1. Introduction

Alkali halides activated with ns^2 ions $A^+ (Ga^+, In^+, Tl^+)$ are well known for their luminescent properties and have many uses as effective laser media and as thermo- or photostimulable detectors in dosimetry [1 to 5]. A variety of colour centres (F, M, V_2, A^0, A^{2+}, and others) are produced and stabilized in these crystals at room temperature (RT) under ionizing irradiation [1 to 8]. Some of them occur in the form of close pairs, for instance, $F-A^+$ [1 to 3, 5], $F-A^{2+}$ [4, 8 to 13]. Work on the $F-A^{2+}$ pais in alkali halides has been in progress for some years, and a considerable amount of data reflecting their properties has been gathered [4, 8 to 13].

$F-A^{2+}$ pairs can be created either by optical creation of excitons in the fundamental exciton absorption band [4, 8 to 12] or by X-ray [4, 12, 13] and electron irradiation [4]. As shown for optical creation of excitons, these pairs are produced with the quantum yield η ranging from 10^{-4} to 1.5×10^{-1} [8, 10]. The value of η is dependent on the history of the crystals.

In order to destroy $F-A^{2+}$ pairs the crystal should be illuminated with the F-light. Due to the absorption which is characterized by an effective optical absorption cross-section σ the electrons are excited and captured by A^{2+}-centres. This capture is accompanied by activator emission which is called photostimulated luminescence (PSL). Recent observations have shown that the decay time τ of optical recovery of the PSL using constant F-light depends on the F-light intensity I_F as $\tau \sim 1/I_F$ [4, 10 to 13]. This feature of the decay time is typical for close luminescent defect pairs in alkali halides [4, 10 to 13] and europium-activated barium halides [14]. The conclusion suggests that the absorption process of the F-photon is the slowest one in the PSL recovery process [4, 10, 12] and the decay time τ

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may be represented as follows:

$$\tau = \frac{1}{\sigma I_F}.$$ (1)

The purpose of the present paper is to investigate this dependence for KBr–In crystals irradiated in the fundamental exciton absorption band, paying special attention to the quantitative estimation of the effective absorption cross-section σ of F-centres entering the F–In^{2+} pairs.

2. Procedure

The crystal KBr–In was grown by the Stockbarger method in our laboratory. The concentration of In$^+$ was estimated to be 9×10^{16} cm^{-3}. The crystal was placed in a special box and UV-irradiation was performed with a LDD-400 lamp. The UV-light from the LDD-400 lamp passed through a SPM-1 monochromator before entering the crystal. The UV-light power was monitored with a PTH-30 °C thermoelement. For exciting PSL the irradiated crystal was illuminated with He–Ne laser or halogen lamp in combination with an interference filter. The PSL was detected with a photomultiplier and its decay as a function of time was recorded by an ENDIM-662.01 recorder.

For our purpose it was necessary first of all to obtain a highly homogeneous coloration of the crystal. This required the use of spatially uniform UV light intensity as well as a sufficiently thin crystal sample ($d = 0.028$ cm). In order to provide a more uniform distribution of F-centres along the exciton penetration depth the crystal was irradiated equally on both sides. For this procedure a special turning mechanism had been made. Estimates show that the unevenness of the F-centre distribution along the depth amounts to approximately 20%. This unevenness is quite allowed because the value of the concentration has a purely illustrative character and is not used for the definition of σ by means of (1).

In order to determine the optical absorption cross-section by means of (1) it is necessary to have a constant stimulated F-light intensity I_F in the irradiated crystal. An appropriate method was described in [10].

3. Results and Discussion

UV irradiation of a KBr–In crystal in the fundamental exciton absorption band at RT leads to energy accumulation in the form of F–In^{2+} defect pairs. These pairs may be identified by means of the characteristic photostimulated luminescence, which is composed spectrally of the intrinsic In$^+$ emission. It is excited by the F-band light after radiation-induced afterglow has completely ceased in the dark. Thus, F and In^{2+} centres are the main defects which take part in the PSL. On the other hand, In^0 centres are unstable at RT [15, 16] and thus do not participate in the PSL. Stability of the F–In$^+$ pair in KBr is unknown, but the analysis of their stimulation spectra of the PSL of KBr–In crystals together with F–In$^+$ centre absorption data [5] shows that F–In$^+$ centres are not produced under UV irradiation in the fundamental exciton absorption band [12].

Under UV irradiation ($\lambda = 200$ nm, $I_\lambda = 4.2 \times 10^{10}$ photons/cm^2 s) in the fundamental exciton absorption band of the KBr–In crystal with a dose ranging from 1.2×10^{12} to 6.0×10^{13} photons/cm^2, the PSL decay has exponential behaviour (Fig. 1). The corresponding decay time τ, exposure dose value D, and effective absorption cross-section σ,
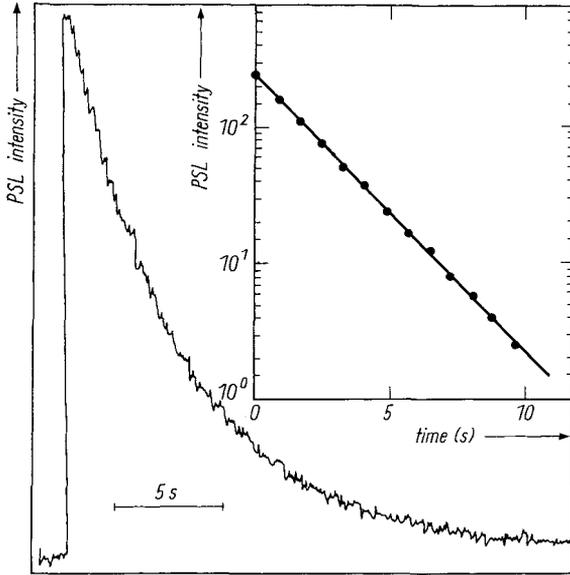
Fig. 1. PSL decay curve of UV irradiated KBr–In crystal ($\lambda = 200$ nm, $D = 8.4 \times 10^{12}$ photons/cm^2) under F-light illumination ($I_F = 9.2 \times 10^{14}$ photons/cm^2 s); in the insert this decay curve is plotted on a semilogarithmic scale

which are calculated by means of (1), are shown in Table 1. As follows from column 5 of Table 1, the value of σ defined by us is in good agreement with the value of σ_F obtained in [17] by means of an absorption method and is equal to 2.0×10^{-16} cm^2. The absorption method for σ_F determination requires the knowledge of the value of absorption coefficient and F-centre concentation and therefore it may be used at sufficiently high concentration of F-centres ($N_F > 10^{16}$ cm^{-3}). The method under consideration may be applied at small F-centre concentrations (see column 3 of Table 1) and does not require knowledge of the absorption characteristics of F-centres. For a confirmation of the above reasoning the value of maximum possible concentration N_F^{max} of F-centres is shown in column 3 of Table 1. N_F^{max} was estimated according to the relation [10]

$$N_F = \frac{\alpha \eta_{max} D}{d}, \tag{2}$$

where α is the fraction of absorbed photons, η_{max} the maximum possible quantum yield of F–In^{2+}, which is equal to 1.5×10^{-1} [8 to 10], D the number of incident photons, and d

Table 1

sample No.	D (photons/cm^2)	N_F^{max} (cm^{-3})	τ (s)	σ (10^{-16} cm^2)
1	1.2×10^{12}	4.97×10^{12}	5.2	2.1
2	5.0×10^{12}	2.1×10^{13}	5.4	2.0
3	8.4×10^{12}	3.48×10^{13}	5.4	2.0
4	2.7×10^{13}	1.11×10^{14}	6.1	1.8
5	5.0×10^{13}	2.1×10^{14}	5.3	2.0
6	6.0×10^{13}	2.48×10^{14}	5.2	2.1
			average	2.0

the crystal thickness. The fraction of absorbed photons was estimated using formula $\alpha = 1 - \exp(-\varkappa_\lambda d)$. Taking into account that $\varkappa_\lambda = 53 \text{ cm}^{-1}$ [17] at $\lambda = 200$ nm, α is equal to 0.774. The number of absorbed photons D was determined from the relation $D = I_\lambda t_{\text{irrad}}$, where I_λ is the UV light intensity ($I_\lambda = 4.2 \times 10^{10}$ photons/cm^2 s) and t_{irrad} the irradiation time.

As follows from Table 1, the upper estimate of the maximum possible concentration N_F^{max} of F-centres in our experiments could be in the range 5×10^{12} to 3×10^{14} cm^{-3}. Therefore, unlike the absorption method, the above luminescent method of effective absorption cross-section determination is very sensitive because it is capable of determining σ at very low defect concentration (up to 10^{10} cm^{-3}). The agreement of the value of the effective absorption cross-section defined by us with the data in [15] also shows that optical creation of excitons in activated alkali halides actually leads to the formation of close F$-$In^{2+} defect pairs. The distance between F- and In^{2+}-centres is $4a$ to $8a$, where a is the lattice constant of KBr [12].

The luminescent method of effective absorption cross-section determination is not universal because it is unapplicable to non-activated crystals and also not to activated crystals with a non-luminescent impurity. In this paper the validity of this method was proved only for the case of exciton defect creation. Apparently, it cannot be applied to other defect creation mechanisms without a careful checking, for example, of electron$-$hole defect creation or F-centre creation in alkali halides activated with ns^2 ions by thermo-optical ionization by activator C-band irradiation. When a crystal is irradiated in the activator C-band ($\lambda = 245$ nm), the Schottky vacancies capture electrons, thus creating F-centres. In this case the corresponding decay time τ_c of optical recovery of the PSL using constant F-light ($I_F = 9.2 \times 10^{14}$ photons/cm^2 s) equals $\tau_c = 450$ s. This value reflects probably a succession of repeated processes, namely: F-centre excitation, its ionization, electron capture by an anion vacancy, repeated F-centre excitation, and so on, until electron capture occurs in the anion vacancy which is situated close to the A^{2+}-centre [10, 12]. The number of such repeated processes could be estimated as $\tau_c/\tau_{\text{exc}} = 450/5.3 \approx 85$. The photostimulated migration of excited F-centres is possible, too [18, 19]. More detailed data about this are to be published.

4. Conclusions

A new, very sensitive, method of quantitative estimation of the effective absorption cross-section σ_F of F-centres has been discussed. The validity of the method is shown for an F$-$A^{2+} pair by excitation creation, whereas its application to F-centre creation under thermo-optical ionization of A$^+$-centres in the C-band is not suitable.

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