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The Observation of a New D-Absorption Band in KBr–In Crystals

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Excitation spectra of the activator luminescence directly excited by UV light and creation spectra of the photostimulated luminescence are investigated for KBr–In crystals with different In⁺ concentrations. It is shown that the electronic states responsible for these two kinds of luminescence differ. Careful analysis of the excitation spectra allow us to find a new D-absorption band having Gaussian shape with the following parameters: peak position at $E_0 = 6.375$ eV and halfwidth $\Delta E = 0.14$ eV. The oscillator strength $f = 0.12$ of the D-band is also determined.

1. Introduction

Optical properties of ns^2 ions known also as the mercury-like activator impurities have been intensively studied in alkali halide crystals [1, 2]. Their absorption spectra exhibit four bands designated as A, B, C, and D, in order of increasing energy. The three absorption bands A, B, C are due to the $^1A_{1g} \rightarrow ^3T_{1u}$, $^1A_{1g} \rightarrow ^3T_{2u} + ^3E_u$, and $^1A_{1g} \rightarrow ^1T_{1u}$ transitions, respectively [1, 2]. Beside these three bands, one or more D-bands may be observed, which are assumed to be due to perturbed excitons and electron-transfer states [1 to 5].

In spite of a rather extensive research performed on the ns^2 doped alkali halide crystals, their luminescence properties related, in particular, to excitation in the fundamental exciton band are not sufficiently well understood.

The subject of the present paper is the In⁺-luminescence excitation in KBr–In crystals in the spectral range between the C-absorption band and the low-energy edge (the so-called Urbach tail) of the exciton fundamental absorption band, covering the region of the D-band. The strong overlap of the D-band with the Urbach tail causes a number of problems complicating a detailed analysis of the excitation spectra (ES). Similar problems were discussed earlier in [6] where the luminescence of the α -centres absorbing also at the low-energy edge of the exciton fundamental absorption was studied in alkali halide crystals.

In this paper we will (i) demonstrate that the excitation spectrum of the directly UV-light excited activator luminescence differs from that for the creation of the photostimulated luminescence (PSL) centres in KBr–In crystals and (ii) discover a new activator D-band and the determination of its absorption characteristics (effective absorption cross-section and oscillator strength).

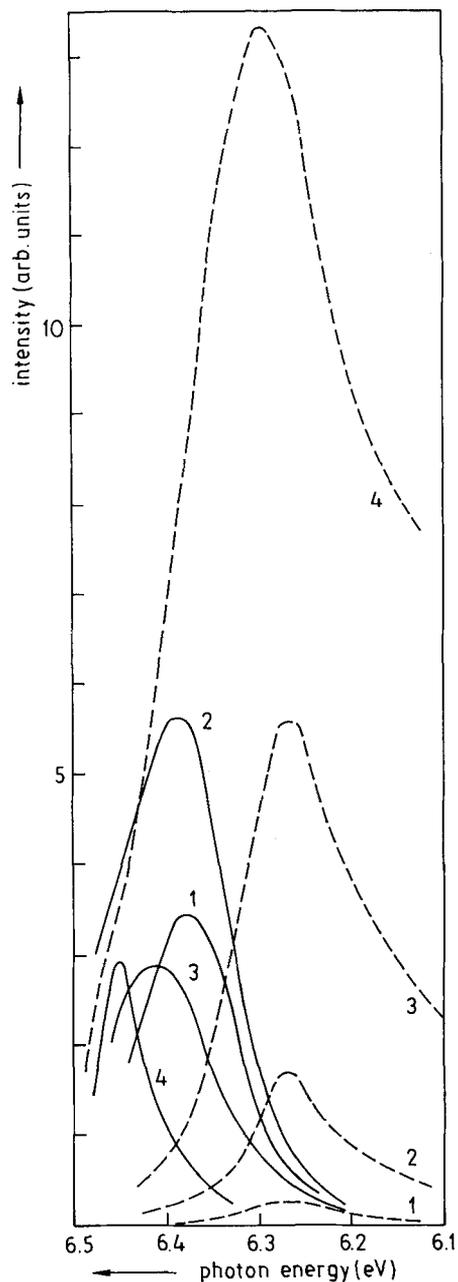
KBr–In crystals were chosen because of their effective PSL properties [7 to 9] and their application as prospective storage material for radiation imaging [8].

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2. Experimental

A series of In^+ -doped KBr crystals were grown by the Stockbarger method. The four types of KBr–In crystals with different In^+ ion concentrations (1.8×10^{16} , 1.6×10^{17} , 1.2×10^{18} , and $1.2 \times 10^{19} \text{ cm}^{-3}$) have been investigated. For measurements of the ES as well as PSL



creation spectra, a water-cooled 400 W deuterium lamp was used as the excitation source. The excitation wavelengths were selected by SPM-1 "Carl Zeiss" prism monochromator. The emission was detected with a photomultiplier and was recorded using an ENDIM 662.01 X–Y recorder. As a stimulation light source, a halogen lamp with appropriate filters was used. The excitation and creation spectra were corrected for the lamp intensity using sodium salicylate as a standard. All investigations were performed at room temperature (RT).

3. Results and Discussion

The ES were measured in the energy range from 6.0 to 6.5 eV. Fig. 1 shows these spectra for both simultaneously detected A_T and A_X bands of the In^+ -ion luminescence. As can be clearly seen from Fig. 1 the shape of the ES is slightly dependent on the In^+ concentration up to $1.2 \times 10^{18} \text{ cm}^{-3}$, whereas the luminescence intensity monotonously increases with increasing In^+ concentration. It was found that the results for KBr–In crystal with high In^+ concentration of $1.2 \times 10^{19} \text{ cm}^{-3}$ differ from those typically observed for lower In^+ concentrations. This point will be discussed below. Fig. 1 shows also the creation spectra of the PSL, excited by F-band light in a monochromatic UV-light (6.1 to 6.5 eV) irradiated crystal. These spectra are shown for all crystals after sensitization. As in [9], the sensitization procedure means the enhancement of the PSL-centre production and

Fig. 1. Excitation spectra (dashed lines) and PSL creation spectra (full lines) of KBr–In crystals with the following In^+ ion concentrations: (1) 1.8×10^{16} , (2) 1.6×10^{17} , (3) 1.2×10^{18} , and (4) $1.2 \times 10^{19} \text{ cm}^{-3}$

consists of the performance of two subsequent irradiations. Firstly, the sample is irradiated at RT in the region of the C-band ($\lambda_{\max} = 245 \text{ nm}$). As a result, the excited electrons from In^+ ions are partly released into the conduction band and are captured in excited states of the lattice imperfections (anion vacancies etc.). Thus, In^{2+} hole centres and electron centres are created. Secondly, the sample is irradiated in the F-band region. Although, such irradiation in the F-absorption band leads to the destruction of some part of the A^{2+} centres, a certain amount of the A^{2+} centres survives, nevertheless, as if nothing had happened. Its influence on the exciton decay leads to a considerable enhancement of the PSL light sum. Fig. 2 shows the creation spectra of both sensitized and nonsensitized crystals and gives clear evidence for the sensitization effect. Another conclusion that can be drawn from Fig. 2, is that the influence of the sensitization on the ES of the activator luminescence is very low.

Next, we shall consider the origin of the ES of the activator luminescence. From an analysis of the excitation and creation spectra of the PSL, shown in Fig. 1, one observes that the electronic states responsible for the above discussed luminescence are different. If the F centres (the main partners involved in the PSL process which are known to be generated by the exciton mechanism, as proposed by Pooley and Hersh (see for example recent reviews [10])) manifest themselves in the PSL creation curves shown in Fig. 1, the excitation peaks of the activator luminescence shifted to the long-wavelength side could be ascribed to the D-band excitation. As is known, such D-bands typically appear in the region between the high-energy side of the C-band and the fundamental absorption edge of the host crystal and are seldom observed in the form of a separate absorption peak [1].

In order to determine quantitatively the spectral position of the D-band in KBr-In and its real shape on the basis of the excitation spectra, we should take into account the fact that although under UV-light excitation in the absorption tail the light absorption occurs in both the host lattice as well as in the D-band resulting from excitation of lattice sites near In^+ ions, the directly observed activator luminescence is excited *only* by photons absorbed in the D-band. Thus, their intensity I_{lum} is expected to be

$$I_{\text{lum}} \sim \frac{I_0 k_D}{k_D + k_{\text{exc}}}, \tag{1}$$

where I_0 is the intensity of the incident photon flux, k_D and k_{exc} are the absorption coefficients of the D-band (or Br^- ions near In^+ ions) and of the exciton band of KBr, respectively. Taking into account that the number of Br^- ions next

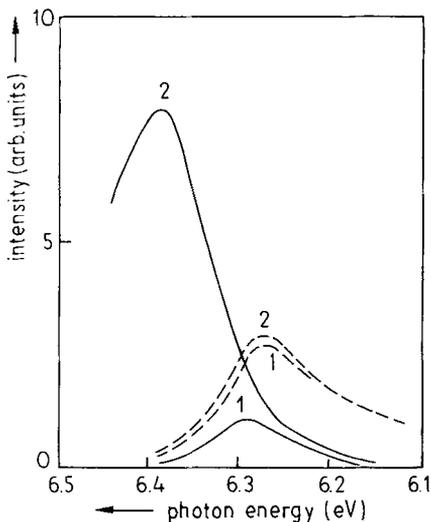


Fig. 2. Excitation spectra (dashed lines) and PSL creation spectra (full lines) of (1) nonsensitized and (2) sensitized KBr-In crystal ($1.6 \times 10^{17} \text{ cm}^{-3}$)

to the In^+ ion is six and introducing the effective absorption cross-section σ_D of the D-band (i.e. of Br^- ions near In^+ ion), k_D could be written as

$$k_D = 6\sigma_D N_A,$$

where N_A is the In^+ -ion concentration.

Thus, for the luminescence intensity I_{lum} , we can rewrite (1) as

$$I_{\text{lum}} \sim \frac{I_0 6\sigma_D N_A}{k_{\text{exc}} + 6\sigma_D N_A}. \quad (2)$$

Using the quantitative absorption coefficient of the exciton band in KBr available from Martienssen's paper [11], we have restored the excitation spectrum shape in Fig. 1 and thus obtained the following shape function

$$\sigma_D = 6.9 \times 10^{-16} \exp(-140(E - E_0)^2). \quad (3)$$

Equation (3) gives a single Gaussian band with maximum at $E_0 = 6.375$ eV and half-width of $\Delta E = 0.14$ eV (see Fig. 3). Let us use now the modified Smakula formula for the determination of the oscillator strength via the effective absorption cross-section σ_M in the absorption band peak [12], which for the Lorentz local field and Gaussian shape of the absorption band can be rewritten in the following way:

$$f = 8.79 \times 10^{16} \frac{n}{(n^2 + 2)^2} \sigma_M H, \quad (4)$$

where H (eV) is the half-width of the absorption band and n the refractive index. The value $n = 3.75$ in the band peak was determined by us from the reflectivity spectrum at $E = 6.375$ eV. Thus we obtain $f = 0.12$.

As was pointed out, the peak position in the excitation spectrum is practically independent of the In^+ -ion concentration (with the exception of $N_A = 1.2 \times 10^{19} \text{ cm}^{-3}$). This seems to be evident when taking into account the maximum value of the intensity (1). Indeed, if we differentiate it, introducing

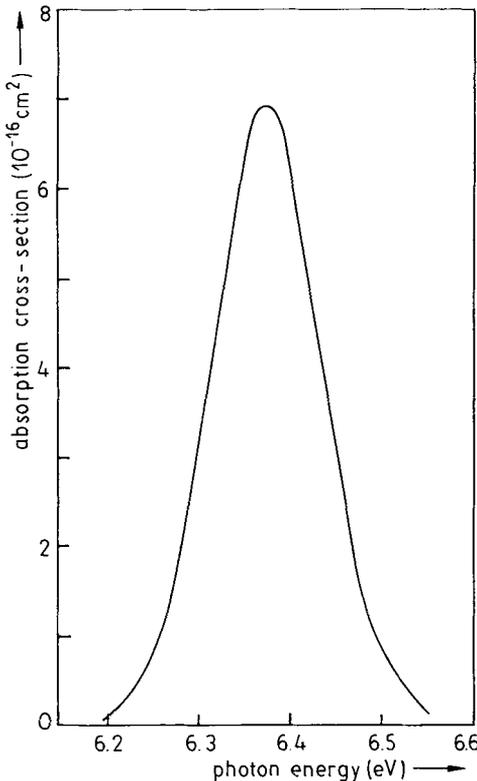


Fig. 3. A real shape of the D-band calculated using (3)

the Gaussian band $\kappa_D(E) = \kappa_{D_0} \exp(-\alpha(E - E_{D_0})^2)$ for the D-band and

$$\kappa_{exc}(E) = \kappa_0 \exp(A(E - E_0)) \quad (5)$$

for the Urbach tail of the fundamental absorption and putting the derivative zero, we will obtain easily for the peak value E_{max} of the excitation spectrum the following self-evident expression:

$$E_{max} = E_{D_0} - \frac{A}{2\alpha}. \quad (6)$$

From this it is clear that the position of the excitation spectrum peaks depends on the parameters of both the Gaussian D-band and the exponent of the Urbach tail, but is not dependent on the activator concentration. Furthermore, from (6) it is possible to understand the reason of the above-mentioned short-wavelength shift of the excitation spectrum for KBr-In crystal observed for high In^+ concentration ($1.2 \times 10^{19} \text{ cm}^{-3}$) – this may be caused by the change of the parameter A . This variation in A is well seen in the Urbach tail data reported in [13] for many pure and heavily-doped crystals and crystalline solid solutions.

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