DELOCALIZATION OF IMPURITY-ELECTRON EXCITATIONS IN BaS-Bi PHOSPHORS

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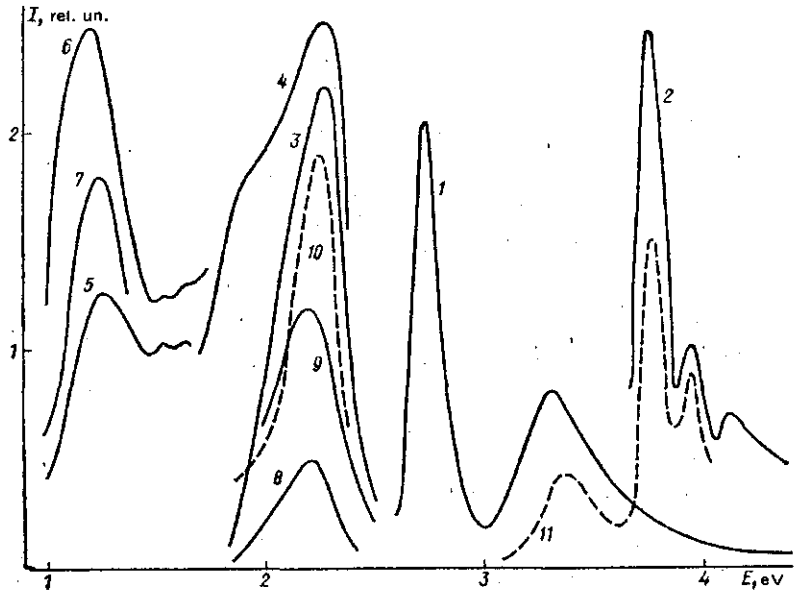
Delocalizations of the A and C excitations of a mercury-like ion in the "bismuth" center of BaS-Bi phosphors at 80° K is investigated by considering the characteristics of a photostimulates scintillation. It is found that excitations in the A band are not accompanied by delocalization of impurity-electron excitations, whereas excitation in the C band is accompanied by delocalization involving "memorization" of the ionization location upon electron breakoff.

Delocalization of impurity excitation has been explored in greatest detail for alkali-halide crystals, activated by mercury-like ions. Lushchik with his coworkers [1] showed that excitation of activator absorption in the C band, corresponding to the $^1S_0 \rightarrow {}^1P_1$ electron transition in the mercury-like ion involves ionization of a part of the luminescence nuclei. Ionization of local nuclei was also detected for A and C excitations in CaS, activated by mercury-like ions [1, 2]. It is emphasized by Lushchik and his coworkers [1] that in all the above cases there is no direct optical ionization of the nuclei, but the system, upon transition to the A or C excited state, is either thermally or self ionized.

Delocalization is detected from the appearance of processes in which the crystal lattice participates, such as: recombination luminescence, electron and hole conductivity, production of electron and hole color centers, etc.

The present study investigated the delocalization of electron excitations of the BaS-Bi crystalline phosphors, manifesting itself in the formation of color centers, by examining the characteristics of infrared stimulation of the scintillation.

The scintillation properties of the phosphor was investigated with a facility, consisting of three monochromators. Excitation was obtained by a DMR-4 monochromator, with IR stimulation provided by an IKS-12 monochromator. The luminescence was recorded by an FEU-70 photomultiplier via a ZMR-3 mirror-type monochromator. The excitation light source was provided by a DKsSh-1000 high-pressure xenon lamp. The stimulating IR source consisted of an SI8-200 calibrated incandescent ribbon-filament lamp. Powdered specimens were placed in a cryostat. The measurements were performed at liquid-nitrogen temperature. In all the presented spectra allowance was made for the energy distribution of photons in the emission of the SI8-200 lamp, for the intensity distribution in the emission spectrum of the DKsSh-1000 lamp, the spectral sensitivity of the photomultiplier, and the variance of the monochromators.



Spectral and luminescence characteristics of activated BaS phosphors. Excitation temperature of 80°K. 1) Excitation of the green band of the stationary luminescence of BaS-Bi; 2) excitation of the blue band of stationary luminescence of BaS-Bi; 3) stationary luminescence of BaS-Bi, E_{exc} = 3.35 eV; 4) stationary luminescence of BaS-Bi, Na, E_{exc} = 3.35 eV; 5) IR stimulation of BaS-Bi; 6) IR stimulation of BaS-Bi, Na; 7) IR stimulation of BaS-Cu; 8) scintillation luminescence of BaS-Bi upon excitation in the 3.35 eV band; 9) scintillation luminescence of BaS-Bi upon excitation in the exciton absorption band; 10) scintillation luminescence of BaS-Bi, Na upon excitation in the 3.35 eV band; 11) excitation of BaS-Bi scintillation. The above spectra were drawn without allowance for the relationship between the intensities of the stationary luminescence and scintillation.

For bismuth-activated BaS phosphors we obtained spectra of luminescence and excitation of stationary luminescence, the spectrum of the infrared stimulation of scintillation, and also the scintillation luminescence and excitation spectra.

An intense band of about 1.25 eV was detected in the spectrum of the IR stimulation of BaS-Bi and BaS-Bi, Na (curves 5 and 6 in the figure). A similar band was detected for BaS-Cu phosphors (curve 7), so that it is natural to associate it with the intrinsic defect of the principal diffraction grid.

The excitation and the spectral composition of the luminescence were investigated in the maximum of this stimulation band.

Active excitation of the scintillation of the BaS-Bi phosphor starts at energies above 3 eV (curve 11). The spectrum clearly displays the approximate 3.35 eV band, the energy location of which is identical with the stationary luminescence excitation band (curve 1). Most probably, excitation in this band involves

freeing of electrons from luminescence centers to the conductivity zone, and active filling of traps. After IR irradiation electrons are freed from capture centers and subsequently recombine with "their own" luminescence centers, since the spectral composition of the scintillation (curve 8) coincides with the green band of the stationary activator luminescence (curve 3). Koz'menko [3] associates the 3.35 eV excitation band with the $^1S_0 \rightarrow {}^1P_1$ transition in the Bi^{3+} bismuth ion. The aforementioned excitation of scintillation in this band possibly indicates that delocalization of C excitations with "memorization: of the ionization location upon breakoff of an electron occurs in BaS-Bi. The existence of "memorization" of the ionization location is additional confirmed by the fact that the spectral composition of scintillation, in BaS-Bi, Na phosphors, exhibiting greeen and red stationary luminescence (curve 4), excited in the 1.25 eV band, also coincides with the green activator band (curve 10). The red band is not present in the scintillation spectrum. There is apparently no relationship between this trap and the "bismuth" scintillation center, since, as was previously noted, the 1.25 eV stimulation band is also observed in copper-activated phosphors.

It can thus be assumed that delocalization of C excitation in BaS phosphors occurs according to the model suggested by Lushchik [1]:

$$L + h\nu \rightarrow L^* \rightarrow Le^+ + e^-,$$

where L and L* are impurity nuclei in the fundamental and excited state, whereas e^- and e^+ are the electron and the hole.

The 2.78 eV excitation band in BaS-Bi is associated, in the paper by Koz'menko [3], with the $^1S_0 \rightarrow {}^3P_1$ electron transition in the Bi^{3+} ion, i.e., with the A band of activator absorption. There is virtually no scintillation in the A band in BaS-Bi (curve 11), which may indicate that, unlike in CaS-Bi [4], there is no delocalization of A excitations in BaS-Bi, or that it occurs to a very small degree.

Delocalization of C excitations in CaS-Bi phosphors occurs due to self ionization of "bismuth" luminescence centers. It is of interest to clarify whether delocalization of C excitations in BaS-Bi occurs by self ionization or thermal ionization. We could not clarify this matter, since this required performing measurements at temperatures below 80° K, which was impossible with our equipment.

The IR scintillation in BaS-Bi is actively excited in the region of the exciton absorption band (curve 11). The structure of scintillation excitation bands in this region coincides with the excitation spectrum of blue stationary luminescence (curve 2) [5]. The scintillation excited in the exciton band also has the same spectral composition as the green activator band of stationary luminescence (curve 9).

Possibly, in this case there occurs one of the exciton reactions, in which the exciton reacts with a local center with attendant freeing of an electron. This may be a reaction such as [6]:

$$L + e^0 \rightarrow Le^0 \rightarrow Le^+ + e^-,$$

since this reaction results in freeing of an electron and formation of a type Le^+ center, which ensures "memorization" of the ionization location, manifesting itself in coincidence of the spectral composition of the scintillation and stationary activator luminescence.

The validation of this assumption requires further study.

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