Preparation and luminescent properties of KBr-TlBr systems

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Luminescence and excitation spectra of the systems on the basis of the nanoporous glass impregnated with KBr-TlBr and TlBr solutions as well as KBr single crystals surface-doped with thallium were studied in visible and ultraviolet regions at $T = 77$ K. It was shown that each of the studied systems has its peculiar optical properties, which differ from those of the corresponding macroscopic single crystals. The results are discussed taking into account the physicochemical features of the thallium insertion in the preparation of samples from solutions.

Keywords: KBr:Tl, luminescence and excitation spectra, low-dimensional KBr-TlBr system.

1. Introduction

The optical characteristics of alkali halides doped with heavy metals strongly depend on the methods and mechanisms of crystallization processes at the stage of the formation of absorption and luminescence centers [1].

KBr:Tl has been studied for more than 60 years (see, for example, [2, 3]), and significant progress has been made in understanding the optical characteristics of this system. The main result is that two well-resolved emission bands are observed in the UV region of the luminescence spectrum of KBr:Tl single crystals. It is generally accepted that these doublet luminescence bands (the so-called A_X and A_T bands), which arise upon excitation in the A-absorption band of KBr:Tl, are due to the coexistence of two types of Jahn–Teller minima on the $^3P_1$ adiabatic potential energy surface [4–6]. Unfortunately, all the features of the luminescence spectra over a wide range of thallium concentrations cannot be explained within the framework of this concept, even for single crystals.

Additional bands appear in the luminescence spectra [7, 8] with the increase in thallium concentration. In paper [7] these bands are ascribed to Tl^+ aggregates statistically distributed in the KBr lattice. The possible presence of microphases of the TlBr or complex salts in the samples with a high Tl^+ ion concentration makes it difficult to identify

the emission bands [9]. Partial covalent interaction of the impurity ion with the environment must be taken into account in such cases.

Local deformations of the lattice in the vicinity of the dopant lead to a change in the spectral characteristics with increasing concentration both in single crystals and in powders. The presence of the grains of small-sized microphases in massive objects, as well as a highly disturbed structure of the centers in low-dimensional systems, can also lead to optical characteristics that differ from those in the undisturbed KBr:Tl. Despite some common features, the optical properties of nano- and macrosystems have noticeable differences, which must be taken into account when discussing the mechanisms of luminescence.

The interest in nanoparticles has arisen because of their unusual optical properties, which are associated with the determining influence of the surface and with the effects of spatial restriction. The main characteristics of nanoparticles and the use of porous glasses as a basis for nanoobjects were considered in review papers [10–12]. The formation of anomalous crystal structures can become more intense in nanoencapsulated systems [13]. The nature of the chemical bond, as was shown in [8], can also affect the optical properties of luminescent low-dimensional systems. One can expect that the identification of the relation between the peculiarities of the investigated object and its luminescent properties can help clarify the distinctive features of the luminescence centers in various KBr-TlBr systems.

The study of low-dimensional samples made from the KBr-TlBr solution with variations in methods of crystallization was performed for obtaining additional information on the optical properties of the KBr-TlBr system. When choosing the method of sample preparation, we were guided by the data of physical and chemical studies [9, 14, 15]. The excitation and luminescence spectra at 77 K of low-dimensional KBr:Tl samples were compared with the corresponding spectra of macroscopic samples and low-dimensional TlBr samples.

2. Experimental procedure

Three types of the low-dimensional samples were studied: the samples KBr:Tl and TlBr embedded in nanoporous glass (NPG-KBr:Tl and NPG-TlBr) and surface-doped samples on the basis of the KBr single crystals (SD).

Nanoporous glass (NPG) with an average pore size about 9 nm and a large specific surface (up to 300 m^2/g) [11] was used as a support for the studied objects. The peculiarities of the used NPG are described in more detail in [16]. The NPG with the open porosity inside the silicate carcass was annealed in an oxygen flow at 260°C in order to remove possible technological contaminants. Then the NPG was annealed in vacuum at 150°C for a long time (~24 hours). The sparing mode of annealing was used because the pore size can decrease with increasing annealing temperature. In the course of preparation, the supports of the studied samples (NPG or plates of KBr single crystals) were kept for 24 hours within the appropriate solutions.

The aqueous solution of KBr-TlBr saturated with respect to both KBr and TlBr at room temperature was used for obtaining NPG-KBr:Tl. After the samples were removed from the solution, the remainder solution was removed from the NPG surface, and the samples were dried in an exsiccator at room temperature. The spectra of NPG-KBr:Tl samples were compared with the corresponding spectra of macroscopic crystals of a hardened melt KBr:Tl (HM).

Optical properties of TlBr were studied using the NPG-TlBr samples. The NPG were dipped into TlBr solution in a rectified ethanol. The TlBr solution was preliminary saturated during a prolonged boiling.

The plates (1–2 mm thick) of freshly cleaved KBr single crystals were placed into the ampoules with a saturated aqueous KBr-TlBr solution at room temperature. KBr concentration in the solution was 4.0 M, and Tl^+ concentration was $C_{Tl^+} = 3.7 \times 10^{-4}$ mol/l. The ampoules were sealed and subjected to mechanical stirring in a special device at room temperature.

Measurements of the luminescence spectra in the region 2.0–4.0 eV and of the excitation spectra in the region 3.0–5.1 eV were performed using the installation described in [8]. All measurements were performed at 77 K. The light transmission edge of pure NPG lies near 5.0–5.1 eV, which impedes the studies of the excitation in a short-wave ultraviolet region.

3. Experimental results

Figure 1 (curve 1) presents the luminescence spectrum of NPG-KBr:Tl under excitation at the maximum of *A*-absorption band.

One can see two well-resolved ultraviolet bands (the so-called A_T and A_X components). The intensity of A_T luminescence is higher than that of A_X component. Moreover, the additional luminescence was observed in the high- (4.2–4.6 eV) and low-energy
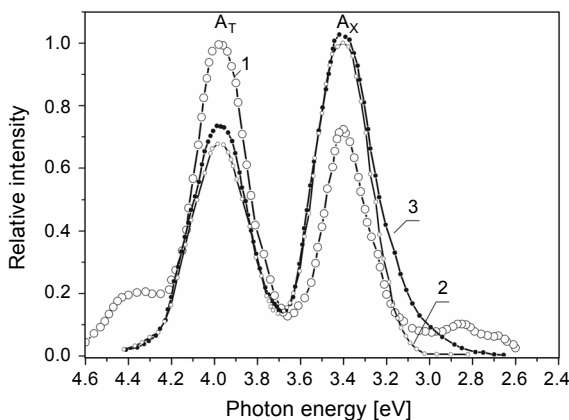

Fig. 1. Luminescence spectra. Freshly prepared NPG-KBr:Tl, E_{exc} = 4.82 eV (curve 1) and HM KBr:Tl, E_{exc} = 4.70 eV, C_{Tl^+} = 0.03 and 1.0 mol% (curves 2 and 3, respectively).

(2.5–3.0 eV) regions. The spectrum of the freshly prepared NPG-KBr:Tl sample (Fig. 1, curve 1) was compared with the spectra of the specially prepared HM KBr:Tl crystals (C_{Tl^+} = 0.03 and 1.0 mol% – curves 2 and 3). Comparing the curves 1 and 2, 3, one can see that, in contrast to the NPG-KBr:Tl samples, the intensity of the A_X component is higher than that of A_T.

The ratio of the intensities of the doublet luminescence components is strongly dependent on temperature and the excitation energy (even when the excitation occurs within the A-absorption band). Three luminescence spectra presented in Fig. 1 were measured under the same conditions, they differ only in the method of manufacturing and in the size of crystals: from nanoscale to macroscopic crystals of the HM with the properties close to the properties of the single crystals. Thallium content in NPG-KBr:Tl and HM samples with a higher Tl^+ concentration is within the same order of magnitude $C_{Tl^+} \sim 10^{20}$ cm^{-3}. A higher intensity of the A_X band (in comparison to the A_T) in the same range of thallium concentration and T = 80 K was also observed for single crystals [7].

The excitation spectra of A_T and A_X components in NPG-KBr:Tl samples have nearly the same position of maxima (~4.8 eV), but are not completely identical (curves 1 and 2 in Fig. 2**a**): excitation of the A_X band is a bit more intensive in the low- and high-energy regions. The excitation spectra of the A_T and A_X components of the HM samples are presented in Fig. 2**b**. The excitation of the A_X component is also more intensive in the low-energy part of the excitation spectrum. The excitation maxima of the doublet components of the NPG-KBr:Tl samples undergo the high-energy ("blue") shift of approximately 0.11 − 0.09 eV in relation to the corresponding excitation maxima of HM. This shift can appear due to the small size of the crystals in the NPG matrix. The half
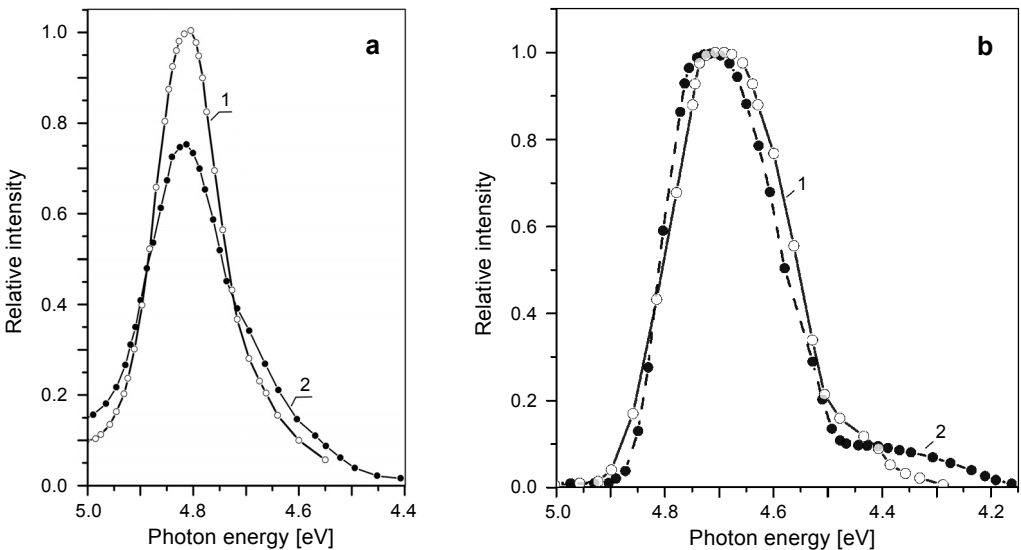

Fig. 2. The excitation spectra KBr:Tl – E_{em} = 3.96 eV (curve 1), E_{em} = 3.41 eV (curve 2). The freshly prepared NPG-KBr:Tl sample (**a**), and HM KBr:Tl, C_{Tl^+} = 1.0 mol% (**b**).

T a b l e 1. Intensity, position of maxima, and half-width of individual components (Fig. 1, curve 1).

Numerical analysis	Region 4.2–4.6 eV	A_T	A_X	Region 2.5–3.0 eV	
Intensity [a. u.]	318.45	1091.99	784.43	172.29	173.70
$E_{i, max}$ [eV]	4.39	3.96	3.39	2.98	2.67
Half-width δ_i [eV]	0.184	0.157	0.154	0.169	0.194

-width of the excitation bands of the doublet components of the HM samples was greater than those of the NPG-KBr:Tl samples.

The random walk method described in [17] was used to clarify the position of the luminescent maxima in NPG-KBr:Tl. The results of the decomposition of the luminescence spectrum (curve 1 in Fig. 1) into 5 individual components are presented in Table 1. Less intense luminescence bands with maxima at 4.39, 2.98 and 2.67 eV were separated in addition to the bands of the ultraviolet doublet. The intensity of the luminescence bands in the high- and low-energy regions is changed significantly with relatively weak external influences on the sample. Annealing of NPG-KBr:Tl samples at 150°C resulted in the disappearance of the additional maximum in the high-energy region, while the luminescence intensity in the low-energy region increased. The storage of the annealed samples in an exsiccator during two months results in almost complete disappearance of the luminescence in 2.5–3.0 eV region. Based on this, it can be assumed that the high-energy band is most likely associated with defects that anneal at 150°C, and low-energy bands are due to the presence of water molecules, whose luminescence maxima in the KBr-H_2O system are present in this part of the spectrum [18]. Positions of the A_T and the A_X maxima for the HM samples are slightly different from those for NPG-KBr:Tl, especially for HM with a higher thallium concentration. The last can be due to the broadening of the A_X band in the low-energy region.

Table 2 presents the parameters of the ultraviolet doublet for all studied KBr:Tl systems. The estimated half-width of the A_T and the A_X components for the HM samples with the high thallium concentration (comparable with the concentration of thallium in NPG-KBr:Tl) was 0.157 and 0.162 eV, respectively. The half-width of the A_T band was the same for NPG-KBr:Tl and HM samples, while the half-width of the A_X for NPG-KBr:Tl was less than the one for HM.

A study of the optical properties of the centers on the surface of KBr single crystals surface-doped with thallium in the aqueous KBr-TlBr solution (SD samples) was performed to clarify the role of the luminescence centers associated with the surface

T a b l e 2. Position of maxima and a half-width of luminescence bands.

Type of the sample	Position of maximum [eV]		Half-width [eV]	
	A_T	A_X	A_T	A_X
NPG-KBr:Tl	3.96	3.39	0.157	0.154
HM C_{Tl^+} = 0.03 mol%	3.96	3.38	0.157	0.155
HM C_{Tl^+} = 1.00 mol%	3.98	3.41	0.157	0.162
SD	–	3.39	–	0.195

incorporation of microphases of complex ions or of TlBr. The parameters of the luminescence spectra under the excitation in the *A*-band can change due to the formation of the centers related to the presence of the thallium complexes in the solution [14, 19] used for preparation of the samples. The possibility of a TlBr insertion in KBr by the adsorption mechanism from the solution was shown in [9] by means of the radiochemical technique. The relative concentration of the inserted complexes will increase for small crystals where the role of the surface increases.

The luminescence spectrum of the NPG-KBr:Tl samples (Fig. 3**a**, curve 1) is compared with the spectrum of the SD samples (curve 2). Only one quite symmetrical luminescence band is observed under excitation of SD in the *A*-absorption band. Position of the maximum of this band (3.39 eV) practically coincides with the position of the A_X component for the samples prepared in other ways. The emission band is signifi-
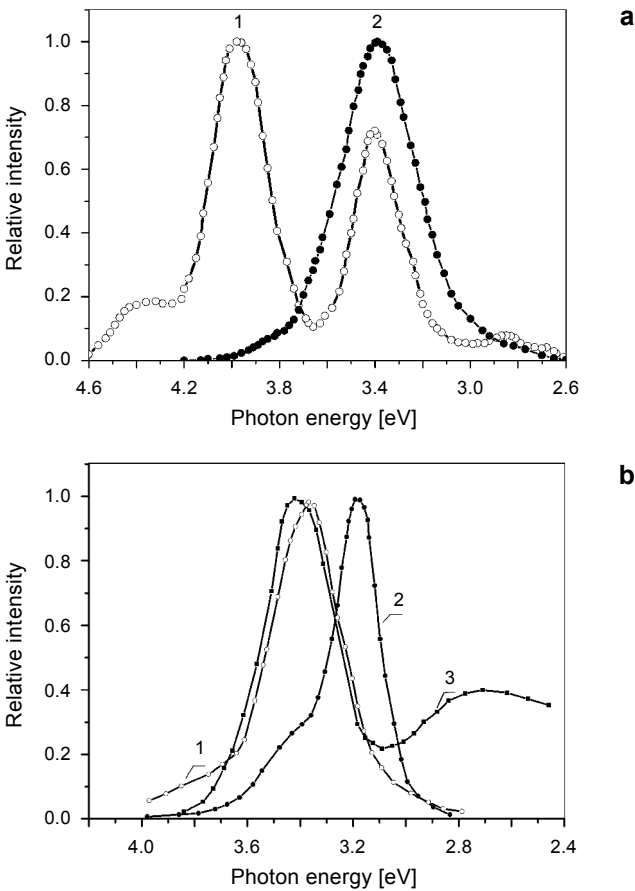

Fig. 3. Luminescence spectra. NPG-KBr:Tl (curve 1) and SD samples (curve 2); excitation at maximum of the corresponding excitation band – **a**. SD samples after annealing at 260°C – E_{exc} = 4.7 eV (curve 1) and E_{exc} = 4.12 eV (curve 3), and after annealing at 560°C – E_{exc} = 4.7 eV (curve 2) – **b**.
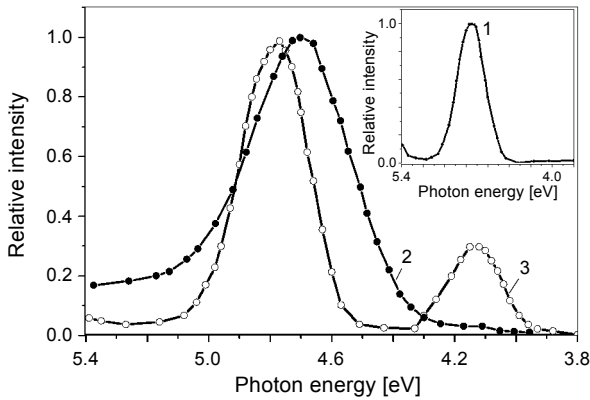
Fig. 4. The excitation spectra. E_{em} = 3.39 eV of the SD samples before annealing (the insert, curve 1). After annealing at 560°C – E_{em} = 3.18 eV (curve 2), and E_{em} = 3.39 eV (curve 3).

cantly broadened compared both with NPG-KBr:Tl and HM and has the large Stokes shift (~1.42 eV).

Annealing at 260°C results in a reduction of the intensity in comparison with the fresh samples, but the shape of the luminescence band under excitation at 4.7 eV remains practically unchanged (Fig. 3**b**, curve 1). After subsequent annealing of the SD samples for an hour and a half at 560°C, the total intensity of the band continued to decrease and a new band with a maximum near 3.18 eV appeared in the luminescence spectrum (Fig. 3**b**, curve 2). The A_T component was not observed in any spectrum.

The excitation spectra of the SD samples before and after the annealing are shown in Fig. 4. A new band with a maximum at 4.12 eV appears in the excitation spectrum after annealing at 560°C. It should be mentioned that this excitation band begins to appear already after annealing at 260°C. This excitation band with a maximum at 4.12 eV partially overlaps the high-energy region of the A_T luminescence of the NPG-KBr:Tl samples. A new luminescence band in the 2.4–3.0 eV region was observed after annealing at 260°C under excitation at 4.12 eV (Fig. 3**b**, curve 3). Annealing at 560°C results in the disappearance of this band, and only the band with maximum at 3.39 eV was observed under excitation at 4.12 eV.

According to [20, 21], various complexes $(TlBr_n)^{1-n}$ can be present in the TlBr solutions. A formation of the complex aggregates in the form of the precipitated nanophase of thallium salt or complex compounds could be expected in the process of the interaction of KBr-TlBr solution with the KBr single crystal. The last can result in the appearance of the additional luminescence bands associated with the presence of TlBr on the surface. For this reason optical properties of the NPG-TlBr samples were studied.

The spectra of the freshly prepared NPG-TlBr samples and of the samples, which were stored for months in a dry air at room temperature, are presented in Fig. 5. The luminescence can be effectively excited in the region 3.0–5.0 eV, *i.e.* in the fundamental absorption region of TlBr and at the edge of the absorption band.
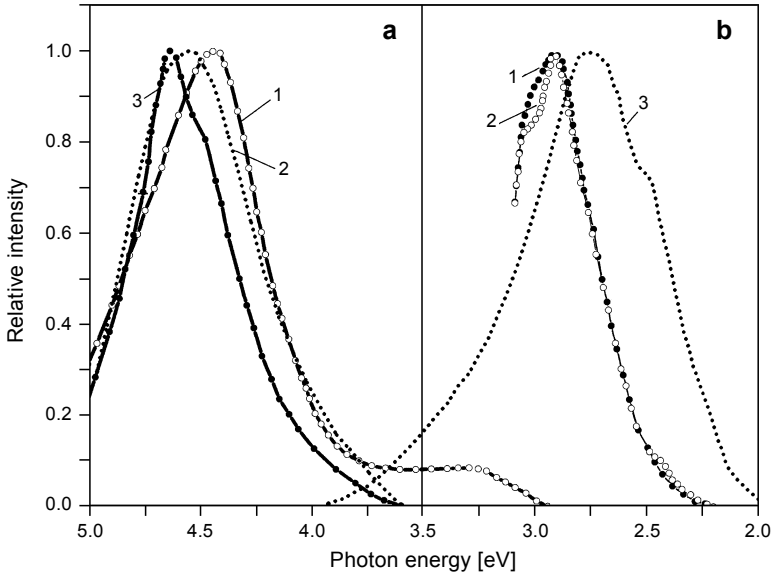
Fig. 5. NPG-TlBr samples. The excitation spectra for the freshly prepared sample E_{em} = 2.92 eV (curve 1), and for the samples stored for several months E_{em} = 2.92 eV (curve 2), E_{em} = 2.50 eV (curve 3) – **a**. The luminescence spectra for the freshly prepared sample E_{exc} = 4.42 eV (curve 1) and E_{exc} = 3.40 eV (curve 2), and for the samples stored for several months E_{exc} = 4.42 eV (curve 3) – **b**.

The luminescence band of the freshly prepared samples is observed near the edge of the absorption band, it has a maximum at 2.92 eV and a shoulder near 3.04 eV. The excitation spectrum has maximum at 4.42 eV and a shoulder in the region of the diffuse edge of the fundamental absorption.

A broad asymmetric luminescence band with a shoulder near 2.5 eV appeared after the storage of the samples. The maximum of the excitation spectrum for emission at 2.92 eV is shifted after the storage of the samples approximately by 0.24 eV toward the high-energy region in comparison to the freshly prepared samples. The maximum of the luminescence spectrum at 2.75 eV for the stored samples is situated in the region of the indirect band-to-band transitions [22]. The emission band in the region 2.2–2.6 eV was ascribed [23] to a radiative recombination of electrons with centers of the type Tl^{2+}.

4. Discussion

All the studied low-dimensional objects have their own peculiarities of the spectral properties. The most interesting result is the absence of A_T band in the luminescence spectra of the SD samples, although the excitation spectra are similar to those of NPG-KBr:Tl and HM samples. The position of the luminescence maximum of this band exactly coincides with the position of the maximum of the A_X band of NPG-KBr:Tl. "A_X-like" band of SD is noticeably broadened, and has a large Stokes shift, which points to a possibility of a nonradiative delocalization of excitation. Although "A_X-like" band

is excited in the region of the *A*-absorption band, the absence of the A_T band allows to suppose that the mechanisms of excitation and luminescence in the SD samples can differ from the generally accepted for KBr:Tl system.

It was expected that the heat treatment of the SD samples could result in the recovery of the doublet structure of the luminescence spectrum due to the diffusion of Tl^+ ions into KBr. But this did not happen. Heat treatment of the SD samples leads to the development of the low-energy part of the luminescence spectrum and of the excitation band at 4.12 eV. The emergence of the luminescence of KBr:Tl single crystals in the low-energy region was observed in many papers, for example in [24], where this emission was associated with a formation of dimeric centers with increasing Tl^+ concentration. One might expect that more complex thallium aggregates will be created in the SD samples upon annealing. However, the observed luminescence with a maximum near 3.18 eV cannot be associated with a higher degree of aggregation of thallium ions. It was shown [7, 24] that luminescence of dimers and other aggregates of thallium ions in single crystals is situated at a lower energy.

A comparison of the NPG-TlBr and SD spectra shows that the excitation spectrum of the luminescence band with the maximum at 2.92 eV for the NPG-TlBr samples covers the part of the spectral region, where the A_T component of the ultraviolet doublet should be observed in the SD samples, and partially overlaps the region of the A_X emission. It can be assumed that more favorable conditions for the formation of nanophase of TlBr can exist on the surface of the KBr single crystal (SD samples). As was shown [25], the local stresses in microcrystals facilitate the formation of the TlBr molecules. It is known that thallium in KBr solutions is present in the form of negative complexes $(TlBr_n)^{1-n}$ or TlBr molecules, which can be captured and adsorbed on the surface of KBr upon crystallization of KBr:Tl [9]. Located in the vicinity of the surface defects or dislocations, the aggregates of complex ions or molecules can form nanophase inclusions.

According to Fig. 5, these inclusions can absorb radiation in the region near 4 eV. Absorption in this region was also observed for TlBr films [26]. It should be mentioned that the excitation band with maximum near 4.12 eV appeared after the annealing of the SD samples at 560°C. But excitation in this band did not result in the appearance of the emission near 3.0 eV characteristic for TlBr (see curves 1 and 2 in Fig. 5). On the one hand, the spectra of the TlBr microphases on the KBr surface can differ from those of NPG-TlBr, but, on the other hand, the presence of emission bands in the low-energy (2.5–3.0 eV) region for all three objects produced from solutions allows to suppose their relation with the TlBr molecules or with the formation of complexes $(TlBr_n)^{1-n}$ with various coordination numbers. Even if these inclusions do not yet have a complete similarity with a free TlBr phase, they can form structural centers with partially covalent bond, which will affect the relaxation processes.

The possibility of the processes of excitation and relaxation, which differ from generally accepted [27, 28], follows also from an examination of the excitation spectra. Though the excitation spectra of SD, HM and NPG-KBr:Tl are located in the region of the *A*-absorption band, the shape of the excitation curves is not the same for the

different objects. Moreover, the excitation spectra of A_T and A_X bands have a different shape for both HM and NPG-KBr:Tl. The excitation spectra in the region of the *A*-absorption band for both doublet components in single crystals [7] have the same shape and position of the maximum (4.7 eV). The difference in the shape of the excitation bands of A_T and A_X components can point to a possibility of different mechanisms of excitation and, hence, of relaxation.

It should be mentioned that the ratio of intensities of A_T and A_X luminescence bands was different in dependence of manufacturing procedure and external actions: from the predominance of A_T emission up to its complete disappearance. In the models proposed to explain the nature of the luminescence [27, 28], the authors do not take into account a possible impact of the halide environment of the thallium ion on a relaxation process. This is probably not the case for low-dimensional systems KBr:Tl prepared from solutions. Apart from Tl^+ ions incorporated in the host lattice, the centers formed in the surface defects via adsorption mechanism should be taken into account in these samples. A role of the covalent bonding increases in such centers, thereby increasing the role of anions in the relaxation process.

According to [29], the presence of quasi-molecules Br_3^- is possible in aqueous solutions of KBr. Similar centers were observed in high-purity single crystals of KBr under creation of radiation defects by means of irradiation in a vacuum ultraviolet region [30]. Linear quasi-molecules Br_3^- can be absorbed near defects on the surface of the SD samples and nanocrystals NPG-KBr:Tl. Taking into account the large surface-to-volume ratio in the investigated objects, it can be assumed that A_X emission in these objects can be at least partially connected with the nonradiative transfer of an electron from the excited Tl^+-ion on Br_3^- -ion and its subsequent excitation. It is possible that a relaxation process of this center could result in the emission near 3.4 eV.

The stability of polyhalide centers can increase in the presence of impurities such as OH^--ions or water, which can contribute to an effective formation of V-centers. The interaction of Br_n^- with the inner surface of the pores via the hydrogen bridge Si-O-[H---O-H] can result in an effective stabilization of V-centers in NPG-KBr:Tl samples. It is supposed [29] that the absorption near 4.7 eV in the aqueous KBr solution is associated with a linear array of halogen molecule and halide ion. Therefore, the possibility of a recombination mechanism of emission connected with a charge transfer from the ligand ions to the central Tl^+ ion should also be taken into account in the explanation of the nature of luminescence of KBr:Tl located in NPG matrix and on the surface of KBr single crystals under excitation within the *A*-band.

5. Conclusion

As follows from the performed study of the objects in KBr-TlBr system prepared from solutions, the generally accepted mechanisms can explain the excitation and relaxation processes in perfect crystals with low thallium concentration only. The presence of microphases, the halide environment of Tl^+-ions and the partially covalent nature of

bonding should be taken into account in discussion of more complex systems. Further research is necessary to clarify the specific role of all the above factors, and a particular attention should be paid to the excitation spectra of the luminescence of individual bands.

It was shown that the optical properties of the low-dimensional systems depend on the conditions of preparation. The last can be associated with various locations of thallium in the host lattice and/or on the surface with a strongly disturbed structure. When discussing the mechanism and the nature of electronic transitions one should consider the high sensitivity of optical characteristics to the formed structure of the luminescence center at least for low-dimensional systems. From a practical viewpoint, the results of the study of the optical properties of disturbed low-dimensional systems can help to detect signs of the appearance of defective structures for different alkali halide systems doped with heavy metals. Comprehensive research by structural methods can also bring to light the specific features of the studied objects.

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