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Recombination processes in crystals of solid solutions of $Ba_{1-x}La_xF_{2+x}$

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Abstract

In this work we carry out the investigations of the suppression of the self-trapped exciton emission include measurements of thermoluminescence (TL), optical absorption of hole centers in the temperature range from 77 K to room temperature of the crystals with various La concentration (up to 5%). Exciton luminescence was also investigated in La-doped BaF_2 crystals.Two luminescence bands at 4.0 eV and 3.67 eV were observed. It was concluded that 4.0 eV emission band belongs to weakly perturbed excitons, while the 3.67 eV band belongs to strongly perturbed excitons.

Keywords: luminescence, exciton, scintillator

1. Introduction

A self-trapped exciton emission is significantly suppressed in crystals of solid solutions of $Ba_{1-x}La_xF_{2+x}$ [1-3]. As the La concentration increases to about 5 %, the intensity of this luminescence decreases by a factor 10, whereas the intensity of cross-luminescence remains almost constant. However the mechanism of this suppression has not been studied in detail and is still unclear. The crystal of the solid solution $Ba_{1-x}La_xF_{2+x}$ with the optimal concentration of lanthanum at about 5% looks promising to applying these crystals to high counting rate experiments. The main problem of its possible use as a scintillating detector is preparation of the perfect quality crystals. Therefore the objective of this work is, firstly, to devise a technique for preparation of the perfect quality crystals and, secondly, to improve the present state of knowledge on suppression of the self-trapped exciton emission in the crystals of solid solutions $Ba_{1-x}La_xF_{2+x}$.

In previous work we found that the interstitial fluorine levels are above the fluorine valence band of $Ba_{1-x}La_xF_{2+x}$ crystals. With increasing La-concentration up to percents the interstitial F levels create a subband. Formation of the interstitial fluorine subband leads to decreasing of band gap and to appearing a new high-energy crossluminescence band [3]. We presume also that the high-energy emission at about 7.2 eV arises from a radiation transition between the electron state of the interstitial F_i^- -ion, its electron state is located in the forbidden band at low concentration of lanthanum, and the outermost Ba^{2+} 5p core band

In this work we carry out the investigations of the suppression of the self-trapped exciton emission include measurements of thermoluminescence (TL), optical absorption of hole centers in the temperature range from 77 K to room temperature of the crystals with various La concentration.

2. Experimental technique

The crystals of undoped and La-doped BaF_2 (with the concentration of lanthanum up to 5 mol %) were grown using the combined Shteber-Stocbarger method. The anomaly of the melting of heterovalent solid solutions is the direct consequence of strong chemical interactions in non-stoichiometric $Ba_{1-x}La_xF_{2+x}$ crystals accompanied by the formation of clusters of structural defects, cellular structure and banding. This problem is remedied by severe thermal conditions of crystal growth. We have developed the method of the growth of the large size crystals of solid solution of $Ba_{1-x}La_xF_{2+x}$. The samples were of high optical quality and no indication of oxygen contamination.

3. Results

3.1. Hole centers

When the undoped barium fluorides are x-irradiated at 77 K the V_k center is predominant hole center formed and the TL spectrum exhibits the intense glow peak at about 110 K, which is associated with the destruction of V_k centers. Aside from this there are additional weaker features above 200 K (Fig.1). This is in agreement with previous reports [4,5]. The intensity of V_k - glow peak constantly decreases with increasing of La concentration and the TL peak at about 110 K is not observed at the concentration above 1 % whatever. At low concentration of lanthanum weak glow peaks in temperature region from 140 to 200 K are appeared which are associated with the thermal destruction of V_{kA} and V_H centers [4]. The thermoluminescence curve of BaF_2 doped with 5% LaF_3 exhibits only weak glow peaks at about 130 and 180 K (Fig.1), therewith the integral

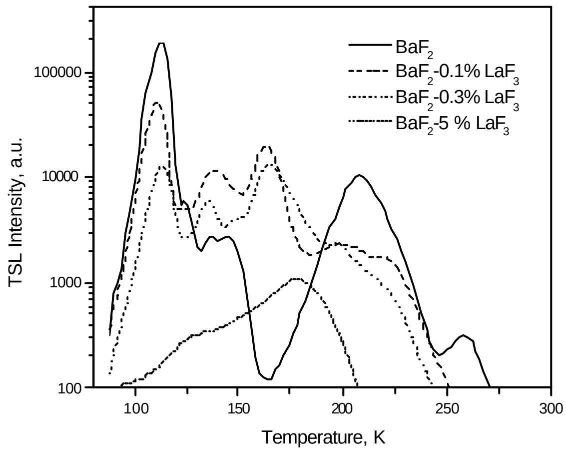

Figure 1 Thermoluminescence of the $Ba_{1-x}La_xF_{2+x}$ crystals, x-irradiated at 77 K

intensity of thermoluminescence is less than that for "pure" BaF_2 by a factor of more than 10.

X – irradiated BaF_2 crystals at 77 K show optical absorption having two maximums at 3.4 (365

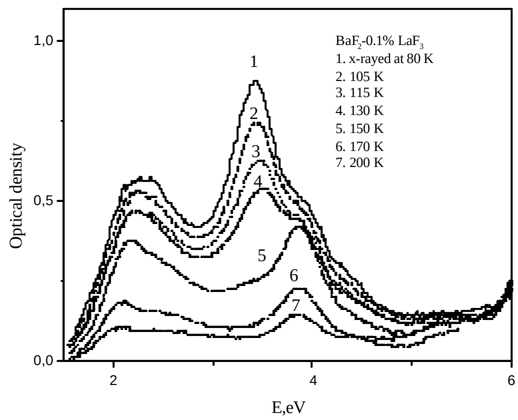

Figure 2 Optical absorption of BaF_2-0.1%LaF_3 crystal after x-iradiation at 80 K (1) and subsequent heating to 105 K (2), 115 K (3), 130 K (4), 150 K (5), 170 K (6) and 200 K (7). The spectra were measured at 80 K.

nm) and 2.3 eV (540 nm). Mutual annihilation of the centers related with these absorption bands occurs below 130 K that correlate with thermal destruction of the V_k -centers and the band at 3.4 eV is apparently associated with V_k -centers. Contrariwise to the thermoluminescence results, the intensity of V_k optical absorption band, which occur at 3.4 eV, increases with increasing of the La concentration (at least for low concentration of lanthanum). Additionally, in the crystals doped with lanthanum an absorption band at 3.85 eV is appeared which also increases with increasing of the La concentration. This absorption band decays at about 170 K (Fig.2). Thermal destruction of V_k centers leads to the formation of a few centers, which are responsible for the band at 3.85 eV. This indicates that the centers are responsible for the band at 3.4 and 3.85 eV have structures related to that of the V_k center. The summary coloration efficiency increases with La-doping up to 20 % [6]. By this it meant that the greater part of self-trapped holes has not been directly implicated in the radiative recombination processes. The results can be interpreted in terms of the

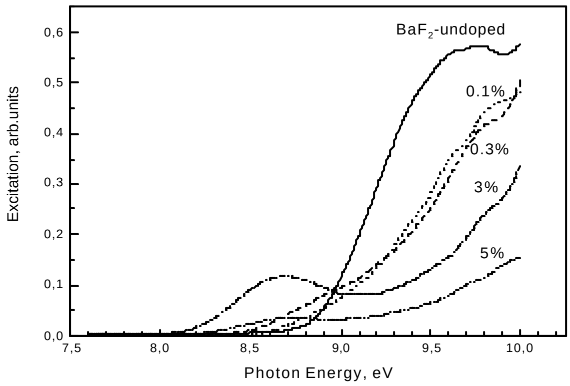

Figure 3. Excitation spectra of luminescence monitored at 4.0 eV of BaF_2 and $Ba_{1-x}La_xF_{2+x}$ crystals at room temperature.

modification of the valence band in the crystal of solid solution of $Ba_{1-x}La_xF_{2+x}$ by the formation of the interstitial anion subband [3]. In the barium fluoride crystals doped with lanthanum, in addition to the pure V_k centers, V_{kA} and V_H centers are formed which are associated with charge-compensating interstitial fluoride ions (F_i^-) (at least V_H centers). However the thermoluminescence spectrum shows only a small increase of emission in the temperature region from 130 to 200 K (Fig. 1). This indicate that the self-trapped holes associated with charge-compensating interstitial fluoride ions (F_i^-) are not efficiently taken part in the radiative recombination processes.

3.2. Excitons

The broad 4.0 eV exciton emission band is excited above 8.8 eV in pure BaF_2 (Fig.3). The band can be fitted by three gaussian bands,which have slightly different decay times. Three bands were associated with different spatial configurations of excitons in BaF_2 [9] With La-doping the excitation spectra efficiency decrease in a region above 9 eV, while increase at lower energies. The excitation intensity of BaF_2-5%LaF_3 at 9.5 eV becomes near 10 times lower than that of pure BaF_2 (see Fig.2). This value is similar to that observed under x-ray excitation [2]. A new excitation band in $Ba_{1-x}La_xF_{2+x}$ is appeared at 8-9 eV region. The band becomes largest in BaF_2 doped with 3% LaF_3 crystals and centres at 8.75 eV at room

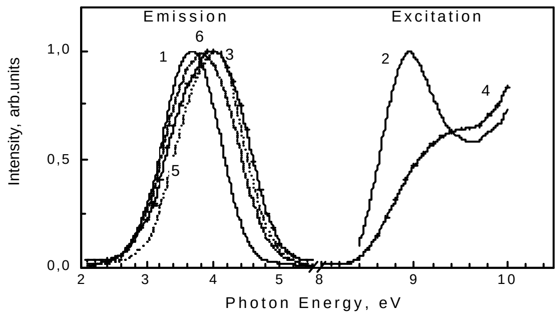

Figure 4. Normalised emission and excitation spectra of BaF_2 (5)and BaF_2 -3%LaF_3 (1-4)crystals at 78 K.Emission spectra were measured with 8.7 eV (1)and 9.5 eV (3,5) excitation.Emission spectrum (6)was measured either 8.6 eV or 9.6 eV at 324 K. Excitation spectra were measured for 3.4 eV (2)and for 4.5 eV (4)emission light.

temperature (see Fig.3).

At optical excitation above 9 eV at 78 K the emission band with maximum at 4.0 eV is observed. The band has the same maximum energy as exciton emission band in pure BaF_2 crystals but has larger halfwidth (Fig.4). The excitation spectra of 4.0 eV emission band are similar in pure BaF_2 and in $Ba_{1-x}La_xF_{2+x}$ compare Fig.3 and 4). One may assume that the 4.0 eV emission band in $Ba_{1-x}La_xF_{2+x}$ belongs to the emission of weakly perturbed excitons. In the emission spectrum of BaF_2-3%LaF_3 excited at 8-9 eV region dominates the band with maximum at 3.67 eV at 78 K. Usually in ionic crystals impurity perturbed exciton emission bands have the excitation bands lying on low-energy tail of exciton absorption [7]. This tendency was observed also in CaF_2 doping with several impurities [8]. Therefore we assume that the emission band at 3.67 eV is due to a perturbed exciton emission. At room temperature the band becomes wider and the maximum of band shifts to higher energy. Using 8.7 eV excitation we observe the increasing of emission monitored at 4.5 eV above 170 K. At 320 K the emission spectra for 8.7 eV and 9.5 eV excitations are similar (see Fig.4). Evidently the emission spectrum at 320 K consists of both 3.67 and 4.0 eV bands. Therefore above 170 K the exciton perturbed by lanthanum ion can leave the impurity and become unperturbed and vice versa. At 320 K both excitons are in thermal equilibrium.

Decay of 4.0 eV emission band in BaF_2-3%LaF_3 is close to exciton decay in pure BaF_2 [9,10]. The decay time of 4.0 eV emission increase from 4.5 µs at room temperature to 16 ms at 78 K. Below 200 K a second slow component of .100 µs appears. Opposite to this the decay of 3.67 eV band consists of single exponential component 4.5 µs, which slightly increased at 78 K.

4. Conclusion

In previous work we found that the interstitial fluorine levels are above the fluorine valence band of $Ba_{1-x}La_xF_{2+x}$ crystals. With increasing La-concentration up to percents the interstitial F levels create a subband. Formation of the interstitial fluorine subband lead to decreasing of band gap and to appearing a new high-energy crossluminescence band [3].

In this work we presume that the modification of the valence band by the formation of the interstitial anion sub-band in the crystal of solid solution $Ba_{1-X}La_XF_{2+X}$ leads to the suppression of the thermoluminescence emission by trapping of the V_k holes by fluorine interstitials forming the hole centers which take no efficiency part in the radiative recombination processes.

On the other hand the formation of the subband leads to the creation of the perturbed exciton. During excitation by 8-9 eV photons of $Ba_{1-x}La_xF_{2+x}$ electron transfer from interstitial fluorine level to conduction band or to exciton states leaving hole on fluorine interstitial. We suppose that this hole very fast become self-trapped. Therefore the structure of 3.67 eV exciton in La-doped BaF 2 can be considered as F_2^- interstitial (V_H centre) near the La_3^+ ion plus trapped electron. One may conclude that apart to unperturbed exciton, where outmost electron localised on anion vacancy, the electron of perturbed 3.67 eV exciton have to be localised on La ion.

We assume that the conversion of weakly perturbed configuration to perturbed one, which we observed in BaF_2 -3% LaF_3, play a role in suppression of exciton emission. Indeed, the exciton created in a perfect lattice can easy transform to La perturbed exciton above 170 K, which have considerably less light output. In $Ba_{1-x}La_xF_{2+x}$ the La perturbed exciton quantum yield drastically decreased above 3% of LaF_3 possibly due to concentration quenching. In general the process of transformation of weakly perturbed exciton to perturbed ones do not depend on sort of Re_3^+ impurity. In accordance to this the exciton luminescence suppression was observed in BaF_2 crystals doped with different Re_3^+ ion

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