



OLEDs based on some mixed-ligand terbium carboxylates and zinc complexes with tetradentate Schiff bases: Mechanisms of electroluminescence degradation

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ABSTRACT

Mixed-ligand terbium carboxylates—Tb(Carb)₃(TPPO)₂ (HCarb = HSal (salicylic acid), Hpobz (2-phenoxybenzoic acid); TPPO = triphenylphosphine oxide) and zinc complexes with tetradentate Schiff bases—ZnSB (H₂SB = H₂SAL1, H₂SAL2 (derivatives of salicylic aldehyde); H₂MO1, H₂MO2 (derivatives of *o*-vanillin)) were used as electroluminescent (EL) layers in organic light emitting diodes (OLEDs). These devices have undergone reversible and irreversible mechanisms of EL degradation. The reversible one is mainly associated with charge carrier trap filling. At the same time several mechanisms of irreversible degradation were observed under UV light irradiation, heating and ageing in ambient conditions. The degradation mechanisms of OLEDs under heating from 293 K to 320 K were related to the changes in the interface regions. The initial degradation was eliminated by (1) an application of alternating bias voltage; (2) a decrease of the substrate temperature and the velocity of the thermal evaporation of materials. The degradation of OLEDs was not observed under low UV irradiation that is promising for OLEDs operation under day light.

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1. Introduction

The operational stability of organic light emitting diodes (OLEDs) is the key problem for their successful widespread application in displays, as well as for lighting and other practical purposes. Therefore, the investigation and enhancement of this characteristic is very important [1–3]. Nowadays, the following mechanisms of OLEDs degradation have been distinguished [1]: (1) dark-spot degradation, (2) catastrophic failure and (3) intrinsic degradation. The first one is associated with the formation of nonemissive regions primarily through the degradation at the device electrodes [4–7]. The second one is connected with the formation of defects in the organic layers which facilitate the origination of short circuits [8,9]. Finally, the third one is related to the decrease of OLEDs brightness without any obvious change in the device's appearance [10].

The first two mechanisms are called “extrinsic” degradation of OLEDs. The considerable advancement has been achieved in its elimination [1,4]. For example, it is the improvement of the device

packaging as well as the enhancement of purity and mechanical properties of the materials [11]. At the same time the mechanism of “intrinsic” degradation is not clear yet [1,12,13]. The most important models proposed to explain the intrinsic degradation of OLEDs [1] are (1) morphological instability model, (2) unstable cationic tris(8-hydroxyquinoline)aluminum (Alq₃) model, (3) indium migration model, (4) mobile ionic impurities model, and (5) immobile positive charge accumulation model. Among various mechanisms, underlying these models, put forward the most widely accepted one offers chemical degradation of the emissive materials [1]. During OLEDs operation the molecules can be destroyed into the radical fragments which take part in further reactions leading to other products. The last one may act as nonradiative recombination centers, luminescence quenchers, and deep charge traps.

Numerous investigations of OLEDs using Alq₃ as EL layer have shown that their “intrinsic” degradation mainly caused by the unbalanced hole or electron injection. That in turn results in the formation of cationic and anionic Alq₃ species. They are unstable, react with each other and act as quenchers. The charge density determines the rate of degradation (whether they are holes or electrons) [14,15]. The degradation can be also induced by heating of OLEDs in operation. It has been shown that the optical failure of OLEDs based on Alq₃ (emissive layer and electron transport layer

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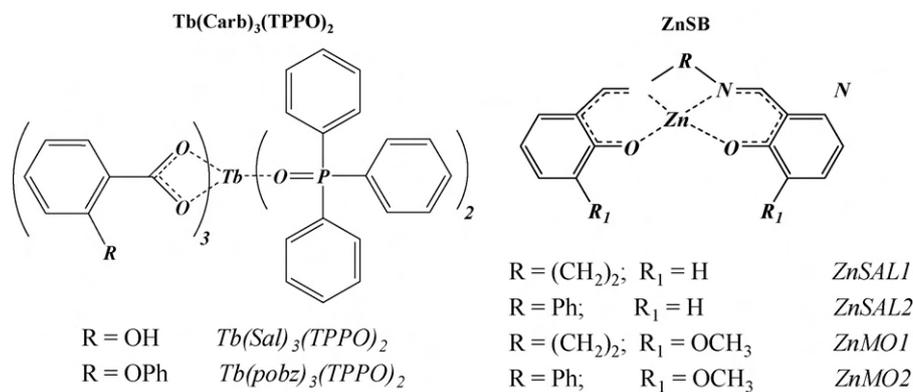


Fig. 1. Chemical structures of emissive materials.

(ETL) and TPD (*N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine, as hole transport layer (HTL)) is strictly related to the glass transition temperature (T_g) of TPD [16]. While the electrical one has been reached only at temperatures higher than T_g . The thermal stress has been generated by the voltages resulted in the optical failure of OLEDs. This stress is a reason of the considerable increase of hole traps at the HTL/ETL interface. The traps can act as non-radiative recombination centers [13] leading to the reduction of EL. Thus, thermal stress results the optical failure via formation of nonradiative zones that are still electrically active.

The similar investigations have been also done for the OLEDs utilizing carbazole derivatives [17]. From one side, it has been established that the key step of operational degradation is homolytic cleavage of weaker bonds in the excited state followed by the radical addition reactions to yield stabilized π radicals. For example, in case of CBP (4,4'-bis(*N*-carbazolyl)biphenyl; carbazole-derived host) it is an exocyclic C–N bond. OLED operation leads to the accumulation of the neutral radical species and their reduced or oxidized forms acting as nonradiative recombination centers and luminescence quenchers. On the other side it has been shown that OLEDs using mCBP (4,4'-bis(3-methylcarbazol-9-yl)-2,2'-biphenyl) as the host material [18] exhibit the luminance loss and increase of the voltage versus time and current density. These effects have been observed due to exciton–polaron annihilation reactions and it has been explained by the model of defect sites acting as deep charge traps, nonradiative recombination centers and luminescence quenchers.

In spite of considerable research progress in the field of “intrinsic” OLEDs degradation the complete picture of the processes is still missing [1]. Up till now the operational stability of OLEDs is not sufficient for practical applications. Thus, the interest to the scientific research of their stability and degradation mechanisms retains.

The possible applications of the terbium complex $\text{Tb}(\text{Sal})_3(\text{TPPO})_2$ (HSal = salicylic acid; TPPO = triphenylphosphine oxide) and zinc complexes with Schiff bases ZnSB ($\text{H}_2\text{SB} = \text{H}_2\text{SAL1}, \text{H}_2\text{SAL2}$ (derivatives of salicylic aldehyde); $\text{H}_2\text{MO1}, \text{H}_2\text{MO2}$ (derivatives of *o*-vanillin)) as EL materials were shown in our previous works [19–24]. Herein we investigate the degradation mechanisms of OLEDs based on $\text{Tb}(\text{Sal})_3(\text{TPPO})_2$ and ZnSB as well as new OLED structures based on $\text{Tb}(\text{pobz})_3(\text{TPPO})_2$ (Hpobz = 2-phenoxybenzoic acid).

2. Experimental details

2.1. Materials

The mixture of poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) in water (PEDOT:PSS, 2.8 wt.%, Bayer AG); poly(*N*-vinyl carbazole) (PVK, Aldrich) and 4,4'-bis[*N*-(1-naphthyl)-

Table 1

The structures of OLEDs.

No.	OLED structures
I	ITO/PEDOT:PSS/PVK/Tb(Sal) ₃ (TPPO) ₂ /CaAl/Ag
II	ITO/PEDOT:PSS/PVK/Tb(pobz) ₃ (TPPO) ₂ /CaAl/Ag
III	ITO/ α -NPD/ZnSal1/CaAl
IV	ITO/ α -NPD/ZnSal2/CaAl
V	ITO/ α -NPD/ZnMO1/CaAl
VI	ITO/ α -NPD/ZnMO2/CaAl

N-phenyl-amino]biphenyl (α -NPD, Aldrich) were used as hole transport layer (HTL) while 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, Aldrich) as electron transport layer (ETL). The emissive layers of $\text{Tb}(\text{Carb})_3(\text{TPPO})_2$ (HCarb = HSAL, Hpobz) and ZnSB ($\text{H}_2\text{SB} = \text{H}_2\text{SAL1}, \text{H}_2\text{SAL2}, \text{H}_2\text{MO1}, \text{H}_2\text{MO2}$) were synthesized and characterized as described in [20,24,25] (Fig. 1).

2.2. OLEDs fabrication

Thin films of PEDOT:PSS with thickness ~ 30 nm for OLEDs with the structures I and II (Table 1) were obtained by spin-coating from its commercial solution on ITO-coated glass (Merk). The polymer γ -glycidoxypropyltrimethoxysilan (Silquest A 187 Epoxysilan, from Witco) was added (concentration ~ 0.2 wt.%) to PEDOT:PSS in order to improve adhesion properties and film stability. Then the film was dried on a hotplate under an ambient atmosphere to crosslink the Epoxysilan at 110 °C for 20 min. Thin films of PVK (~ 25 nm) and $\text{Tb}(\text{Carb})_3(\text{TPPO})_2$ (~ 20 nm) were obtained by spin-coating from toluene and benzene solutions, respectively. The rotation speed varied in the range 2500–3000 rpm. Thin films of ZnSB (~ 60 nm), α -NPD (~ 40 nm) and BCP (~ 40 nm) (OLEDs with structures III–VI (Table 1)) as well as electrodes (CaAl, Ag) were thermally evaporated (Univex-300, Leybold-Heraeus) under a pressure below 3×10^{-5} mbar. The thickness of the deposited electrodes was ~ 100 nm that was controlled by the quartz indicator. The contacts were attached to the electrodes, and the device was sealed with epoxy resin. The emitting areas were 2 mm \times 3 mm.

For the investigation of photoluminescent (PL) and morphological properties the thin films of $\text{Tb}(\text{Carb})_3(\text{TPPO})_2$ and ZnSB were obtained on a quartz substrates by the same methods.

The EL spectra of OLEDs I and II (Fig. 2(a)) contain linelike Tb^{3+} transitions: 490 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_6$), 545 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$), 590 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_4$), 620 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_3$) (for more details, see [20]). The EL spectra of OLEDs based on ZnSB (Fig. 2(b)) exhibit broad emission bands corresponding the π – π^* transitions of ZnSB molecules.

2.3. Physical measurements

Transmission spectra of layers on quartz substrates were measured at $T = 293$ K using a mask with diameter 2.5 mm on

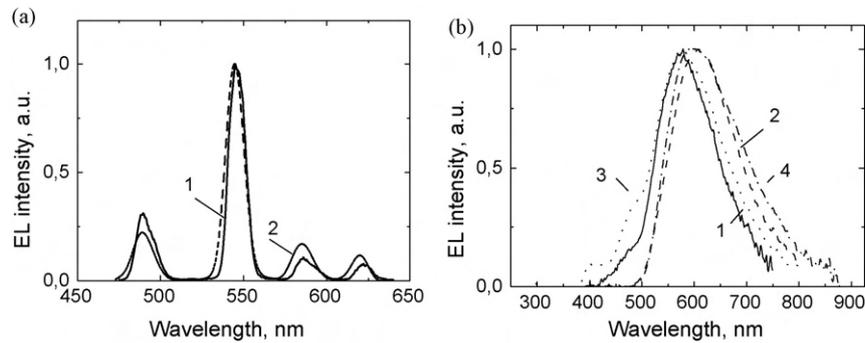


Fig. 2. (a) 1—EL spectrum of OLED II with and without hole-blocking BCP layer between emissive layer and CaAl cathode; 2—EL spectrum of OLED I (applied bias: 26 V; current density: 0.8 mA/cm²); (b) EL spectra of OLEDs based on ZnSB; 1—III (18 V, 5.6 mA/cm²); 2—IV (16 V, 450 mA/cm²); 3—V (16 V, 14.5 mA/cm²); 4—VI (16 V, 17.1 mA/cm²); $T=293$ K.

spectrometer “Specord M–40”. The jump of transmission near wavelength 333 nm was caused by lamp change.

Luminescence spectra were measured with the multichannel spectrometer S2000 (Ocean Optics). A nitrogen laser (wavelength 337 nm, pulse frequency 100 Hz, pulse duration 10 ns, average power ~ 1 mW) was used as an excitation source. The evolution of luminescence intensity versus time was measured using the grating monochromator, a photomultiplier connected with microvoltmeter and a plotter at wavelengths near the emission maxima. The samples were cooled inside a cryostat, pumped to a pressure $\sim 2 \times 10^{-2}$ mbar.

The voltage was applied to OLEDs using a stabilized power supply and a special form signals generator. The voltage was measured by a digital voltmeter, while the current—by amperemeter and the current sensing circuit of the digital voltmeter.

The thin film surfaces were investigated by atomic force microscopy (AFM) including the research complex NTEGRA, a scanner and a detecting head. The software NT-MDT was used for the image processing.

3. Results and discussion

3.1. EL degradation of OLEDs

The evolution of OLEDs (Table 1) EL intensity in time were detected and analyzed in order to investigate the degradation mechanisms. The experiments were carried out at 293 K. It should be noted that, in general the EL intensity decreases for all OLEDs and the character of decays differs considerably (Fig. 3(a)). The latter could be a result of different factors, the nature of these is out of the frames of this article. If one switches on the voltage after “time pause” the EL intensity sharply increases with following relaxation (Fig. 3(b) and (c)). The scheme of experiment is exemplified for OLED VI (Fig. 3(b)). The maximum value of EL intensity rise depends on the duration of “time pause” and exceeds the saturation when the latter is more than 5 min (Fig. 3(b)). In this case, two processes should be considered: (1) charge carrier trapping and (2) drift of ionic impurities [26–29]. The internal electric field arisen opposite to an external one reduces the electric

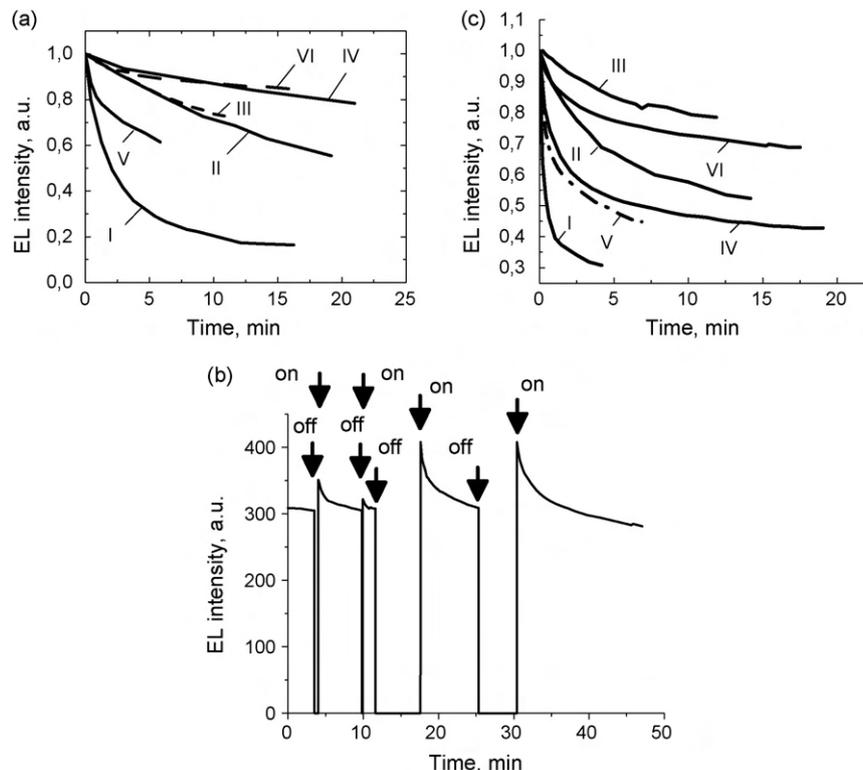


Fig. 3. (a) Initial EL intensity decays; (b) the EL intensity decays after switch off/on the voltage for OLED VI; (c) EL intensity relaxation after “time pause”; types of OLEDs are depicted in the figure; $T=293$ K.

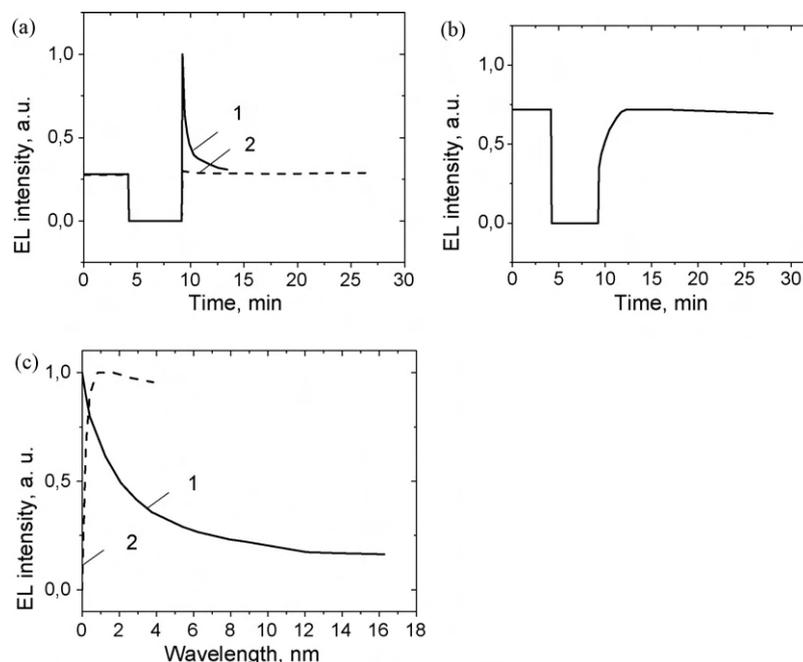


Fig. 4. OLED I: (a) EL intensity decay or growth after “time pause” at constant electric bias: 1— $T=293$ K, 2— $T=77$ K; (b) EL intensity growth after “time pause” at alternating electric bias: $T=293$ K, $f=100$ Hz; (c) initial EL intensity decay or growth at $T=293$ K: 1—constant electric bias, 2—alternating electric bias ($f=100$ Hz).

current flow and the EL intensity. The carrier release occurs during the “time pause” and results in the jump of EL intensity.

The same experiments were carried out at 77 K for OLED I (Fig. 4(a)). The initial EL intensity decay after switch on the voltage is similar to the one at 293 K (Fig. 3(a)). However, after “time pause” the sharp increase of EL intensity was not observed and a quasi-stationary value of the latter was achieved. It can be the result of insufficient thermal energy for the release of charge carriers from the traps during “time pause”. This confirms that the initial decrease of EL intensity is determined by the trap filling process.

For the better understanding the reasons of initial decrease and the nature of OLEDs degradation the EL intensity dependence on time was investigated for OLEDs under alternative voltage bias at 293 K (Fig. 4(b) and (c)). Van Slyke et al. have shown that OLEDs operation under alternative bias prevents the capture of charge carriers in organic layers [30]. Indeed, in OLED I under square shaped bias (0.1–100 Hz) another character of EL intensity variation was observed (Fig. 4(c)): an increase with the following slow decrease. Furthermore, the EL intensity after “time pause” gradually rises without any sharp jumps. This confirms the existence of charge carrier traps in the studied organic layers. The reasons of the slow character of initial- and after “time pause” increase of EL intensity are associated with heating of the samples upon electric current flow and frequency dependent processes. The last one should be investigated more carefully. An increase of the alternating symmetric sinusoidal electric stress frequency (up to 5 Hz) for OLEDs based on ZnSB results in significant decrease of EL intensity and remaining on this low level at higher frequencies (up to 50 Hz). Thus, the investigation of these OLEDs operating at alternating bias was not performed.

Further, in order to examine the degradation of OLEDs dealing with the processes of capture and release of charge carriers the behavior of OLEDs operating at constant electric bias under UV irradiation was executed (Fig. 5). After the initial decrease of the EL intensity (Fig. 3(a)) OLEDs were irradiated by short-term (1.5 min) unreduced UV light. First, this results in rise of EL intensity. But after switching off the light the decay to the quasi-stationary value

(Fig. 5(a)) occurs after stopping illumination. The sharp jump of EL intensity can be associated with the photorelease of charge carriers from traps. However, the release of charge carriers may be also caused by additional heating of the samples upon absorbing the UV light. Thus, the influence of heating on the EL intensity of operating OLEDs should be investigated. Therefore, the characteristics of OLEDs were investigated under heating from 293 K up to 320 K. If one heats the OLEDs after initial decrease of EL intensity up to quasi-stationary value, the latter rises (Fig. 6(a)). In some cases it increases up to the starting value observed when OLED was switched on for the first time. The observed phenomena are in agreement with the carriers capture and release processes. In this case the release of carriers from traps is caused by the temperature enhancement. Thus, the system comes back to the initial state with following decrease of the internal electric field opposite to the external one. Furthermore, if OLEDs are heated up to 320 K during the “time pause” the EL intensity jumps become considerably higher compared to OLEDs operating without heating (Fig. 3(b) and (c)). This indicates that the heating of switched off devices results in the release of trapped carriers.

During slight heating at 305 K of OLEDs II and VI the decays of EL intensity were not observed, and new quasi-stationary state was achieved. If the heating of OLEDs is switched off the following decrease of EL intensity up to the initial quasi-stationary value appears (Fig. 6(a), curve 1) due to the trap filling. Therefore, the process of thermal release of charge carriers from the traps during heating is reversible.

So, both shot-time UV irradiation and heating results in enhancement of EL intensity. As a consequence, it is possible to conclude that an increase of EL intensity under UV illumination originates not only due to the photorelease of charge carriers from traps but also because of the thermal release caused by heating of OLEDs by absorption of UV light.

For all OLEDs the long-term heating at 320 K results in the decrease of EL intensity (Fig. 6(a)) possibly caused by the irreversible sample degradation. Moreover, such heating of OLEDs leads in the decrease the magnitude of EL jumps noticed after “time pause” up to their disappearance. Thus, the irreversible

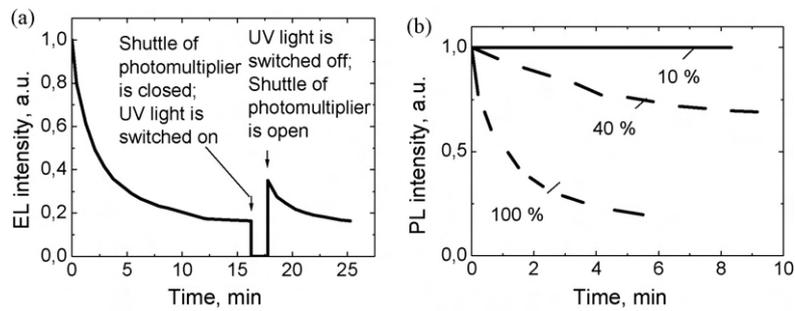


Fig. 5. (a) The influence of short-term UV nitrogen laser irradiation (~ 1.5 min) on the EL intensity of OLED I; (b) the change of PL intensity of $\text{Tb}(\text{Sal})_3(\text{TPPO})_2$ thin film at different power of irradiation (the percents correspond to the relative intensity of the laser light to the unreduced one); $T = 293$ K.

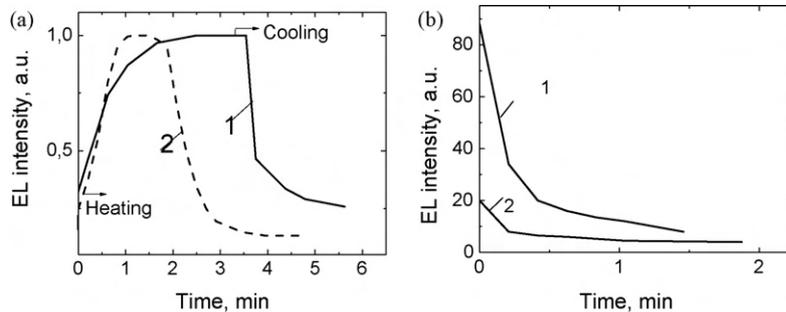


Fig. 6. (a) The influence of thermal heating on the EL intensity of OLEDS: 1—OLEDS II, IV at slight heating up to 305 K; 2—all other OLEDS heated up to 305 K and OLEDS I–VI heated to 320 K. In the latter case the heating was not switched off (initial temperature of OLEDS was 293 K); (b) the EL intensity jumps of the OLED I after “time pause”: 1—before heating; 2—after heating the operating OLED for 6 min at 320 K. The curves indicate the relationship of the absolute as well as relative jumps amplitude to the quasi-stationary value of EL intensity.

thermodegradation has a strong influence on the processes of capture and release the charge carriers from traps.

From the other hand, if unreduced UV laser irradiation is applied to OLEDS for long time, the EL intensity decreases down to the value lower than the one before illumination. After that if one switch off and then applies again the UV irradiation the magnitude of the EL intensity jumps diminishes and finally disappears. This demonstrates the presence of irreversible photodegradation processes. To clarify if the irreversible changes occurred in OLEDS under heating and UV irradiation are connected with the degradation of the emissive layer materials, the PL decays of the latters were investigated under the similar conditions.

3.2. PL degradation of emissive materials

It was established that the rate of PL intensity decrease depends on the intensity of UV irradiation (Fig. 5 (b)). At 10 times reduced UV intensity no changes of PL intensity were observed. The similar behavior was observed for all other emissive materials studied

in this work. This is promising for OLEDS operation under day light.

The comparison of Figs. 6(a) and 7(a) shows that PL intensity decreases contrary to the increase of EL intensity under heating. The reason of such dependences for thin films of emissive materials can be associated with thermal quenching. So, the processes taking place in OLEDS at heating cannot be simply transferred to ones occurred in the materials of their emissive layers under photoexcitation. It should be noted that each heating cycle results in lowering of quasi-stationary value of PL intensity. Thus, the irreversible degradation occurs in studied materials even under 10 times reduced laser light. To demonstrate the irreversible processes taking place in thin films they were irradiated by unreduced laser light during heating. It was shown that PL intensity at room temperature under the thermal treatment up to 690 K decreases (Fig. 7(b)).

Summarizing the results it is possible to conclude that the irreversible degradation develops for OLEDS under long-term unreduced UV irradiation or heating and for thin films of emissive materials under: (1) heating at 320 K and 10 times reduced UV

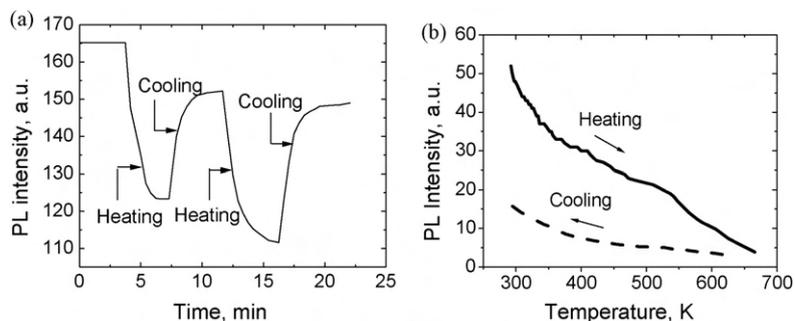


Fig. 7. (a) The PL intensity of ZnSAL2 thin film heated from 293 K to 320 K (PL was excited by 10 times reduced intensity of the nitrogen laser; $\lambda_{\text{ex}} = 337$ nm); (b) the thermal quenching of the PL intensity for ZnSAL2 thin films (PL was excited by unreduced nitrogen laser light): 1—heating; 2—subsequent cooling.

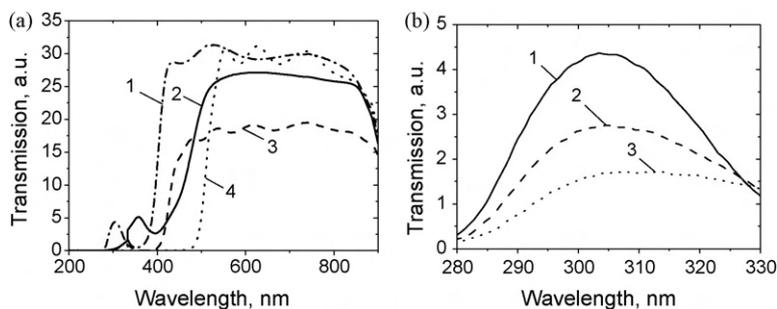


Fig. 8. (a) Transmission spectra of untreated layers: 1—ZnSAL1; 2—ZnSAL2; 3—ZnMO1; 4—ZnMO2; (b) short-wave region of ZnSAL1 transmission spectra: 1—initial, heated in darkness or irradiated by 10 times reduced nitrogen laser light without or with heating; irradiated by unreduced nitrogen laser light; 2—without or 3—with heating (duration of all treatments was 30 min; $T = 320$ K).

irradiation; (2) strong heating and unreduced UV irradiation; (3) unreduced UV irradiation. It can be detected by (1) decreasing the magnitude of EL intensity increment caused by UV illumination, after long-term UV irradiation; (2) reduction the values of EL intensity jumps after “time pause” and heating at 320 K.

To elucidate is the irreversible degradation under UV irradiation connected with the development of photobleaching process, the transmission spectra of ZnSB thin films after different treatments were measured (the irradiation by unreduced and 10 times reduced laser light under or without heating at 320 K). Transmission spectra of untreated layers are shown in Fig. 8(a). The transmittance for ZnSAL1 layers near the excitation wavelength (337 nm) is the same for untreated layers and for layers heated for 30 min in darkness or irradiated by 10 times reduced nitrogen laser with or without heating (Fig. 8(b)). The similar dependences of transmittance under various treatment conditions were observed for ZnSAL2 and ZnMO1. Thin films of ZnMO2 possess low transmission in the mentioned spectral region. As a consequence, the role of photobleaching processes is difficult to establish in this case. It should be mentioned that for ZnSAL1 and ZnMO1 the treatment of the layers was carried out subsequently. Only in the case of ZnSAL2 the experiments were performed in different points of the film and it was observed that dependences were the same as for ZnSAL1. Thus, photobleaching process plays negligible role in irreversible PL degradation of thin films noticed in heating experiments (Fig. 7(a)).

However, irradiation by unreduced nitrogen laser light for 30 min decreases transmission (Fig. 8(b)). The same relative reduction of transmission was observed when going from curve 1 for untreated sample to curve 2 and from curve 2 to curve 3. Therefore, the role of heating in the increase of absorption at high intensity of UV irradiation seems to be insignificant. It was shown that only 10 times reduced UV light (Fig. 5(b)) or heating in darkness have no influence on PL intensity of thin films. Summarizing the obtained results one could conclude that only mutual influence of reduced UV light and heating lead to lowering of the quasi-stationary value

of PL intensity and thus to irreversible degradation of thin films (Fig. 7(a)).

An enhancement of thin films absorption under unreduced UV irradiation should lead to increase of its PL intensity. But the experimental results show a contrary behavior (Fig. 5(b)). Hence, the chemical transformation occurs. The similar discussion could be considered as valid for explaining the decrease of quasi-stationary value OLEDs EL intensity under unreduced UV light.

The chemical transformations can be explained by the low thermal stability of the emissive materials [31–33]. Here, we could trace back to Fig. 7(b) where the decrease of PL was observed under heating the thin films up to high temperatures (~ 670 K). However, the thermal stability of the complexes used as emissive materials shows that $\text{Tb}(\text{Carb})_3(\text{TPPO})_2$ and ZnSB have no weight loss up to 450 K [20–24,34]. This means that the main role in the degradation under the heating up to the high temperatures plays the irradiation by unreduced UV light. Probably, processes of EL light reabsorption could be the reason of irreversible OLED degradation. However, the comparison of the EL spectra of OLEDs (Fig. 2) with transmission spectra of films (Fig. 8(a)) reveals that the spectral region of OLEDs emission does not practically overlap the spectral region of films absorption.

Thus, it was shown that emissive materials used in this work are thermally stable and the degradation processes of OLEDs is not related to the heating or the light reabsorption. Thus, because the same EL intensity changes were observed upon heating for OLEDs of different emissive and hole-transporting layers the nature of materials and their interaction in interfaces have no special role in these processes. Probably, the degradation processes taking place in the interfacial regions during OLEDs operation changes the current flow conditions.

It is well known that the morphological properties of thin films have an influence on OLEDs characteristics. The preparation of smoother films can not only reduce the current densities but also eliminate the interfacial traps. Thus, the investigation of thin

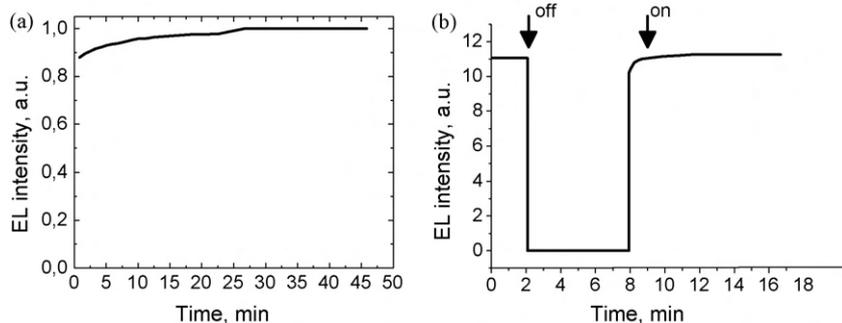


Fig. 9. OLED IV made in modified preparation conditions (for more details, see the text): (a) the initial change of the EL intensity, (b) the relaxation of the EL intensity after “time pause” (the arrows indicate the voltage off/on); $T = 293$ K.

films morphology was performed depending on the deposition rate and substrate temperature. The thin films of ZnSB with roughness ~ 10 – 15 nm were obtained at $T \geq 400$ K and deposition rate 15 \AA/s . The most smooth (rms ~ 5 nm) and homogeneous thin films were deposited at lower temperature (~ 300 K) and deposition rate (1 \AA/s). These conditions were further used for thin films deposition in OLEDs. It was shown that in fresh OLEDs IV an improvement of properties was established, namely the initial EL intensity decay and jumps after “time pause” disappeared (Fig. 9(a) and (b)). This means that the degradation processes described above are absent in this new devices. Unfortunately, after 2 weeks these OLEDs aged and the initial EL intensity decays and jumps after “time pause” changed to the forms shown in Fig. 3.

For further understanding the mechanisms of irreversible degradation of OLEDs the influence of water and oxygen should be considered. These experiments are under way.

4. Conclusions

The investigation of OLEDs (Table 1) operation and characteristics under different conditions let us to prove the existence of reversible and irreversible degradation. The first one is associated with the initial increase of the EL intensity due to the charge carriers trapping process. The charge carrier release with the following recovery of the EL intensity can be achieved by (1) switching off the voltage, (2) short UV light exposure, (3) heating of the OLEDs or (4) switching to the alternating voltage. The last one can also enhance the life-time of OLEDs. However, if one decreases the temperature of OLEDs from 293 K to 77 K the charge carrier release is not occur during switching off the voltage. The irreversible degradation occurs at the prolonged heating as well as under the intense UV nitrogen laser irradiation and during ageing at ambient conditions. On the other hand, the irradiation of OLEDs by nitrogen laser with 10 times reduced intensity does not lead to the noticeable degradation of EL intensity. The same EL intensity changes originated by heating from 293 K to 320 K were clearly observed for OLEDs with different structure (Table 1). In addition, $\text{Tb}(\text{Carb})_3(\text{TPPO})_2$ and ZnSB are thermally stable up to 450 K. Thus, the degradation in this temperature range (293–320 K) is more related to the changes in the current flow conditions due to the development of degradation processes in the interface regions than with chemical transitions in the emissive layers. Using the literature data one may suppose that variations of electron injection barrier height occur due to the diffusion of cathode material molecules into emissive layer. However, the formation of hot spots which undergo thermal runaway and eventually short electrically should not be ruled out.

The working characteristics of OLEDs depend on the morphological properties of emissive layers. For example, the decrease of evaporation velocity and temperature of the substrate lead to evening-out the surface of ZnSB thin films. Thus, the initial decrease of EL intensity as well as the jumps of the EL intensity after “time pauses” disappears. However, these new OLEDs are not sufficiently brighter than previous one and ageing leads to the decrease of their performances.

The luminance of the studied OLEDs achieved the value (was reached) $\sim 50 \text{ cd m}^{-2}$. This characteristic can be improved if one stops the evolution of the degradation processes.

Herein, we found the way to avoid the irreversible degradation under UV irradiation by means of lowering the UV intensity that is

promising for stabilization of OLEDs performances at the day light operation.

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