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BRIEF COMMUNICATIONS

LUMINESCENCE OF THIN FILMS BASED ON BENZOATE DERIVATIVES OF TERBIUM(III)

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Thin films (~100 nm) of complexes of terbium(III) with 2-benzoylbenzoic, 2-(4-chlorobenzoyl)benzoic, and 3,4-diethoxybenzoic acids were obtained. By means of the data from electron and optical microscopy it was found that the complexes crystallize during formation a film. In order to improve the surface quality of the films, the complexes were doped into a poly-(N-vinylcarbazole) polymer matrix in ratios between 1:1 and 10:1. On the basis of the dependence of the integral luminescence intensity of the films on the mass ratio of the components it is supposed that the polymer takes part in luminescence excitation of the complexes.

Keywords: *complexes, luminescence, lanthanide, thin film, organic light emitting diode.*

Complexes of lanthanides are of considerable interest as prospective electroluminophores [1] in that they have a series of advantages in comparison with other similar compounds: narrow luminescence bands, high quantum yield of electroluminescence, and the possibility of changing their physical characteristics (conductivity, solubility, thermal stability) without loss of luminescence quality [2]. A significant number of papers have been devoted to the use of terbium(III) and europium(III) complexes with derivatives of β-ketones [3–7]. However, not much attention has been paid to the study of lanthanide compounds with derivatives of benzoic acid in spite of their good prospects for use as electroluminophores [7]. Only a few papers have been devoted to study of compounds and materials based on them as electroluminophores (e.g., see [8–10]) in spite of the fact that such investigations could make it possible to predict the effectiveness of electroluminescence before the construction of actual devices.

The aim of the present work was to study the photoluminescence of thin-film materials based on complexes of terbium(III) with 2-benzoylbenzoic (HBBz), 2-(4-chlorobenzoyl)benzoic (H4Cl-BBz), and 3,4-diethoxybenzoic (H3,4DEBz) acids.

Thin films of both the individual complexes and those doped into poly(N-vinylcarbazole) (PNVC) were prepared by spin coating. A solution in chloroform (or a mixture of the substance in the case of the PNVC:complex systems) was deposited on a glass substrate by means of a microdispenser, and rotation was then started. The solutions for deposition were prepared by dissolving a weighed amount of the substance in the volume of solvent required to obtain the required concentration. The mixed PNVC:complex solutions were obtained by mixing solutions of the individual compounds. The procedure for cleaning the substrates included washing successively in three different media (soap solution, deionized water, and isopropanol) with ultrasonic treatment.

The microstructure of the films was studied by means of a Bruker Hyperion 2000 IR microscope, which was used as a normal optical microscope with reflected and transmitted light. Pictures with high magnification were obtained on a JSM 7500F scanning electron microscope. The thicknesses of the films were monitored by means of a LOMO-4M MII microinterference microscope. The excitation and emission spectra of the thin films were recorded on a Lumex Fluorate-02-Panorama spectrofluorimeter at room temperature with the Lagushka attachment for solid samples.

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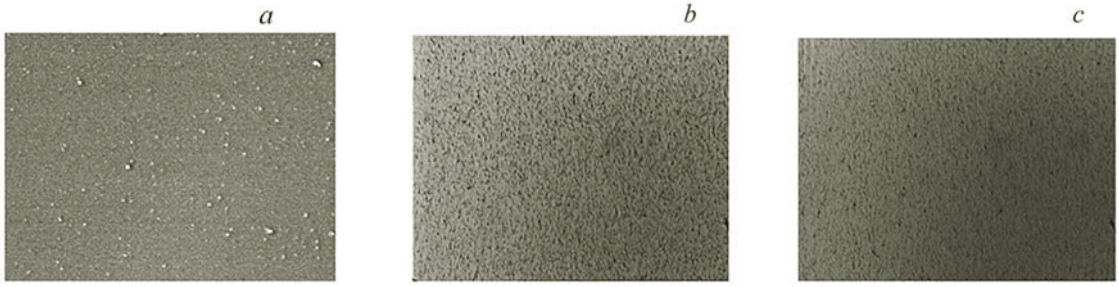

Fig. 1. Photomicrographs of the surface of $Tb(BBz)_3$ (a), $Tb(3,4DEBz)_3$ (b), and $Tb(4Cl\text{-}BBz)_3$ (c) films.

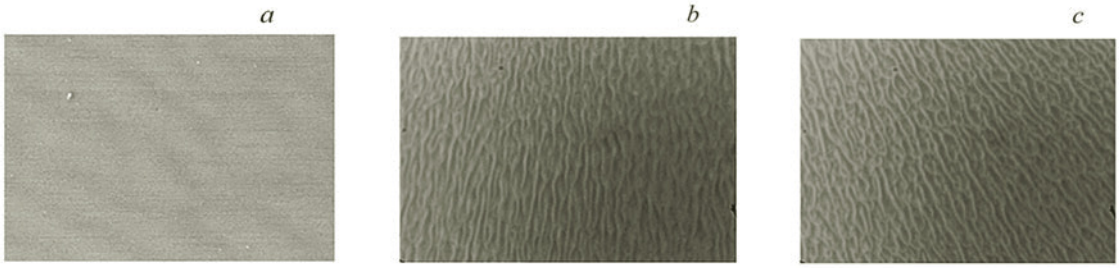

Fig. 2. Photomicrographs of the surface of PNVC:$Tb(BBz)_3$ (a), PNVC:$Tb(3,4DEBz)_3$ (b), PNVC:$Tb(4Cl\text{-}BBz)_3$ (c) films.

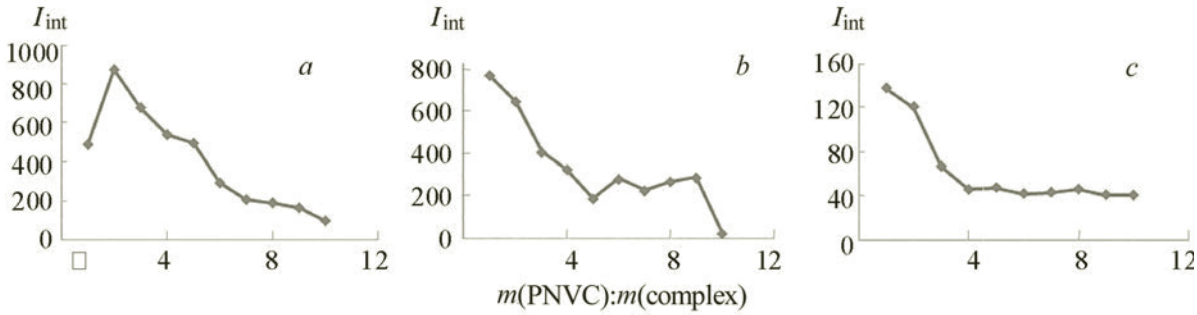

Fig. 3. Dependence of the integral photoluminescence intensity of the terbium(III) complexes on the mass ratios PNVC:$Tb(BBz)_3$ (a), PNVC:$Tb(3,4DEBz)_3$ (b), and PNVC:$Tb(4Cl\text{-}BBz)_3$ (c).

As seen from the photomicrographs of the surface of the obtained thin films of terbium(III) complexes (Fig. 1), active crystallization of the complex occurs during formation of the film, and this leads in turn to the formation of multiple defects. This property of the films does not meet the conditions for their use in organic light-emitting diodes (OLED) since the presence of such defects will lead to electric breakdown, and the device will stop working. Moreover, the presence of a large number of crystalline inclusions makes it difficult to control the thickness of the films by the interference method.

In order to improve the quality of the films the terbium(III) complexes were doped into PNVC. The choice of this polymer was based on its widespread use as a hole-type conducting material in organic OLEDs. Figure 2 shows photomicrographs of the surface of mixed PNVC:complex films. It is seen that the amount of small point defects is significantly reduced. Greatly extended irregularities, evidently formed at the last stage of film formation as a result of flow of the greatly thickened solution, are observed. However, such defects do not have a significant effect on the operation of the OLED since they have a significantly larger surface area. In order to establish the optimum ratio of polymer and complex in the mixture and also to determine the nature of participation of the polymer in the photoluminescence of the mixed film a series of samples (film thickness ~90 nm) with PNVC:complex mass ratios from 1:1 to 10:1 were obtained, and their photoluminescence spectra were recorded. These spectra were used to obtain the dependence of the integral luminescence intensity of the complex in the film on the mass ratio of the components (Fig. 3).

For the series of samples based on $Tb(BBz)_3$ a maximum is observed at a ratio of 2:1. Maxima are not observed in the case of the samples based on $Tb(3,4DEBz)_3$ and $Tb(4Cl\text{-}BBz)_3$, but the integral intensity does decrease with decrease of the content of the complex in the film. It can be concluded from these relationships that the polymeric matrix is only involved the photoluminescence process in the case of $Tb(BBz)_3$.

It can thus be stated that of the three investigated terbium(III) complexes (2-benzoylbenzoate, 2-(4-chlorobenzoyl) benzoate, and 3,4-diethoxybenzoate) in the polymer the mixed PNVC:complex film is only involved in excitation of the luminescence of the complex in the case of terbium(III) 2-benzoylbenzoate. The film with a mass ratio of 2:1 can be recommended for use in organic light-emitting diodes.

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