THIN FILMS OF LUMINESCENT TERBIUM AROMATIC CARBOXYLATES FOR OLED APPLICATION

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Rare earth elements (REE) coordination compounds possess such unique luminescent properties as quasi-monochromatic luminescence, which makes them perspective materials for a wide range of applications. One of the main goals in use of such materials today is to obtain compounds with the high UV stability [1]. Among such materials substituted REE benzoate take a noticeable place since they also exhibit high photoluminescence quantum yield, which riches 100% in case of $Tb(bz)_3$ [2]. However the problem of their low solubility and volatility arise since they have a polymeric structure which makes coating their thin films almost impossible, which limits considerably their use in planar devices. Thus, it is necessary to create new methods of deposition of REE aromatic carboxilates thin films of high quality.

This work is devoted to the development of two new methods of aromatic terbium carboxilates $Tb(Carb)_3$ thin films deposition, where HCarb is benzoic acid (Hbz) and *o*-phenoxybenzoic acid (Hpobz). We offer two different methods of thin films deposition, both of which are based on the chemical reactions leading to the formation of $Tb(Carb)_3$ thin films. The first method of reactive chemical vapor deposition (RCVD) is based on the exchange reaction between volatile precursors: REE β-diketonate and aromatic carbonic acid.

$$Ln(dik)_3\uparrow + 3HCarb\uparrow \rightarrow \mathbf{Ln(Carb)_{3(film)}}\downarrow + 3Hdik\uparrow$$

Initially basics of this reaction were established on example of interaction between $Ln(dpm)_3$ (Ln = Tb, Lu) and *o*-substituted benzoic acids: Hbz (benzoic acid), HSal (salicylic acid), Habz (aminobenzoic acid), HPA (phenylantranilic acid), and Hpobz (*o*-phenoxybenzoic acid), which differs by chemical stability and volatility [3]. Afterwards experimental conditions for smooth, even and transparent thin films of $Tb(bz)_3$ and $Tb(pobz)_3$ with the thickness of 50-100 nm were found, which was necessary for organic light-emitting diod (OLED) fabrication. OLED based on $Tb(bz)_3$ with the structure glass/ITO/PEDOT:PSS/TPD/$Tb(bz)_3$/Ca:Al demonstrated electroluminescence caused by current flow through the $Tb(bz)_3$ film.

The second approach is based on the spin-coating of the thin film of soluble mixed-ligand complex (MLC) $Ln(Carb)_3(Q)_n$ (Q – triphenylphosphine oxide, TPPO; acetylacretone imine, Hacim) with its following thermal decomposition:

$$Ln(Carb)_3\downarrow + nQ \rightarrow Ln(Carb)_3(Q)_n$$

$$Ln(Carb)_3(Q)_{n(film)} \rightarrow \mathbf{Ln(Carb)_{3(film)}} + nQ\uparrow$$

Neutral ligand Q has to: 1) form MLC with $Tb(Carb)_3$, 2) remove easily from MLC at heating, and 3) be highly volatile. Because of the low film thickness (100-200 nm) it is difficult to examine their composition via convenient methods, so we used combination of spectroscopic methods: 1) IR and Raman spectroscopy, which demonstrates different C–H vibrations and also P–Ph vibration in case of TPPO; 2) excited state lifetime (Tb(III); $^5D_4$); 3) excitation spectra character. It was shown that TPPO removal at high temperature leads to the partial complex decomposition in the film, while complexes with Hacim can be easily obtained in thin film state and transferred to the $Tb(Carb)_3$. At the same time thermal treatment leads to the surface smoothen and film roughness reduces from 9 nm to 4 nm.

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