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# Red Emitting Phosphors Doped with Mn and Eu Ions for pc-WLEDs

Y.A. Nekrasova[1,*], V.A. Aseev[1,†], N.V. Nikonorov[1,‡], E.B. Kolobkova[1,§], O.A. Usov[2,**], A.V. Nashchekin[2]

[1] *St. Petersburg National Research University of Information Technologies, Mechanics and Optics, 49, Kronverkskiy pr., 197101 Saint-Petersburg, Russia*
[2] *Ioffe Physical-Technical Institute of the RAS, 26, Politekhnicheskaya Sr., 194021 Saint-Petersburg, Russia*

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A new red emitting phosphors based on oxyfluoride glass and glassceramics doped with europium and manganese ions were synthesized and their optical properties and structure were studied. The transparent ceramic matrices for phosphors were selected because they overcome traditional powder phosphors due to high chemical and thermal stability and low temperature sensitivity. The fluoride based red emitting phosphors combined with green one and blue emitting chip used to fabricate phosphor converted white LEDs with warm color temperature and improved color rendering indexes.

**Keywords:** Red Phosphor, White LED, Fluoride Glassceramics, Color Rendering Index, Color Temperature.

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## 1. INTRODUCTION

One of the problem of modern solid state white lighting technology is the development of an effective inorganic single or multiple phosphors for down conversion of blue or UV light-emitting diode (LED) light into photons of other (green, red) visible spectral range with intensity ratio between components to produce by mixing white light with specific chromaticity parameters: correlated color temperature (CCT), color rendering index (CRI), luminous flux and efficacy [1, 2]. In this work, a new type of red phosphors representing a oxyfluoride glass and glassceramics doped with rare-earth ($Eu^{3+}$) or transition metal ($Mn^{2+}$) ions, was synthesized using technology developed by authors earlier [3]. The fluoride glass were used as the host materials due to their features, such as high chemical and thermal stability, high optical transparency, and high solubility for optically active dopants and low temperature sensitivity [1, 4]. These red phosphors with combination of green-yellow phosphors and blue InGaN chip were used to fabricate the pc-WLEDs.

## 2. TECHNOLOGY AND EXPERIMENTS

In the present work samples of glass and glassceramics based on oxifluoride matrix were synthesized. $MnF_2$ and $EuF_3$ compound was added as activator in various concentrations (1–20 mol%) and (0.5-3 mol%), respectively. The crystalline phase of the lead fluoride is segregated in these systems upon heat treatment at 1050°C for 30 min in a capped corundum crucible. To obtain colorless high transparent glasses with high transmission in the visible range it is important to use materials of special purity grade (purity >99.9 %), to prevent the escape of fluoride compounds and decrease crystallite size to the nanoscale range about 15 – 40 nm using additional heat treatment at 405°C during 2 hours.

The photoluminescence and excitation spectra of the samples were recorded by means of monochromator (Model Acton-300, Acton Research Corp.) and PMT-detector (Model Hamamatsu R928) and spectrofluorimetr LS 50B Perkin Elmer. The phosphor-converted white LEDs (pc-WLEDs) based on the green YAG:$Ce^{3+}$ phosphors, were prepared and measured in the flat remote phosphor-on-top arrangement [5].

Luminescence properties of original and thermal treated samples with various concentrations of ions were investigated in visible range (400–800 nm) with a step of 0.5 nm. Various industrial LEDs and pulsed laser LS-2131M Lotis TII attachment with radiation-transducer HG-T were used to excite the samples. The laser wavelength was 355 nm. The values of the color temperature from the obtained spectra were determined. To fabricate the white LED, we used standard LED based on YAG:$Ce^{3+}$ phosphors.

## 3. RESULT AND DISCUSSION

The experiments showed that glass and glassceramics doped with $Eu^{3+}$ and $Mn^{2+}$ ions have intensity bands of luminescence in red range of spectrum excitation by UV radiation at 355 nm and blue light at 465 nm: radiation of trivalent europium at 618 ($^5D_0 \rightarrow {}^7F_2$) and 701 nm ($^5D_0 \rightarrow {}^7F_4$), luminescence band of manganese with maximum at 620 nm ($^4T_1 \rightarrow {}^6A_1$).

Increasing of concentration of manganese ions results to shift of luminescence band maximum at more length wavelength range.

The emission spectra of the fabricated pc-WLEDs are shown in Fig. 1. The spectrum of each pc-WLED consists of two bands: a sharp band with peak at 452 nm due to the emission from InGaN diode, and a broad

* Nekrasova@oi.ifmo.ru
† Aseev@oi.ifmo.ru
‡ Nikonorov@oi.ifmo.ru
§ Kolobok106@rambler.ru
** Oleg.Usov@mail.ioffe.ru

 

bands due to the emission from the green (YAG:$Ce^{3+}$) and red europium and manganese doped phosphors, respectively.

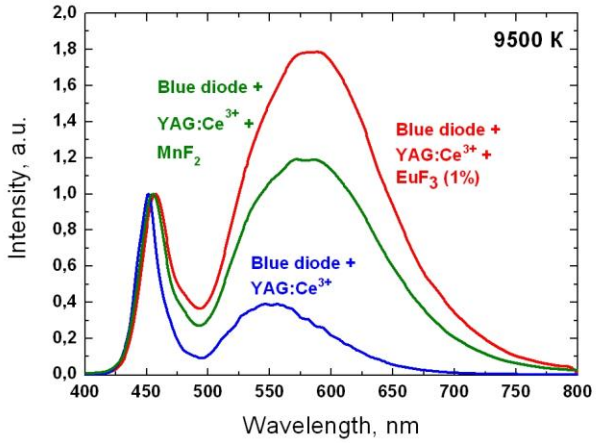


**Fig. 1** – Spectral power distributions of fabricated pc-WLEDs with green-yellow and red phosphors doped with europium and manganese ions and YAG:$Ce^{3+}$.

The location of pc-WLEDs on the CIE 1931 chromaticity diagram are shown in Fig. 2. The chromaticity coordinates, CCT, CRI and spectral characteristics of the pc-WLEDs are listed in the Table 1.

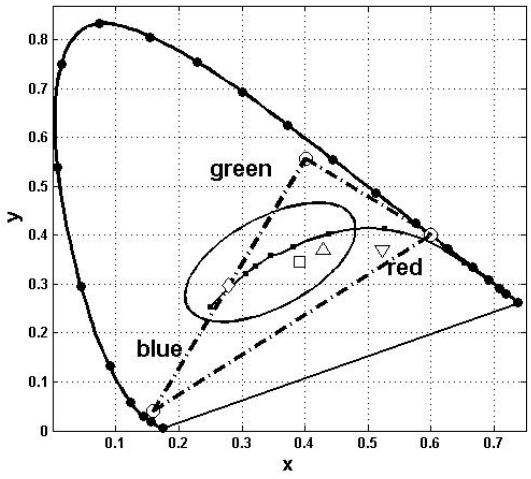


**Fig. 2** – The CIE 1931 chromaticity diagram with Planckian locus for CCT in the range from 1000 to 25000 K (filled circles) and the ellipsoid sketched out a white region. The location on diagram of the pc-WLEDs for YAG (di-amond), $EuF_3$ (1 mol%) (triangle up), $EuF_3$ (3 mol%) (triangle down), $MnF_2$ (2 mol%) (square) and the gamut (circles and dash-dot lines).

The gamut region: blue (0.163, 0.044), green (0.401, 0.556) (0.600, 0.400), and Planckian locus in the range from 1000 to 25000 are also displayed on the chromaticity diagram in Fig. 2. The external quantum efficiency (EQE) of the produced phosphors was calculated using their experimental photoluminescence emission and excitation spectra. The power performance efficiency of the phosphors was also calculated from luminescence spectra of the pc-WLED capped and uncapped with phosphors, respectively. These results showed that prepared red phosphors are promising materials for light emitting in the amber-red 600-620 nm range. Optimization composition and structure of the glass ceramic phosphors and fabrication of pc-WLEDs with improved chromaticity parameters are in progress now.

**Table 1** – Optical properties of the fabricated pc-WLEDs

| pc-WLED | CIE (x,y) | CCT(K) | CRI | $\lambda_{max}$ (nm) |
|---|---|---|---|---|
| Blue chip | 0.1633, 0.0436 | - | - | 452 |
| YAG: $Ce^{3+}$ | 0.2792, 0.2984 | 9540 | 65 | 553 |
| $EuF_3$ (1 mol%) | 0.4292, 0.3694 | 2830 | 75 | 599 |
| $MnF_2$ (2 mol%) | 0.3918, 0.3466 | 3450 | 81 | 598 |

## 4. CONCLUSIONS

The synthesized new type red emitting phosphors based on a fluoride glass and glassceramics doped with europium and manganese ions having a high chemical and thermal stability and low temperature sensitivity comparing with a traditional powder phosphors were shown to be an attractive materials for fabrication the phosphor-converted white LEDs with warm color temperatures and improved color rendering indexes.

According to the results of work, it was concluded that the best features on the sample activated by $Mn^{2+}$, it was the color temperature of 3450 K and value of color rendering index around 81.

Such sources can be used in light systems for streets and interior illumination and in liquid crystal displays and monitors.

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