Near-Infrared-to-Blue Up-conversion Luminescence in Transparent Eu$^{3+}$/Yb$^{3+}$ Doped Oxyfluoride Phosphors

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Abstract: In this paper transparent glass ceramics co-doped with Eu$^{3+}$ and Yb$^{3+}$ ions has been synthesized by melt quenching and subsequent heat treatment of the precursor glass. X-ray diffraction and transmission electron microscopy studies show precipitation of distorted PbF$_2$ crystallites in the glass ceramics. Excitation at 976 nm leads to the appearance of UCL (up-conversion luminescence) with the strong bands characteristic to Eu$^{3+}$ ions. Luminescence studies suggest that Eu$^{3+}$ emission appears as the result of cooperative excitation of Yb$^{3+}$ ions and subsequent energy transfer to europium ions. The presence of Er$^{3+}$ and Tm$^{3+}$ impurities, identified in the course of the experiment, leads to the white up-conversion emission of phosphors under the study.

Key words: Up-conversion luminescence, photoluminescence, rare-earth ions, phosphors.

1. Introduction

The development of modern high technologies, including nanotechnologies opens great prospects for the development of new nanostructured composite materials with the widest range of applications. In optics, one of such technologies is based on the spectral conversion of radiation, in particular, on the effect of the up-conversion luminescence in optical matrices. This effect, representing a kind of the anti-Stokes radiation, can be effectively used in the producing of materials for photovoltaic systems, short wavelength lasers, various optoelectronic devices, biophosphors, etc. [1-4].

RE (rare earth) doped materials are very attractive for various phosphors applications due to their emissions in a wide spectral range. The energies of the transitions are almost independent on the particular matrix where RE is positioned leading to the appearance of sharp emission lines in the spectrum, which is due to effective shielding of 4f-4f transitions by 5s$^2$, 5p$^6$ electrons.

Currently, much attention is paid to the search and investigation of materials that will increase the efficiency of the UCL processes. Oxyfluoride glass-ceramics activated with rare-earth elements, such as erbium, europium, thulium, praseodymium, ytterbium, etc., are among the most promising materials for phosphors. The matrices obtained on the basis of oxyfluoride glass-ceramics represent a good alternative to chalcogenide and halide materials, the synthesis of which is complex and expensive due to the need to prevent the interaction of it with the circumambient in the process of synthesis. In addition, the oxyfluoride matrices combine in itself the properties of both crystal and glass that allows: extruding them, creating of large size samples, pulling the fiber, as well as carrying of ion exchange processes to produce waveguide structures. Oxyfluoride matrixes are well known for their relatively low effective phonon energy (approximately 400 cm$^{-1}$ [5]) due to fluorides and the optimal size of ionic radius for doping RE phosphors that provides minimization of non-radiative losses and, as a result, more efficient UCL [6-8]. Besides, oxyfluoride
glasses are characterized by high chemical and mechanical stabilities related to oxides.

Among other RE elements europium is considered as one of the most perspective elements for phosphors applications due to its high quantum efficiency in the orange-red range of the spectrum and, as a result, it can be used as a red phosphor for television displays, fluorescing lamps, etc. [9]. However, the lack of any absorption bands in the NIR range makes it impossible to excite UCL in Eu3+ in the range, where powerful sources of radiation are present (~ 1 m). In this regard, the system requires the addition of an ion-donor, which should have effective absorption cross section in the near infrared range. In particular, Yb3+ ion has an absorption cross section $\sigma = 1.78 \times 10^{-21} \text{ cm}^2$ in NIR range. The only $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition of Yb3+ ion is in near resonance condition with the $f-f$ transitions of the others RE ions such as: Er3+, Eu3+, Tm3+, Ho3+ making it promising and effective candidate as a sensitizer donor [10].

2. Materials and Methods

2.1 Glass Synthesis and Characterization of Oxyfluoride Phosphors

The detailed technology utilized in the synthesis of samples is presented in Ref. [11]. Here we will briefly mention only some points: the initial glass samples were synthesized in the SiO2-PbO-PbF2-CdF2 system, activated with fixed Eu2O3 (1 mol%) and varying YbF3 (1.0, 1.5, 2.0, 3.0 mol%) concentrations. Synthesis of glass was held at a temperature of 900 ± 50 °C in 25 mL corundum crucibles in electric furnace in air atmosphere during 0.5 h. The glass was poured on a smooth metal surface, then annealed at a temperature of ~300 °C and slowly cooled down to room temperature. The secondary heat treatment of the initial glass at the temperature of 400 °C during 20-30 h results in $\beta$-PbF2 nanocrystalline phase formation which was initially identified by the XRD analysis (Fig. 1).

The XRD pattern of the precursor glass (black curve) exhibits broad humps characteristic of the amorphous structure. Glass ceramics pattern (red curve) is composed of a series of sharp peaks attributed to the cubic face centered lattice of PbF2 nanocrystalline phase precipitated in the glassy matrix. The positions of the peaks are slightly shifted to higher angles. This could be explained by the different ion sizes for eight-fold coordination of Pb2+, Eu3+ and Yb3+ ($r_{\text{Pb}^{2+}} = 129 \text{ pm}$, $r_{\text{Eu}^{3+}} = 107 \text{ pm}$, $r_{\text{Yb}^{3+}} = 99 \text{ pm}$) in PbF2 lattice [12], which in the case of RE incorporation into the crystalline lattice of $\beta$-PbF2 would lead to its contraction. Another explanation of the peak shift is the formation of (Pb,Cd)F2 solid solution rather than stoichiometric $\beta$-PbF2 compound. Indeed, $r_{\text{Cd}^{2+}} = 110 \text{ pm}$, which means that the incorporation of Cd2+ ions in the PbF2 crystalline lattice would also lead to its contraction and as the result it would induce the shift of the XRD peaks to higher angles. In the present work we did not analyze the chemical composition of the nanocrystallites in details, since the shift of the peaks is insignificant, therefore, further in the text the nanocrystals are treated as PbF2:Eu3+. The average crystallite sizes were found to be about 14 nm by using the Scherrer equation.

The microstructures of the samples were analyzed by a transmission and scanning electron microscopy (TEM, SEM, “FEI Tecnai”).

Fig. 1 XRD patterns of 1% Eu3+, 1.5% Yb3+ co-doped precursor and heat-treated SiO2-PbO-PbF2-CdF2 phosphor samples.
Fig. 2 presents TEM micrographs and their corresponding SAED (selected area electron diffraction) patterns of the heat-treated sample which reveal the formation of homogenously distributed PbF$_2$ spherical nanocrystals with relatively small variations in diameter. The detailed lattice structure of an individual PbF$_2$ nanocrystal in 1% Eu$^{3+}$, 1.5% Yb$^{3+}$ doped sample was presented by the HRTEM image in Fig. 2b. Fig. 2c shows that nanocrystals have a face-centered cubic lattice crystal, typical for β-PbF$_2$.

3. Results and Discussion

For the excitation of the UCL processes we used a continuously tunable between 690-990 nm wavelengths laser source (model EKSPLA PT257). The beam was focused into the sample by a 40× objective lens. The UCL spectra were analyzed with the monochromator-spectrograph MS-5004i coupled with CCD camera. The room temperature UCL emission of fixed Eu$^{3+}$ and different doping level Yb$^{3+}$ co-doped precursor samples have been recorded upon excitation at 976 nm corresponding to the maximum value of absorption coefficient of Yb$^{3+}$ ions (Fig. 3).

As it is seen from Fig. 3a the UCL intensity growth is almost proportional to the doping level of Yb$^{3+}$ ions. At the same time the spectra consist of UCL bands centered from 450 nm up to 700 nm. Such results seem incompatible with the possible transitions of Eu$^{3+}$ ions presented in the energy level diagram Fig. 3b. To understand and to clarify the origin of the all UCL bands in the obtained spectra we assume the presence of some impurities in the optical system, in particular of Er$^{3+}$ and Tm$^{3+}$ ions as the positions of the UCL bands in the range of 450-550 nm well fits the...
corresponding UCL spectra of those two RE elements [13-16]. In order to confirm this assumption we implemented two control experiments: direct photoluminescence studies of the same optical system, and comparison measurement of the UCL spectra of the precursor and glass-ceramics samples. The UCL control experiment results are shown in Fig. 4.

The UCL mechanism can be briefly described as follows: a pair of Yb$^{3+}$ ions, as an effective acceptor in the IR spectral range, absorbs two pump photons at 976 nm and are firstly excited to the $^2F_{5/2}$ state. Then one of them via cooperative energy transfer mechanism occupies the virtual energy state (V) located in the near-resonance condition with $^5D_1$ energy state of Eu$^{3+}$ ion. The next step is accompanied with the energy transfer from the excited Yb$^{3+}$ ions to the ground state Eu$^{3+}$ ions and promoting them to the $^5D_1$ or $^5D_0$ level. After the nonradiative relaxation from the $^5D_1$ state the process ends up by the radiative emissions of Eu$^{3+}$ ions from the $^5D_0$ state to the $^7F_j$ states. The obtained UCL spectrum is presented in Fig. 4. The UC emission bands centered around 578 nm, 593 nm, 612 nm, 650 nm and 699 nm correspond to the transitions assigned as $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, $^5D_0 \rightarrow ^7F_4$ transitions, respectively [17-19]. The weak and narrow yellow line with a maximum centered around 578 nm is forbidden by the both electric- and magnetic dipole selection rules of angular momentum which is of special interest. Its appearance can be explained by the effect of mixing of the angular momentum in crystal (J-mixing), described in more details in a number of works [20, 21].

The UCL spectrum of glass ceramics reveals the redistribution of the intensities of the bands at 592 and 613 nm. This feature of the two most intensive emission bands was observed and interpreted earlier by the other authors and deals with the hypersensitivity of the $^5D_0 \rightarrow ^7F_2$ transition to the local environment of Eu$^{3+}$ ions. The details can be found in Ref. [17].

Besides, we paid attention to the significant intensity increase of the bands in the green region of the spectrum. From the literature and our own previous studies we know that this can occur for the Er$^{3+}$ ions in the heat treated phosphors due to the inter-ion interaction processes described in Ref. [10].

For the blue band peaking at 476 nm and most probably attributed to Tm$^{3+}$ ions we did not record the intensity increase in the glass ceramics.

The room temperature photoluminescence emission of the precursor glass was measured under the laser excitation at the wavelengths of 463 and 522 nm. Fig. 5 presents the obtained spectra.
The mechanism of the photoluminescence can be explained as follows: $\text{Eu}^{3+}$ ion directly absorbs photons leading to population of higher energy states ($^5\text{D}_2$, $^5\text{D}_4$), and nonradiatively relaxes to metastable state $^5\text{D}_0$. Afterwards, radiative transitions to $^7\text{F}_J$ levels lead to the observed luminescence. The proposed involvement of $\text{Er}^{3+}$ ions in the up-conversion process is shown in Fig. 5, where 3 different excitation wavelengths are used. Excitation at 522 nm corresponds to direct excitation of $\text{Er}^{3+}$ ions ($^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$). After the excitation intense luminescence bands at 525 nm and 540-550 nm are observed. Similar luminescence bands in combination with the band at 650 nm are observed under excitation at 973 nm. The additional red luminescence band corresponds to $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition. Several cross relaxation processes (for example, $(^4\text{S}_{3/2}$, $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$, $^4\text{I}_{9/2}$) and $(^4\text{S}_{3/2}$, $^4\text{I}_{13/2} \rightarrow ^4\text{F}_{9/2}$, $^4\text{I}_{11/2}$)) might be responsible for the appearance of the red band. The fact that neither of the green bands appears under excitation at 463 nm (direct excitation of $\text{Eu}^{3+}$ ions) signifies that bands centered at 525 nm, 540 nm are related to $\text{Er}^{3+}$ ions. As to the band at 650 nm we suggest the superposition of contributions from both: $\text{Er}^{3+}$ and $\text{Eu}^{3+}$ ions. Thus, two control experiments confirmed our assumption on the presence of rare-earth elements impurities in the synthesized optical system.

4. Conclusions

Oxyfluoride glass and glass ceramics samples co-doped with $\text{Yb}^{3+}$ and $\text{Eu}^{3+}$ have been successfully synthesized. The heat treatment of the precursor glass promotes the crystallization of $\text{PbF}_2$-$\text{Yb}^{3+}$, $\text{Eu}^{3+}$ nanocrystallites. Excitation at 976 nm leads to the appearance of cooperative up-conversion luminescence of $\text{Eu}^{3+}$ ions. Analysis of photo- and up-conversion luminescence spectra reveals the presence of $\text{Er}^{3+}$ and $\text{Tm}^{3+}$ impurities in the phosphors leading to the emission in the blue-green region of the spectrum.

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References

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