Up-conversion Photoluminescence in a Fluorophosphate Glass Matrix Doped with Yb/Er – Effects of Doping Levels

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Abstract—In this work, two series of glasses of the $NaF–Al_2O_3–P_2O_5$ ternary system with the $Na_3Al_2(PO_4)_2F_3$ nominal composition, doped with Er^{3+} (1% and 0.5%) and Yb^{3+} ions, were synthesized by a standard melt-quenching method, and their up-conversion photoluminescence properties were studied. The as-received amorphous materials were excited by the IR laser radiation with a wavelength of 976 nm, and their emission spectra in the visible range were measured. The optical measurements were focused on the up-conversion photoluminescence spectra in the visible range. It was found that stronger up-conversion effects were observed for the series containing 1 wt% Er_2O_3. In the case of 0.5 wt% Er_2O_3, the emission response was weaker, comparable with the background noise.

In the quest for photoluminescent sources of white light resembling natural daylight, one does not necessarily be limited to down-conversion (DC) processes but can attempt to use the up-conversion (UC) ones as well.

Up-conversion processes are those photoluminescence (PL) phenomena in which absorption of two or more low-energy photons of the exciting light promotes the emission of a single photon of higher energy [1–3]. In most practical UC cases, the excitation radiation of the infrared range is converted into light in the visible or near-UV range [4]. The UC scheme is active in many solids containing ions of rare-earth elements (REE) and has already found applications in chemistry, medicine, biosensing, photovoltaics, photocatalysis, and other areas, including white-light sources (reviewed, e.g., in Ref. [5]). The basic mechanisms responsible for those processes have been identified and described in several excellent reviews and textbooks (e.g., in Ref. [6]). Generally, it has been established that a broad class of these processes in REE-containing solids occur via the energy-transfer up-conversion (ETU) mechanism [5]. The process requires the presence of two types of active centers: sensitizers and activators, both of which are REE ions. The sensitizers' ions are excited by the incident low-energy radiation. Then, the energy of the sensitizer's excited states is sequentially transferred to the excited states of an activator [4]. The final stage of up-conversion photoluminescence is the optical transition of the activator ion from its excited state to the ground state, resulting in the emission of a high-energy photon [4]. Besides the ETU, other mechanisms are also responsible for the up-conversion process (e.g., [7]).

The yield of the UC-driven conversion of the exciting IR radiation to the emitted visible (or near UV) light depends primarily on matching the energies of the excited states of the sensitizer and those of the activator, on their concentrations, but also on the REE-containing host. Among many tested sensitizer-activator couples, one has been found especially suitable for applications, namely Yb^{3+} as a sensitizer and Er^{3+} as an activator. It is also of some practical importance that the lowest excited states of Yb^{3+} and Er^{3+} can be attained using the 980 nm IR radiation emitted by common and inexpensive lasers and Xe lamps. The main advantages of using the dual Yb-Er doping are, in principle, the high absorbance of 980 nm radiation of Yb^{3+}, a reasonable rate of the energy transfer of the excited state from Yb^{3+} to Er^{3+}, and a ladder of equally conveniently spaced energy levels of Er^{3+} [8].

The majority of the studied Er^{3+}-Yb^{3+}- containing materials exhibiting UC photoluminescence have been based on crystalline hosts, e.g., $NaYF_4$ [9] or, more recently, on nanocrystalline matrices [10]. All these materials can be prepared by various synthetic routes (e.g., [10]). Unfortunately, some of these syntheses are complicated, time-consuming, and expensive. In addition, several fluoride crystalline matrices, such as $NaYF_4$, besides exhibiting high UC photoluminescence yields due to low-energy phonons mediating in non-radiative energy transfer between sensitizers and activator, often have poor mechanical properties and are sensitive to ambient conditions, e.g., humidity. As a consequence, the prospects for their application in practical devices can be limited. In some of those cases, glassy matrices may be a good solution. Moreover, amorphous hosts can, in principle, be easily thermally nanocrystallized (e.g., [11]), providing an alternative synthetic route to nanostructural UC matrices. In recent years, some studies have been conducted on UC PL in fluorophosphate glasses doped with Er3+-Yb3+ photoluminescent centers (e.g., [12–13]).

In this work, we chose a glass of the $NaF–Al_2O_3–P_2O_5$ system with the nominal composition $Na_3Al_2(PO_4)_2F_3$ as a

UC host material. The composition of this glassy matrix is identical with that of a crystalline phase, whose structure, local order, and some physical properties, including photoluminescence, have already been studied [12, 14]. It should be noted that our group also studied the above-mentioned glasses, but doped with Eu. The resulting materials exhibited strong down-conversion photoluminescence, whose emission spectra could be effectively tuned by the synthesis conditions [11, 15].

Eleven glassy samples of the $NaF–Al_2O_3–P_2O_5$ system with nominal composition $Na_3Al_2(PO_4)_2F_3$ and doped with varying amounts of Er_2O_3 (0.5 or 1 wt. %) and Yb_2O_3 (1 – 9 wt.%), were synthesized using a melt-quenching technique. The concentrations of Er_2O_3 and Yb_2O_3 were selected to keep similar Yb_2O_3/Er_2O_3 ratios in each series. The materials were prepared using the following scheme. Firstly, pre-dried Al_2O_3 (POCh, p.a.) and $NH_4H_2PO_4$ (POCh, 99,5%) were finely ground and mixed in a mortar. Then the mixed powders were preheated in air at 240°C for 4 hours to remove the excess volatiles. Afterwards, the required amounts of NaF (Sigma-Aldrich, ACS reagent, ≥ 99%), Er_2O_3 (Alfa Aesar, 99.9 %), and Yb_2O_3 (Alfa Aesar, 99.99 %) were added to the mixture. The final mixture was heated to 1200 °C and allowed to melt. The melt was kept at this temperature for 15 min. Then it was quickly poured onto a stainless-steel plate held at room temperature and immediately pressed with a second identical plate. The estimated cooling rate during this stage was around 1000 K/s. This process yielded thin, transparent, visually homogeneous glassy plates, whose amorphousness was confirmed by X-ray diffraction.

The measurements of the emission spectra resulting from the up-conversion process were carried out using a setup consisting of a Nd: YAG pulse laser source, Continuum Surelite II (10 ns pulse-width at 10 Hz), followed by an optical parametric oscillator (OPO) allowing for tuning of the emission wavelength, a 2500i double set monochromator, PMT, and SR-400 photon counting system. The up-conversion emission spectra were observed after excitation at 976 nm.

The emission spectra were measured using a PTI setup, consisting of a steady state xenon lamp, a set of double set monochromators both at the input and output legs, as well as Hitachi PMTs for both UV/VIS and NIR spectral ranges. Wherever necessary, a set of bandpass filters was used to isolate the desired signal from other emission wavelengths, such as those originating from the order of deflection of the Bragg grating. The measurements were carried out at a single power setting. All optical measurements were carried out at room temperature on as-received materials with naturally smooth surfaces, so no polishing was required. With a material thickness of 0.7–0.9 mm, this factor only slightly affected peak visibility in transmission studies and didn't alter the overall conclusions.

Unlike crystalline materials that produce sharp Bragg peaks in XRD patterns, characteristic for the long-range order, amorphous solids, including glasses, are characterized by broad halos, typical for amorphous solids. Diffraction patterns of all studied samples contained only wide halos without any Bragg reflections. This proves the amorphous nature of the synthesized materials.

Erbium (Er^{3+}) ions, when introduced into various host materials, exhibit several absorption bands spanning the range from the infrared to visible. The specific absorption wavelengths can depend slightly on the host material, the concentration of ions, and other factors.

Optical transmission spectra of the materials under study, for the series with 1% wt. % Er_2O_3 are presented in Fig. .

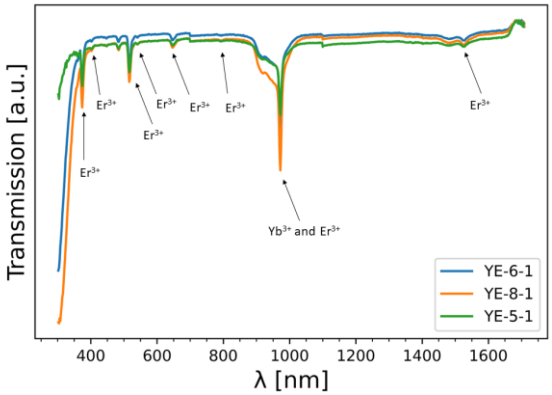

Fig. 1. Optical transmission spectra for samples containing 1 wt. % of Er_2O_3 and 5, 6 and 8 wt. % of Yb_2O_3, collected in the 350–1700 nm range. The characteristic features of these spectra are marked by arrows. The transitions are listed in the text.

The absorption maxima (corresponding to the observed transmission minima) were identified as due to the following electronic transitions of Er^{3+} centers [16]: ${}^4I_{15/2} \rightarrow {}^4G_{11/2}$(380-390 nm), ${}^4I_{15/2} \rightarrow {}^4G_{11/2}$ (400-410 nm), ${}^4I_{15/2} \rightarrow {}^2H_{9/2}$, (ca. 520 nm), ${}^4I_{15/2} \rightarrow {}^2H_{11/2}$ (550 nm), ${}^4I_{15/2} \rightarrow {}^4S_{3/2}$ (ca. 650-660 nm), ${}^4I_{15/2} \rightarrow {}^4F_{9/2}$ (ca. 800 nm), ${}^4I_{15/2} \rightarrow {}^4I_{9/2}$. The absorption near 980 nm is due to the ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition. The band near 1530 nm, corresponds to the ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+}. Ytterbium ions have a broad and strong absorption band in the near-infrared region around 900-1000 nm, which corresponds to the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition [17]. From the optical spectra shown in Fig. 1, one can see that the absorption lines, and especially that at 980 nm, related to the photoluminescence process, are relatively strong.

To investigate the UC photoluminescence spectra of the as-synthesized materials, the samples were excited with an IR laser at 976 nm. Samples of the series with 0.5 wt. % of Er_2O_3 dopant emitted faint green light. Unfortunately, their spectra, especially beyond 600 nm, were too weak and noisy for rigorous, reliable analysis. On the other hand, the

emission intensities of the samples of the series with 1 wt. % of Er_2O_3 were substantially stronger in the 500-560 nm range, but still weak beyond 600 nm. The spectra of the samples of the latter series are shown in Fig. 2.

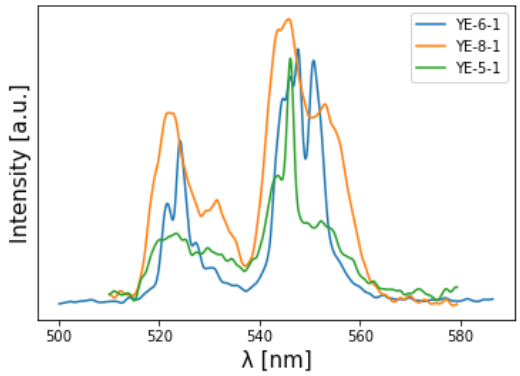

Fig. 2. Photoluminescence spectra of a series of glassy samples doped with 1 wt. % Er_2O_3, and 5, 6 and 8 wt. % of Yb_2O_3. Series labels YE-n-1, where n=6,8,5 denote samples with *n* wt. % of Yb_2O_3 and 1 wt. % of Er_2O_3. Excitation IR radiation wavelength was λ=976 nm.

In Fig. 2, one can distinguish two broad bands, centered at ca. 520 nm and 550 nm, respectively. The positions of these PL bands correspond to the following transitions from the excited states of Er^{3+} to its ground state: the band 520 nm corresponds to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition, while 550 nm emission is due to the transition $^4S_{3/2} \rightarrow {}^4I_{15/2}$ [3]. One can see that the peak intensities increase with the Yb/Er ratio. In the case of the series with 0.5 wt. % Er_2O_3, the PL spectra presented similar behavior, but the intensities were lower and noisy, therefore they are not shown here.

The above transitions are preceded by the following major steps (e.g., [14]):

a) Initial Absorption: The 976 nm excitation light is primarily absorbed by the Yb^{3+} ions (much higher absorbance of individual Yb^{3+} vs. Er^{3+} ions and a larger amount of Yb), leading to the transition of Yb^{3+} ions from their ground state $^2F_{7/2}$ to the excited state $^2F_{5/2}$.

b) Energy Transfer: Once the Yb^{3+} ions are excited, they can transfer their energy in a non-radiative way to nearby Er^{3+} ions. This process effectively and sequentially "pumps" the Er^{3+} ions to their consecutive higher energy levels.

The final up-conversion emission of Er^{3+} ions depends on several factors, including the content of Er^{3+} and Yb^{3+} ions, their relative distances, and the properties of the matrix, e.g., its phonon energy. It should be noted that in the case of our samples, the contents of Er_2O_3 were relatively low: 0.5 wt% and 1% wt. Moreover, the fluorophosphate glassy matrices, especially those containing higher amounts of phosphates, are characterized by phonon energies much higher than the best UC materials like $NaYF_4$. Comparing the relatively strong absorption band near 980 nm seen in Fig. 1 and moderate intensities of the photoluminescence spectra in Figure 2, one can postulate that the high phonon energy of the matrix used is mainly responsible for the final suppression of the UC PL efficiency.

In UC PL studies of fluorophosphate glasses doped with Yb/Er carried out by Kolobkova *et al.* [13], the PL signals were stronger than ours. However, in their case, the content of fluoride components, promoting low phonon energies, was much higher than in our glasses.

In conclusion, it was demonstrated that the Yb/Er-doped fluorophosphate glasses under study exhibit up-conversion photoluminescence in the visible range when excited by IR radiation. The relatively weak intensities of PL light originate from two factors: a low doping level insufficient to produce stable and measurable photoluminescence in the whole visible range, and high phonon energies of the fluorophosphate glassy matrix used, suppressing the energy-transfer processes between ions of sensitizers (Yb^{3+}) and activators (Er^{3+}). The optical transmission measurements carried out on the series with 1 wt. % Er_2O_3. Working conclusions from the study indicate that to get stronger UC PL spectra in the visible range, one should replace the fluorophosphate glassy matrix with one with considerably lower phonon energies and provide higher Yb/Er doping levels.

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