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## MECHANISMS OF UPCONVERSION LUMINESCENCE IN GLASS-CERAMICS CONTAINING Er:PbF<sub>2</sub> NANOCRYSTALS<sup>\*\*</sup>

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Transparent oxyfluoride germanosilicate glass-ceramics containing  $Er:PbF_2$  nanocrystals is synthesized on the basis of SiO<sub>2</sub>–GeO<sub>2</sub>–PbO–PbF<sub>2</sub> initial glass doped with  $Er_2O_3$ . The glass-ceramics is characterized by yellow-green luminescence, the intensity of which is ~12-times higher than that for the initial glass. The redistribution of the intensity between green and red emission bands after the glass heat-treatment is explained using data of the lifetime measurements for six excited states of  $Er^{3+}$  ions from  ${}^{4}I_{11/2}$  to  ${}^{2}H_{11/2}$ . A substantial increase of the lifetime of the  ${}^{4}F_{9/2}$  state (from 0.6 to 71 µs) is detected for the glass-ceramics as compared to the initial glass. UV up-conversion luminescence is observed for the glass-ceramics. The mechanisms of the up-conversion for 11 emission lines in the UV, blue, red, and deep-red spectral regions are discussed.

Keywords: oxyfluoride glass, glass-ceramics, erbium ion, upconversion, luminescence decay.

## МЕХАНИЗМЫ UP-КОНВЕРСИОННОЙ ЛЮМИНЕСЦЕНЦИИ В СТЕКЛОКЕРАМИКЕ, СОДЕРЖАЩЕЙ НАНОКРИСТАЛЛЫ Er:РbF₂

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Прозрачные оксифторидные германатно-силикатные стеклокерамики, содержащие нанокристаллы  $PbF_2$ : Er, синтезированы на основе исходных стекол системы  $SiO_2$ -GeO<sub>2</sub>-PbO-PbF<sub>2</sub>, допированных  $Er_2O_3$ . Они характеризуются интенсивной желто-зеленой люминесценцией, которая усиливается в ~12 раз по отношению к исходному стеклу. Перераспределение интенсивности между полосами люминесценции в зеленой и красной областях спектра после термической обработки стекла

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интерпретировано на основе измерения времен жизни ионов  $Er^{3+}$  в возбужденных состояниях от  ${}^{4}I_{11/2}$  до  ${}^{2}H_{11/2}$ . Обнаружено существенное увеличение времени жизни для состояния  ${}^{4}F_{9/2}$ , от 0.6 мкс для исходного стекла до 71 мкс для стеклокерамики. Для стеклокерамики зарегистрирована  $V\Phi$  ирконверсионная люминесценция. Обсуждаются механизмы ир-конверсии для 11 переходов в  $V\Phi$ , синей, красной и ИК областях спектра.

**Ключевые слова:** оксифторидное стекло, стеклокерамика, ион эрбия, ир-конверсия, затухание люминесценции.

**Introduction.** Up-conversion is a process where absorption of several pump photons is followed by emission of one high-energy photon (with a shorter wavelength). In this way, near-IR-to-visible conversion is possible typically with the rare-earth ions. Trivalent erbium,  $\text{Er}^{3+}$ , is suitable for such conversion due to the special structure of energy levels allowing for population of higher-lying excited states via the excited-state absorption, cross-relaxation, and energy-transfer mechanisms. Intense green and red (centered at ~540 and 650 nm) up-conversion luminescence (UCL) from  $\text{Er}^{3+}$  ions was studied previously for a large variety of glasses, glass-ceramics, single-crystals and nano-powders following the pioneering work of F. Auzel et al. [1]. The potential applications of such Er-doped phosphors are in the field of solid-state lightning [2], biological labeling [3], or enhancing solar-cell efficiency [4]; Er up-conversion visible lasers were also reported [5].

An important point for the efficient up-conversion is the rate of non-radiative relaxation from the involved excited-states. This rate depends on the maximum phonon frequency of the host; so fluoride materials provide better up-conversion properties due to lower phonon frequencies,  $\sim$ 500–600 cm<sup>-1</sup> (as compared with their oxide counterparts). Oxyfluoride glass-ceramics (GC) is the compromise material with fluoride nanocrystals nearly uniformly distributed in the residual predominantly oxide glassy phase [6]. It allows for a combination of good spectroscopic properties of fluorides with chemical stability and good thermal and mechanical properties of oxide compounds [7]. GC can also be synthesized by a standard melt-quenching technique with subsequent heat treatment [8].

Transparent GC containing Er-doped fluoride nanocrystals like MF<sub>2</sub> (where M denotes Pb [9], Ca [10], Sr [11], Ba [12] etc.), LnF<sub>3</sub> [13, 14], or NaLnF<sub>4</sub> [15, 16] (where Ln can be La, Y, Lu, or Gd) were studied in recent years. Among MF<sub>2</sub> compounds, PbF<sub>2</sub> crystal is one of the most attractive. The structure and crystallization features and the optical absorption and up-conversion luminescence were studied for various GC containing Er:PbF<sub>2</sub> nanophase. A "standard" composition of the initial glass in this case is a two-component 50SiO<sub>2</sub>–50PbF<sub>2</sub> glass doped with ErF<sub>3</sub> [17]. A modification of this composition by introduction of CdF<sub>2</sub> was presented in [18, 19]. It resulted in crystallization of Pb<sub>x</sub>Cd<sub>1-x</sub>F<sub>2</sub> solid solution with a reduced unit-cell constant similar to that of ErF<sub>3</sub>, as well as in slightly modified position of energy levels providing stronger upconversion [20, 21]. Also, introduction of GeO<sub>2</sub> (which is favorable from the point of view of lower melting temperature) was considered [22–24].

An interesting feature of  $Er:PbF_2$ -containing GC is the redistribution of the intensity of green and red emission bands in the up-conversion spectrum for high Er content [25]. Complete understanding of this feature can be useful for controllable color tuning of the potential phosphors. In the present paper, we aimed to explain this phenomenon, involving a detailed study of the luminescence decay and comparing Er-doped initial glass in the modified system of SiO<sub>2</sub>–GeO<sub>2</sub>–PbO–PbF<sub>2</sub> and transparent GC with Er:PbF<sub>2</sub> nanocrystals. It is important that we obtain enhanced luminescent properties for GC when introducing Er in the form of oxide  $Er_2O_3$ , while previously it was typically doped as fluoride,  $ErF_3$  [9–19]. Also, we aimed to study shortwavelength up-conversion emissions (blue-violet), which results in a comprehensive analysis of the up-conversion mechanisms for 11 emission lines in the blue, green, red, and deep-red spectral ranges.

Glass synthesis and structural studies. The studied oxyfluoride glass with the composition of  $43SiO_2$ – 6GeO<sub>2</sub>–38PbO–13PbF<sub>2</sub> (in mol.%) was synthesized by a standard melt-quenching technique and doped with Er<sub>2</sub>O<sub>3</sub> (1.0 mol.%). The raw materials (99.9% purity) were weighed and homogenized in a 25 cm<sup>3</sup> corundum crucible. The synthesis was performed at ~950 ± 50°C in the electric furnace in air. The synthesis duration at maximum temperature was 0.5 h. The melt was then cast onto a steel surface and annealed at ~300°C for 2 h in a muffle furnace. Then the glass boule was cooled down to room temperature. It was transparent with a slight rose coloration and did not contain any signs of opalescence and air bubbles. X-ray diffraction (XRD) confirmed the amorphous nature of the as-cast glass. The glass density  $\rho$  was measured by a hydrostatic method,  $\rho = 6.05\pm0.01$  g/cm<sup>3</sup>, so the concentration of active ions  $N_{\rm Er} = 4.4 \times 10^{20}$  cm<sup>-3</sup>. The differential scanning calorimetry (DSC) curves for pure and Er-doped glasses are shown in Fig. 1a. Erbium doping of the glass results in the increase of glass transition temperature  $T_{\rm g}$ , from 354 to 386°C, and leads to the formation of exothermic peak centered at  $T_{\rm p} = 522$ °C. This peak is attributed to the crystallization of Er-containing cubic  $\beta$ -PbF<sub>2</sub> (space group *Fm3m*) phase, as determined from XRD analysis. These data indicate that  ${\rm Er}^{3+}$  ions assist the formation of crystallization nuclei for PbF<sub>2</sub> in the as-cast glass. The difference  $\Delta = T_{\rm p} - T_{\rm g}$ , which is called the glass thermal stability factor, equals 123°C. Such a large value indicates that the studied glass has a good potential for the synthesis of transparent GC containing Er:PbF<sub>2</sub> nanocrystals. For comparison, we also synthesized the "standard" two-component oxyfluoride glass in the system  $50SiO_2-50PbF_2$  doped with the same amount of Er. For this glass,  $\Delta = 56$ °C, confirming the beneficial properties of the proposed composition. Thermal expansion of the glass was measured with a horizontal dilatometer, Netzsch 402 PC,  $\alpha = (10.3 \pm 0.2) \times 10^{-6} \text{ K}^{-1}$ .

For the preparation of GC, the as-cast glass was heat-treated at 350°C (slightly below the  $T_g$  temperature) for 10–30 h. The glass-ceramics was transparent with a slight rose color. Its XRD pattern is shown in Fig. 1b, together with the peaks corresponding to a bulk  $\beta$ -PbF<sub>2</sub> crystal. In addition to a characteristic halo of the residual glassy phase, sharp diffraction peaks are observed corresponding to that of PbF<sub>2</sub> compound. The mean size of the nanocrystallites determined with the Scherrer equation is  $8.5\pm0.5$  nm. The shift of the peaks on the pattern to the larger diffraction angles 20 as compared with the bulk PbF<sub>2</sub> corresponds to the decrease of the unit cell parameter *a*. Indeed, for the synthesized nanocrystals, *a* = 5.810 Å (compare with 5.940 Å for a bulk crystal). This is in agreement with the difference of ionic radii of VIII-fold coordinated Pb<sup>2+</sup> (1.45 Å) and Er<sup>3+</sup> (1.14 Å). The tendency for the evolution of the unit cell parameter *a* with Er doping for ErF<sub>3</sub>–PbF<sub>2</sub> solid-solution was discussed in [26, 27]. Using these data, we estimated the concentration of ErF<sub>3</sub> in our case to be ~20 mol%, corresponding to local concentration of Er<sup>3+</sup> ions as high as ~39×10<sup>20</sup> at/cm<sup>3</sup>.



Fig. 1. Differential scanning calorimetry curves for the undoped and Er-doped oxyfluoride-germanosilicate glass (a); XRD pattern of GC heat treated at 350°C/30 h; vertical lines correspond to the peaks of the bulk  $\beta$ -PbF<sub>2</sub> crystal; the inset represents an HR-TEM image (b); intensity of the small-angle neutron scattering (SANS) vs the modulus of the scattering vector, Q, for the as-cast glass and GC; the inset represents a modeled shape of the nanocrystals (c).

The inset in Fig. 1b represents a high-resolution transmission electron microscope (HR-TEM) image for GC treated at 350°C/30 h. Based on the HR-TEM studies, we estimated the volume fraction of the Er:PbF<sub>2</sub> nanocrystalline phase as  $\sim$ 35±10% and the average diameter of the nanocrystals as 7±2 nm. The shape of Er:PbF<sub>2</sub> nanocrystals is close to a spherical one; they are near-uniformly distributed in the glass matrix. For a structural characterization of the GC, we also used small-angle neutron scattering (SANS), with an IBR-2 reactor as the source of the pulsed neutron flux and an YuMO spectrometer [28]. The scattering intensity vs modulus of the scattering vector Q for both the as-cast glass and GC treated for 30 h is plotted in Fig. 1c. The heat treatment induces a substantial change of the glass structure, which is clear from the scattering curves with a characteristic peak. To model the shape of the nanocrystals (inset in Fig. 1c), we used the ATSAS software [29]. The mean size of PbF<sub>2</sub> nanocrystals is around ~10 nm, which is consistent with XRD and HR-TEM data.

**Optical absorption.** Thin (2 mm) polished plates of the as-cast glass and GC were used for the spectroscopic studies. The refractive index of the glass,  $n = 1.61 \pm 0.01$ , was measured at 650 nm by the immersion method. The absorption spectrum was determined with a Varian Cary-5000 spectrophotometer in the range of 0.3–1.6 µm, and the spectral bandwidth (SBW) was 0.1 nm. The absorption spectrum of the as-cast glass and GC is shown in Fig. 2. The characteristic bands of  $\text{Er}^{3+}$  ions related to the transition from the groundstate  ${}^{4}I_{15/2}$  to the excited ones (denoted on the graph) are detected. The heat treatment leads to the structuring of the bands, related to the change of the local environment of  $\text{Er}^{3+}$  ions in the fluoride PbF<sub>2</sub> crystalline phase and increased Stark splitting. The glass-ceramics demonstrate low scattering losses. The position of the UV absorption edge is 346 ±5 nm ( $E_g = 3.58\pm0.05$  eV). It is only slightly shifted as compared with the as-cast glass, where  $\lambda_{\text{UV}} = 340$  nm as determined from Tauc plots. This indicates the good optical quality of the material.



Fig. 2. Absorption bands of Er<sup>3+</sup> ions in the GC treated for 30 h as compared with the as-cast glass; the background losses are subtracted.

The band around 1  $\mu$ m is related to the  ${}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2}$  transition and is used for the excitation of  $\text{Er}^{3+}$  ions with InGaAs laser diodes. For the as-cast glass, it is centered at ~973 nm with the corresponding peak absorption coefficient of 1.3 cm<sup>-1</sup>. The heat-treatment results in the enhancement of the peak absorption to 1.7 cm<sup>-1</sup> (at 972.2 nm); the full width at half maximum (FWHM) of this band is 14 nm. It is slightly larger than that of SiO<sub>2</sub>-PbF<sub>2</sub> glass-ceramics with the same treatment (synthesized for comparison), namely 12.5 nm, which is beneficial from the point of view of possible temperature drift of the diode wavelength.

**Up-conversion luminescence.** The UCL in the glass and GC was excited by a power-scalable InGaAs diode emitting at ~960 nm; the excitation beam was focused on a 200  $\mu$ m spot. The UCL spectrum was detected with a wide-aperture lens, lock-in amplifier, and MDR-23 monochromator (SBW = 0.5 nm) using a sensitive Hamamatsu C5460-01 photodetector. The spectral sensitivity of the set-up was determined using a halogen lamp with calibrated spectral power density. The monochomator itself was calibrated with a Pb and Xe lamps.

The UCL spectra of the Er-doped glass and glass-ceramics are shown in Fig. 3a,b. Both of them are normalized to unity for comparison (the heat treatment resulted in a 12-fold increase of the UCL intensity for GC as compared with the as-cast glass).

For the as-cast glass, the green emission dominates. The two closely located bands centered at 522 and 544 nm are related to the transitions from the  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  excited states to the  ${}^{4}I_{15/2}$  ground state. The weak red band contains two components at 653/667 nm; it is related to the transition  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ . The deepred bands at ~800 and 845 nm are related to the transitions  ${}^{4}I_{9/2} \rightarrow {}^{4}I_{15/2}$  and  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{13/2}$ , respectively. No emission at the wavelength shorter than 500 nm is detected, at least at an excitation power density of ~10<sup>4</sup> W/cm<sup>2</sup>. This determines the green color of the emission from the as-cast glass. The calculated Commission Internationale de l'éclairage (CIE 1931) color coordinates are x = 0.268 and y = 0.608; the dominant wavelength is 545 nm with 0.95 color purity.

The heat treatment results in a substantial change of the UCL spectrum (Fig. 3a), which is observed both in the band shape (as structuring due to a Stark splitting) and intensity redistribution. The most intense emission is red (the transition from  ${}^{4}F_{9/2}$  excited state), and this band is splitt with the local peaks at ~651/667 nm. The relative intensity of both green bands (centered at 522 nm and 540/548 nm for the transitions from  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  excited states) is decreased. Only a slight increase of the intensity of the deep-red band at 800/821 nm is detected, while the band corresponding to the longest wavelength is structured, 843/851 nm, but unchanged in intensity. As a result, the color of the emission is yellow-green. The CIE coordinates are x = 0.374 and y = 0.626; the dominant wavelength is 559 nm with 0.99 color purity.

For the GC sample, we observed also emissions in the blue to UV range (Fig. 3b). They are related to the radiative transitions from higher-lying excited states of  $\text{Er}^{3+}$  ions. In order to assist with the interpretation of the emission channels, we plot a part of the absorption spectrum (Abs) on the same figure. The UCL spectrum is again normalized to unity (which corresponds to 20× magnification with respect to the red emission).

The most intense purplish-blue emission band peaks at 408/412 nm. It is related to the transition from the  ${}^{2}H_{9/2}$  excited state to the  ${}^{4}I_{15/2}$  ground state. The transitions from the  ${}^{4}G_{11/2}$  (382 nm, violet),  ${}^{4}F_{3/2} + {}^{4}F_{5/2}$  (450+454 nm, purplish-blue), and  ${}^{4}F_{7/2}$  (487/492 nm, greenish blue) states to the ground state are also detected. All the above mentioned UCL bands perfectly match the position of the corresponding bands in the absorption spectrum. The transition  ${}^{4}G_{11/2} \rightarrow {}^{4}I_{15/2}$  is visible at 503 nm (green light). These emission channels do not disturb the color of the overall emission from the glass-ceramics due to their weakness.



Fig. 3. Up-conversion luminescence spectra for the GC treated at 350 °C/30 h and the as-cast glass (a,b); the absorption spectrum is shown to assist with the interpretation of the emission bands; (c,d) dependences of the UCL intensity on the excitation power for the GC heat treated at  $350^{\circ}$ C/30 h; points are the experimental data; lines are their fitting for the slope (*n*) calculation; the excitation wavelength is 960 nm.

To analyze the up-conversion mechanisms in the glass-ceramics, we studied the dependence of the integrated UCL intensity,  $I_{\text{UCL}}$ , on the excitation power *P*. These plots are shown in Fig. 3c,d in a log-log scale to reveal the number of pump photons involved (*n*), as  $I_{\text{UCL}} \sim P^n$  [30]. For intense red and green emission, n = 2.1-2.3, confirming a two-photon excitation mechanism. For the bands located lower than 500 nm, typical values of *n* are 2.5–2.9, which indicates that three pump photons are needed to excite these emissions (this also explains their relative weakness).

(this also explains their relative weakness). The scheme of energy levels of  $\text{Er}^{3+}$  ions showing the potential channels of their excitation and observed UCL lines is shown in Fig. 4. Ground-state absorption (GSA) corresponds to  ${}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2}$  transition. Several excited-state absorption (ESA) channels exist for  $\text{Er}^{3+}$  ions. The two main ESA channels are  ${}^{4}I_{13/2} \rightarrow {}^{4}F_{9/2}$  (after the non-radiative decay from an intermediate  ${}^{4}I_{11/2}$  state) and  ${}^{4}I_{11/2} \rightarrow {}^{4}F_{7/2}$ . They are responsible for the population of the excited-states related with the red and green UCL, respectively. ESA from the  ${}^{4}F_{9/2}$  and  ${}^{4}S_{3/2}$  states allows for population of higher-lying excited states. The important mechanism for the enhancement of the efficiency of excitation (as GSA is relatively weak) is the cross-relaxation (CR) process,  ${}^{4}F_{7/2} + {}^{4}I_{15/2} \rightarrow {}^{4}F_{9/2} + {}^{4}I_{13/2}$ . In addition, for high concentrations of  $\text{Er}^{3+}$  ions (as in the present study), energy-transfer up-conversion (ETU) for closely located adjacent ions is possible. Thus, the excitation of red (~650 nm) and green (520/540 nm) luminescence requires two pump photons, while observation of emission in the blue-violet range require at least three photons. This explains well the data from Fig. 3c,d.



Fig. 4. The scheme of the energy levels of  $\text{Er}^{3+}$  ions in the studied GC with the possible mechanisms of excitation (*a*), as well as observed emission channels for the UCL (*b*); GSA and ESA are the ground-and excited-state absorption, CR is cross-relaxation, ETU is energy-transfer up-conversion.

**Luminescence decay.** The UCL intensity depends on the lifetime of the excited state, from which the radiative transition occurs (for longer lifetimes the  $I_{\text{UCL}}$  is higher). For the green UCL, these are the states  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$ ; for the red UCL, this is  ${}^{4}F_{9/2}$ . Also,  $I_{\text{UCL}}$  depends on the lifetime of the intermediate state, from which the excitation steps (like ESA) occurs. If this lifetime is long enough, the probability of further excitation increases (with respect to luminescence to the ground state or non-radiative relaxation). However, the shortening of the lifetime of the intermediate state can also work as a switch of different emission channels. This occurs for the  ${}^{4}I_{11/2}$  state of Er<sup>3+</sup> ions. If its lifetime is long, the  ${}^{4}I_{11/2} \rightarrow {}^{4}F_{7/2}$  ESA process dominates, resulting in the strong green UCL. If it is short, fast non-radiative decay leads to the  ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$  relaxation and alternative  ${}^{4}I_{13/2} \rightarrow {}^{4}F_{9/2}$  ESA channel, leading to the strong red UCL. The change of the environment of the Er<sup>3+</sup> ions from the oxyfluoride (glassy) to pure fluoride (crystalline, PbF<sub>2</sub>) can disturb all the above-mentioned lifetimes.

Thus, we measured the lifetimes of the excited states from  ${}^{4}I_{11/2}$  to  ${}^{2}H_{11/2}$  that determine the UCL color, both for the as-cast glass and glass-ceramics. The luminescence was excited with the output of a ns-range optical parametric oscillator; the decay curves were detected with the MDR-12 monochromator (SBW = 1 nm), fast Hamamatsu C5460 and G5853 photodetectors, and 500 MHz Tektronix digital oscilloscope. The results are presented in Fig. 5. Each graph shows information on the exact excitation and registration wavelengths. The decay curves are plotted in a semi-log scale. In general, they deviate from the linear ones (the decay is not single-exponential, as observed previously for ~3 µm emission from nanocrystalline Er:PbF<sub>2</sub> [18]). The characteristic decay time was then simply calculated on the 1/*e* level.

For the as-cast glass, the lifetimes of  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  states (responsible for the green UCL) are 3.5 and 1.9 µs, respectively. These lifetimes are several times longer than for the  ${}^{4}F_{9/2}$  state (0.6 µs), which is responsible for the red emission. This explains the domination of the green UCL in the spectrum of the as-cast glass. From the other hand, the lifetime of the intermediate level,  ${}^{4}I_{11/2}$ , is not very short (42 µs), so the red emission observation is possible in principle (Fig. 3a).

After the heat treatment of the as-cast glass, the lifetime of the  ${}^{4}S_{3/2}$  state is increased only to 3.2 µs, which means a slight enhancement of the green emission. For the less intense transition from the  ${}^{2}H_{11/2}$  state,

the lifetime is nearly the same (3.6  $\mu$ s). In contrast, the lifetime of the  ${}^{4}F_{9/2}$  state is increased more than 100 times, to 71  $\mu$ s. This is the key point to understanding the redistribution of intensity from green to red bands in the UCL spectrum of the glass-ceramics (Fig. 3a). The lifetime for the intermediate state,  ${}^{4}I_{11/2}$ , is nearly 16 times longer (as compared with the as-cast glass). This prevents complete suppression of the green UCL for the glass-ceramics.



Fig. 5. Decay curves for the visible and IR luminescence of Er-doped as-cast glass and GC treated at 350 °C/30 h (under resonant excitation).

The deep-red emissions occur from  ${}^{4}S_{3/2}$  and  ${}^{4}I_{9/2}$  states. The lifetimes of these states are only slightly increased with the heat treatment (to 3.2 and 1.6 µs), so no profound intensity redistribution is observed. For the observation of the blue-violet UCL, it is important to have a relatively high population of the  ${}^{4}F_{9/2}$  state, being the initial one for the  ${}^{4}F_{9/2} \rightarrow {}^{2}H_{9/2}$  ESA process. This is exactly the case of the studied glass-ceramics, so that the transition from the  ${}^{2}H_{9/2}$  state (peaked at 412 nm) is particularly intense. However, for the as-cast glass, the population of the higher-lying excited states is absolutely not efficient.

To understand the reasons for the overall enhancement of  $I_{UCL}$  for the glass-ceramics (near 12-times as compared with the as-cast glass), one should consider all previous data. The first reason is the increase of the local concentration of  $Er^{3+}$  ions in the PbF<sub>2</sub> nanocrystals (as compared with the as-cast glass), leading to increased efficiency of the CR and ETU processes for the population of the excited-states. The second is the increased efficiency of GSA of pump radiation; see Fig. 2. The third is the substantial enhancement of the lifetimes of several excited states, in particular  ${}^{4}F_{9/2}$  and  ${}^{4}I_{11/2}$  ones. In addition, the lifetime of the lower excited-state,  ${}^{4}I_{13/2}$ , is relatively long (3.4 ms for GC), resulting in a high probability of ESA from this state and supporting the process of the "recirculation" of  $Er^{3+}$  ions over the higher-lying excited-states. The lifetime variations are attributed to the change of the local environment of the  $Er^{3+}$  ions with reduced highest phonon frequencies, and, hence, the rates of non-radiative relaxation.

**Conclusion.** Novel transparent oxyfluoride germanosilicate glass-ceramics containing Er:PbF<sub>2</sub> nanocrystals are synthesized on the basis of the SiO<sub>2</sub>–GeO<sub>2</sub>–PbO–PbF<sub>2</sub> initial glass doped with Er<sub>2</sub>O<sub>3</sub> by a secondary heat treatment. The addition of Er<sub>2</sub>O<sub>3</sub> stimulates the crystallization of the PbF<sub>2</sub> nanocrystals in the glass. The absorption spectrum of the as-cast glass and GC is studied in details. GC is characterized by an intense yellow-green emission (CIE coordinates, x = 0.374, y = 0.626; the dominant wavelength is 559 nm with 0.99 color purity), which is enhanced 12 times with respect to the as-cast glass. The redistribution of intensity between the green and red emissions with the heat treatment is explained from the point of view of the lifetime measurements. In particular, a substantial increase of the lifetime of the <sup>4</sup>*F*<sub>9/2</sub> state (from 0.6 to 71 µs) is detected for the ions entering a purely fluoride nanocrystalline phase, PbF<sub>2</sub>. The UCL in the blueviolet region is also detected. The mechanisms of the UCL for 11 lines in the UV, visible, and near-IR are carefully explained.

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