

UV luminescence and energy transfer during upconversion in wide-gap crystals doped with Pr^{3+} ions

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The study presents the results of investigating interconfigurational $d-f$ luminescence in the ultraviolet (UV) spectral region and energy transfer between rare-earth ions during upconversion in wide-gap compounds doped with Pr^{3+} ions. Compounds with different crystalline and electronic structures were examined, the Stokes $d-f$ - and $f-f$ -luminescence of which had been previously studied. UV upconversion luminescence of Pr^{3+} ions under excitation with a visible-range laser diode was observed in Pr^{3+} -doped crystals with the following structures: garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Lu}_3(\text{Al,Ga})_5\text{O}_{12}$ nanocrystals, quaternary $\text{Gd}_1\text{Y}_2\text{Al}_2\text{Ga}_3\text{O}_{12}$ ceramic); silicate-apatite ($\text{LiLa}_9(\text{SiO}_4)_6\text{O}_2$); orthosilicate (Y_2SiO_5 , Lu_2SiO_5); and lanthanum beryllate ($\text{La}_2\text{Be}_2\text{O}_5$). Furthermore, in gadolinium-containing matrices ($\text{Gd}_1\text{Y}_2\text{Al}_2\text{Ga}_3\text{O}_{12}$ ceramic and CsGd_2F_7) under two-photon laser excitation (450 or 488 nm), resonant energy transfer between excited states of rare-earth ions $4f^15d^1(\text{Pr}^{3+}) \rightarrow {}^6\text{P}_{7/2}(\text{Gd}^{3+})$ was observed, followed by UV emission at 314 nm ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ transition in Gd^{3+} . This resonant energy transfer $4f^15d^1(\text{Pr}^{3+}) \rightarrow {}^6\text{P}_{7/2}(\text{Gd}^{3+})$, interconfigurational $d-f$ -emission, and multiphonon relaxation of excited $4f^15d^1 \rightarrow {}^3\text{P}_J$ states to 3P_J states followed by Stokes $f-f$ -emission in the visible range are competing channels for electron relaxation the $4f^15d^1(\text{Pr}^{3+})$ excited-state band. A necessary condition for observing upconversion luminescence is that the energy position of the $4f^15d^1(\text{Pr}^{3+})$ excited-state band lies below the conduction band, fails to exceed twice the energy of the ${}^3\text{H}_4 \rightarrow {}^3\text{P}_J(\text{Pr}^{3+})$ transitions, and that the efficiencies of multiphonon $4f^15d^1 \rightarrow {}^3\text{P}_J$ -relaxation and energy transfer to crystal-lattice defects are low.

Keywords: Pr^{3+} ion, Gd^{3+} ion, upconversion, interconfigurational $d-f$ -luminescence, energy transfer, wide-gap crystals.

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1. Introduction

Up-conversion (anti-Stokes) luminescence (UCL) may be observed when absorption of two or more low-energy photons causes emission of a photon with higher energy [1,2]. Such conversion of absorbed energy may potentially be used in lighting technology, development of hidden marks, visualization of infrared laser emission, improvement of solar battery efficiency, optical thermometry etc. [3]. To record UCL, it is efficient to use impurity ions Er^{3+} since they have a developed structure of excited electron states and longer life time of excited state ${}^4\text{I}_{11/2}$. Electron transitions from various excited states form UCL mostly in the green or red spectral regions. Besides, using a pair of $\text{Er}^{3+}/\text{Yb}^{3+}$ ions enables improving UCL yield due to the mechanism of subsequent sensibilization, which presumes absorption of infrared emission with Yb^{3+} ion and subsequent transfer of energy between Yb^{3+} and Er^{3+} ions. The efficiency of energy transfer is significantly affected by defects of the crystalline lattice, which act as centers of non-radiative relaxation. Efficiency of energy transfer depends on certain factors related to both the material of the matrix (crystalline structure, defectiveness, size, surface effects) and the properties of impurity ions (qualitative and quan-

titative compositions of donor-acceptor pairs, cross section of absorption, quantum yield and kinetics of luminescence decay). Synthesis of various matrices, determination of optimal concentrations of alloying impurities, establishment of the role of crystalline structure defects are the main objectives for achievement of the maximum efficiency of energy transfer, improvement of UCL efficiency.

Most recent publications in the journals on optical and luminescent subjects are dedicated to the study of UCL in the visible spectral range, using infrared laser diodes, usually with wavelength of 850 or 980 nm, as a source of excitation. The main objective of these studies is to improve efficiency of up-conversion process, which is achieved by synthesis of new matrices or development of best conditions for improvement of the energy transfer efficiency between rare earth (RE) ions [4,5]. At the same time there are scarce papers on the analysis of the opportunity to observe up-conversion luminescence in the ultraviolet (UV) range (UV-UCL) with the radiation of the materials using visible range photons, and the issue is relevant.

Pr^{3+} ion is interesting due to the specific nature of the energy position of excited $4f^n$ -states and $4f^15d^1$ -zone of the mixed electron configuration. In wide-band dielectric materials doped with Pr^{3+} ions it is possible to

observe both bright Stokes $f-f$ -luminescence from ^3P_J -, $^1D_2$ -levels or cascade emission of photons from $^1S_0$ -level with quantum yield up to two, and quick ($\tau = 12-20$ ns) interconfiguration $d-f$ -luminescence in the UV-range. All these types of luminescence are determined both by relative location of $^1S_0$ -level and $4f^15d^1$ -zone of mixed electron configuration and also by the efficiency of energy transfer from the excited states of ions Pr^{3+} to centers of non-radiative relaxation [4]. Population of $4f^15d^1$ -zone of mixed electron configuration of various RE ions with two-photon laser excitation shows the possibility of up-conversion process [5]. However, the most promising here is using exactly Pr^{3+} ions [6–15]. Besides, using Pr^{3+} ions in the up-conversion process made it possible to demonstrate using UV-UCL for multiple applications, including prototypes of current solar cells, biovisualization, photodynamic therapy and especially microbial inactivation and bacteria inhibition [9–11].

This paper searches for and studies UV-UCL with laser excitation of crystals with different crystalline and electron structure alloyed with Pr^{3+} ions. The objects of the study are wide-band crystals and Gd-containing compounds, alloyed with Pr^{3+} ions, the Stokes luminescence of which was previously studied in detail by our research group. These materials are effective quick detectors and converters of various types of ionizing radiations.

2. Experimental details

Absorption spectra were recorded at room temperature using a Helios-Alpha spectrometer with μ Vision 32 software. Spectra of Stokes photoluminescence (PL) in the range of 260–900 nm and PL excitation (PLE) spectra in the range of 230–550 nm were measured using a HORIBA iXR320 FLUOROLOG spectrofluorimeter equipped with a cooled CCD camera as a detector and an 450 W ozone-free Xe-lamp as a source of light. The presented PLE spectra were adjusted to the equal number of exciting photons using a calibrated photodiode. The same spectrometer recorded up-conversion luminescence in UV range of (230–400 nm). Typical spectral resolution in UV-UCL measurement was 1–3 nm, when Stokes PL is measured of not more than 1 nm. The sources of excitation were laser diodes ($\lambda_{\text{exc}} = 405, 450, 490, 505$ nm, $W \sim 100-300$ mW) in a combination with a filter KV400 (transmission band above 400 nm). The laser emission power was controlled by a meter of average power and energy of laser emission IMO-2N. To exclude the influence of the scattered light, a filter UFS-1 was installed in front of the input slot of the recording monochromator (transmission band 220–400 nm). All UV-UCL spectra, apart from lanthanum beryllate, were measured at room temperature. For measurements at low temperatures, a closed cycle cryogenic system and a high-vacuum He-cryostat by „Trade Engineering“ (Russia) with a cryohead RDK-205D2 (Japan) controlled by a thermal regulator LakeShore 335 were used. Working oil-free

vacuum 10^{-4} Pa was maintained using a turbomolecular vacuum pump.

3. Experimental results and discussion

3.1. Interconfiguration $d-f$ (Pr^{3+}) UV-UCL

Lanthanum beryllate single crystals $\text{La}_2\text{Be}_2\text{O}_5:\text{Pr}^{3+}$ (1%) Substantial interest in lanthanum beryllate arose after the bright effect of stimulated emission in $\text{La}_2\text{Be}_2\text{O}_5:\text{Nd}^{3+}$ [16], and after using this crystal in solid-state dosimetry of ionizing emissions and as a quick inorganic scintillator [17]. Crystals grown by Czochralski method were studied. Data of optical and luminescent spectroscopy of $\text{La}_2\text{Be}_2\text{O}_5:\text{Pr}^{3+}$ were summed up in paper [18]. Bandgap width $E_g = 6.8$ eV. The state $^1S_0$ (Pr^{3+}) is located by 1.5 eV above the zone of $4f^15d^1$ -states. Therefore the hypothetical transition to the level $^1S_0$ is fully suppressed by much more intense interconfiguration transitions $4f^2 \rightarrow 4f^15d^1$.

Fig. 1 presents $\text{La}_2\text{Be}_2\text{O}_5:\text{Pr}^{3+}$ absorption spectra compared to a pure crystal, spectra of Stokes PL and UV-UCL, and also excitation spectra of Stokes PL. The absorption spectrum shows both $f-f$ - and interconfiguration $4f^2 \rightarrow 4f^15d^1$ -transitions in Pr^{3+} ions. The Urbach edge of fundamental absorption in a pure crystal is below 230 nm. The spectra of Stokes PL clearly show radiative $f-f$ -transitions and wide bands of $4f^15d^1 \rightarrow 4f^2$ -emission in Pr^{3+} . The excitation spectrum of Stokes PL shows that $f-f$ -PL is efficiently excited when both ^3P_J -states (region of 440–490 nm) and $4f^15d^1$ -states (region 230–270 nm) are populated. From Fig. 1 it follows that laser 450 nm excitation provides for transitions from levels $^3H_4$ of the main state to the term $^3P_2$ of excited state of Pr^{3+} ion. Further, there are two processes of two-photon population of $4f^15d^1$ -states, the mechanisms of which are analyzed, for example, in papers [7,10]. When the excited state is absorbed (the so called excited state absorption — ESA-mechanism), Pr^{3+} ion in ^3P_J state absorbs the other photon and is excited to zone of $4f^15d^1$ -states. Therefore, two serial excitation stages are observed on one Pr^{3+} ion: $^3H_4 \rightarrow ^3P_J \rightarrow 4f^15d^1$. When energy is transferred in the process of up-conversion (the energy transfer up-conversion — ETU-mechanism), two adjacent Pr^{3+} ions absorb exciting radiation and change to excited states ^3P_J . Then one of these ions non-radiatively returns to the main state and transfers energy to the adjacent Pr^{3+} ion, which is excited to a higher $4f^15d^1$ -state. Spectral-kinetic experiments make it possible to establish the population mechanism of $4f^15d^1$ -states [8–13]. ESA is a dominating process of up conversion for low concentration Pr^{3+} , and ETU is a dominating mechanism for higher concentration of Pr^{3+} -ions. Since the concentration of Pr^{3+} ions is low, we believe that in $\text{La}_2\text{Be}_2\text{O}_5:\text{Pr}^{3+}$ the ESA-mechanism is implemented. As a result, UV-UCL is observed as wide bands that fully correspond to the spectrum of Stokes $4f^15d^1-4f^2$ -PL (Fig. 1).

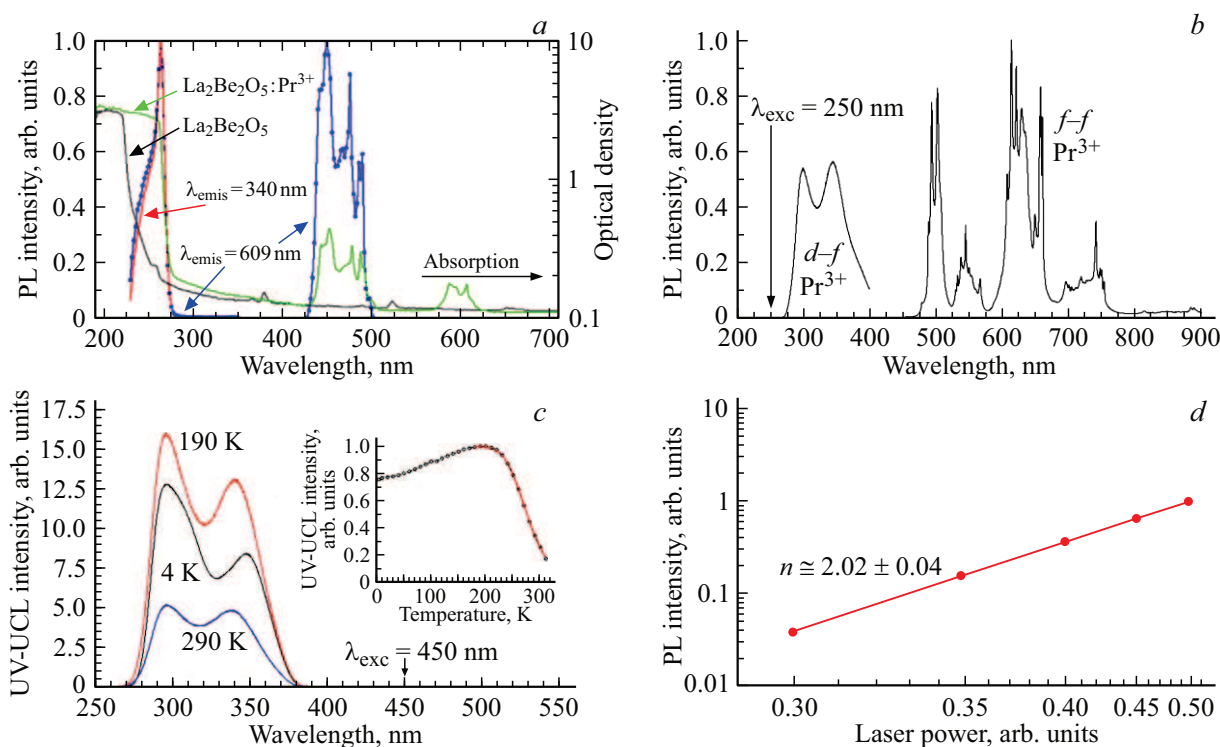


Figure 1. Single crystal $\text{La}_2\text{Be}_2\text{O}_5:\text{Pr}^{3+}$: (a) spectra of absorption and excitation of Stokes PL, (b) spectra of Stokes PL at $\lambda_{\text{exc}} = 250$ nm, (c) UV-UCL spectra at different temperatures at $\lambda_{\text{exc}} = 450$ nm (insert — temperature dependence of integral UV-UCL and its approximation in the field of quenching by Mott's scattering formula), (d) dependence of UV-UCL yield on excitation density.

Dependence of UV-UCL yield on excitation power is important in the study of the up-conversion process. Fig. 1, d shows the dependence of 340 nm UV-UCL yield on the density of excitation of a laser diode with $\lambda_{\text{exc}} = 450$ nm. It is known that intensity of UV-UCL (I) is proportionate to the n th degree of pumping power (W), where n — number of photons necessary to obtain one photon of up-conversion. Value n may be determined from the inclination of the linear curve of dependence $I = f(W)$ in double lg-coordinates. The calculated value of inclination is 2.02 ± 0.04 ($R^2 = 0.999$), which means that two exciting photons of visible range participate in the process of up-conversion.

UV-UCL spectra at different temperatures when excited by a laser with $\lambda_{\text{exc}} = 450$ nm are shown in Fig. 1, c. If temperature goes below 190 K, the maximum of the long-wavelength band shifts to the long-wavelength region, and $\sim 25\%$ reduction of integral UV-UCL yield is observed. At temperatures above 200 K the integral yield of UV-UCL decreases. Temperature dependence of UV-UCL yield in this region is approximated well by the available Mott's formula with activation energy of 314 meV, which describes the competition of radiative and non-radiative electron transitions (Fig. 1, c, insert, red line). Therefore, one may presume that as temperature goes above 200 K, UV-UCL quenching is caused by the growth of probability of energy transfer from $4f^15d^1$ (Pr^{3+}) states to defects — centers of non-radiative relaxation, or, in the second case,

this effect comes from competition between UV-UCL and relaxation of metastable excited state $^3P_0$ by radiation and non-radiative transitions [19].

Crystals with garnet structure Crystals with garnet structure doped with Pr^{3+} were one of the first with the recorded UV-UCL [6]. Therefore, in our experiments the reference was commercial yttrium-aluminum garnet $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Pr}^{3+}$, doped with 1% Pr. Fig. 2 presents the spectra of absorption, Stokes PL, UV-UCL, and also the UV-UCL excitation spectrum measured using a Xe-lamp. The absorption spectrum clearly shows both $f-f$ - and interconfiguration $4f^2 \rightarrow 4f^15d^1$ -transitions. The Stokes PL spectra show radiative $f-f$ -transitions and wide bands of emission $4f^15d^1 \rightarrow 4f^2$ (Pr^{3+}). The UV-UCL spectrum in the range of 270–410 nm under laser excitation $\lambda_{\text{exc}} = 450$ nm fully complies with the spectrum of Stokes PL. The UV-UCL yield is quite high, which made it possible for us to observe UV-UCL even with the use of a Xe-lamp as a source of excitation and to do the measurement of the UV-UCL excitation spectrum. Note that in the literature such UCL excitation spectra using gas discharge sources of light are not presented. This spectrum is shown in Fig. 2, a compared to the absorption spectrum. A clear correlation of peaks is seen in the excitation spectrum of UCL and position of excited ^3P_J - and $^1D_2$ -levels of Pr^{3+} ion in the absorption spectrum. The wavelength

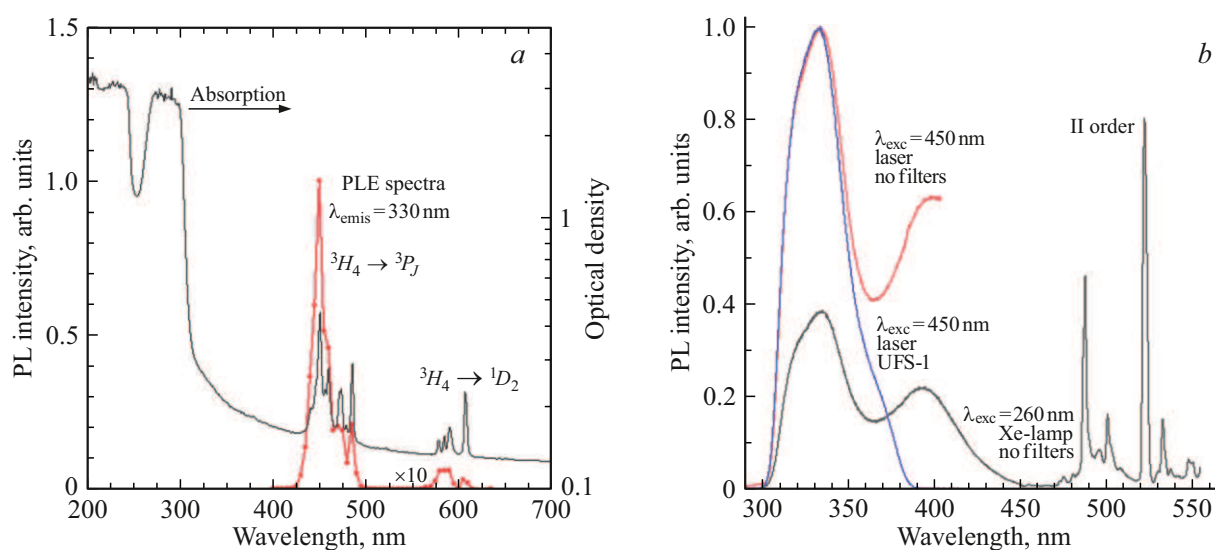


Figure 2. Single crystal $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Pr}^{3+}$: (a) spectra of absorption and excitation of UV-UCL, (b) spectra of Stokes PL (280–560 nm) at $\lambda_{\text{exc}} = 260 \text{ nm}$ and UV-UCL (laser, $\lambda_{\text{exc}} = 450 \text{ nm}$).

of 450 nm corresponds to the population of excited $^3P_2$ -states. Subsequent quick relaxation to the level $^3P_0$ and two-photon absorption provide for implementation of the ESA-mechanism for population of the zone of $4f^15d^1(\text{Pr}^{3+})$ -states. At the same time, when the $^1D_2$ -state was excited, we observed a very weak UV-UCL (at the level of not more than $\sim 1\%$ from intensity of UV-UCL with excited ^3P_J states). This confirms that in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Pr}^{3+}$ the two-photon excitation of the level $^1D_2$ provides for population of $4f^15d^1(\text{Pr}^{3+})$ -states. The possibility to implement such process depends on the position of the zone of mixed $4f^15d^1(\text{Pr}^{3+})$ -configuration. Detailed discussion of the participation of $^1D_2$ level in the up-conversion process in different matrices is analyzed in paper [15].

Anti-Stokes $d-f$ -PL in $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}^{3+}$ crystals (1% Pr) with garnet structure was studied in detail in the temperature range of 80–500 K in paper [20]. Based on these data, we studied UV-UCL in $\text{Lu}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Pr}^{3+}$ micropowders. Fig. 3 shows the spectra of Stokes PL in the area of $f-f$ (450–720 nm) and $d-f$ (250–400 nm) transitions, for comparison, the UV-UCL spectrum is shown under laser emission of ($\lambda_{\text{exc}} = 450 \text{ nm}$). The spectra are measured in the same unit with the same spectral resolution. You can see that they correlate well in the area of $d-f$ -transitions. At the same time the shape of the UV-UCL spectrum differs in the long-wavelength region. Therefore, it follows that interconfiguration transitions from the $4f^15d^1$ -zone of mixed electron configuration to the levels of ^3H_J main state, forming the Stokes luminescence and UV-UCL, happen with different probability or are observed from various $4f^15d^1$ -states of the zone of mixed electron configuration.

Crystals with the structure of orthosilicate

$\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ crystals with orthosilicate structure were one of the first, where UV-UCL was found using Ar⁺-laser

($\lambda_{\text{exc}} = 488 \text{ nm}$) as the source of excitation [7]. In this paper, dependences of UV-UCL on pumping power were measured for crystals with different concentration of Pr^{3+} , and the conclusion was made that at low concentration the ESA-mechanism was dominating in the up-conversion process, and the mechanism with energy transfer (ETU) was relevant at a higher concentration Pr^{3+} (1 mol.% and above). Spectroscopy with time resolution was used to distinguish between ETU and ESA. UV-UCL kinetics under pulse excitation with a 488 nm laser contains the exponential nanosecond attenuation, but without the build-up stage. This made it possible to exclude the ETU-mechanism in the process of up-conversion in $\text{Y}_2\text{SiO}_5:\text{Pr}^{3+}$ (1% Pr) [7,10].

Based on these data, to study UV-UCL in the crystals of orthosilicate, a nanocrystalline $\text{Lu}_2\text{SiO}_5:\text{Pr}^{3+}$ (1% Pr) synthesized with sol-gel-method was selected. Nanocrystalline X2-LSO: Pr^{3+} is included in a new class of nanosized optical materials with potential applications in scintillators and X-ray phosphors. Spectroscopic data, characteristics of this nanocrystal (average grain size $\sim 45 \text{ nm}$) are described in detail in paper [21]. Fig. 4, a shows the spectra of Stokes PL in the region of $d-f$ - and $f-f$ -transitions, and also UV-UCL spectra of Pr^{3+} -ion. The intense UV-UCL is observed at laser excitation with $\lambda_{\text{exc}} = 450 \text{ nm}$. The spectrum of Stokes $d-f$ -PL and UV-UCL spectrum cover one spectral region, however, the shape of spectra in the long-wavelength part slightly differs. As in the crystals with the garnet structure, this fact may indicate that $4f^15d^1 \rightarrow 4f^2$ -transitions forming the Stokes luminescence and UV-UCL, originate from various states of $4f^15d^1$ -zone of mixed electron configuration. Another possible reason for the long-wavelength shift of the spectrum is the effect of reabsorption (reabsorption with Pr^{3+} ions), the possibility of which was specified in the study of UV-UCL in the crystals with the garnet structure [20].

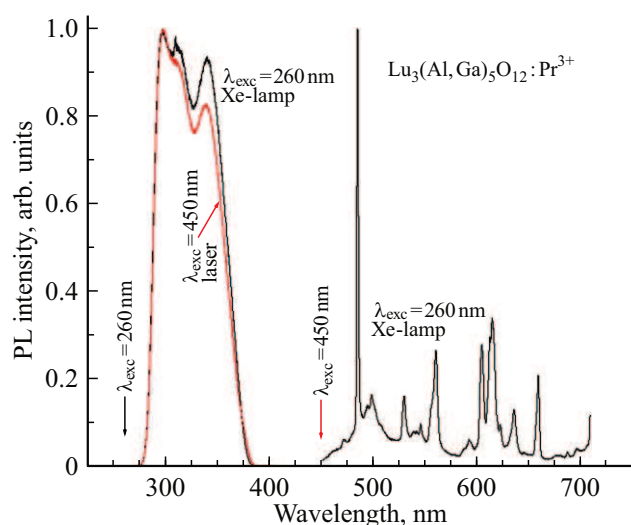


Figure 3. Single crystal $\text{Lu}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Pr}^{3+}$: spectra of Stokes PL at $\lambda_{\text{exc}} = 260 \text{ nm}$ and UV-UCL when excited by laser $\lambda_{\text{exc}} = 450 \text{ nm}$.

Crystals with apatite structure The example selected for the link to the crystalline structure of apatite was $\text{LiLa}_9(\text{SiO}_4)_6\text{O}_2$ (LLSO), doped with 1% Pr. Detailed information on the luminescent spectroscopy and characteristics of the crystalline structure are described in detail in our paper [22]. LLSO is included in the family of alkaline/alkaline-earth double silicates that contain trivalent RE-ions, and is characterized by crystalline structure of apatite and general formula $\text{ARE}_9(\text{SiO}_4)_6\text{O}_2$ (A — alkaline metal) or $\text{AE}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ (AE — alkaline-earth metal). One of the most attractive features of LLSO and other RE-oxyapatites that makes them promising for various applications is related to the ability to include trivalent impurity RE-ions without the need to compensate the charge. This enables growing large bulk crystals doped with optically active RE ions at high doping concentration. The structure of LLSO apatite is characterized by the presence of two coordination geometries for cation positions. The first position is occupied exclusively by La^{3+} , coordinated with seven oxygen ions, forming a distorted pentagonal bipyramid (positions 6h), whereas the second one is occupied partially with La^{3+} (75%) and Li^+ (25%) ions in the random distribution and is nine-coordinated (positions 4f) [22]. This partial structural chaos causes excitation of the crystalline field around RE-ions that substitute La^{3+} in both positions, and noticeably expands the spectral lines of $f-f$ -transitions even at low temperature.

In similar crystals with apatite structure UV-UCL $4f^15d^1 \rightarrow 4f^2$ was studied previously in $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2:\text{Pr}^{3+}$ powders synthesized with the sol-gel method using various concentrations of Pr^{3+} (0–2%) [14]. Indeed, two different types of PL centers Pr^{3+} were identified, which substitute Y ions in two different lattice points: 4f and 6h. Pr^{3+} ions in 4f point show only

$f-f$ -emission, whereas ions in point 6h have PL mostly in the UV-range. Mechanisms of up-conversion were analyzed with account of Pr^{3+} concentrations and excitation mode. It was found that in $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2:\text{Pr}^{3+}$ the ESA-mechanism is the main one in the process of up-conversion [14].

The spectra of Stokes PL and excitation spectra of $d-f$ -luminescence LLSO: Pr^{3+} (1% Pr) are presented in Fig. 4, b and 4, c accordingly. The spectrum of Stokes PL contains a group of wide bands in the UV-region corresponding to interconfiguration $d-f$ -luminescence Pr^{3+} , and a set of intense lines in the visible area, corresponding to the intraconfiguration $f-f$ -transitions (not shown in the figure). As shown above [22], the position of the excited $4f^15d^1$ -states of Pr^{3+} -ions in LLSO: Pr^{3+} depends strongly on the local coordination environment, as a result of which the PL spectrum shows Pr^{3+} ions that occupy two inequivalent crystallographic positions instead of La^{3+} ions. Long-wavelength overlapping bands centered at 330 and 305 nm correspond to PL of Pr^{3+} ions occupying the 4f-position instead of La^{3+} ions. Short-wavelength bands of 300 and 260 nm correspond to PL of Pr^{3+} ions occupying the 6h-position. Similar pattern is observed in LLSO: Pr^{3+} crystals with lower concentration of the activator (0.1% Pr). PL excitation spectra for each pair of UV-bands differ significantly (Fig. 4, c). As it follows from the excitation spectra of $d-f$ -luminescence, two-photon excitation with the UV-UCL laser at $\lambda_{\text{exc}} = 450 \text{ nm}$ provides for population of excited $4f^15d^1$ -states of Pr^{3+} ions in each position. However, the emission band in the UCL spectrum is centered in a shorter-wavelength region. Therefore, it may be concluded that in the process of up-conversion the $d-f$ -emission of Pr^{3+} ions is observed, which occupy mainly the 6h-position. This conclusion agrees with the result of the UV-UCL study in $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2:\text{Pr}^{3+}$ crystals having similar structure of apatite [14].

As shown above, the spectrum of Stokes PL at $\lambda_{\text{exc}} = 450 \text{ nm}$ contains lines of $f-f$ -transitions in the region of 460–750 nm. They are fully identified as electron transitions in Pr^{3+} ion. However, these lines are noticeably wider compared to the PL spectra in the region of $f-f$ -transitions in the compounds studied above or compared to the literature data. As noted in [22,23], this is specific for the crystals with the apatite structure doped with various RE ions. The partial structural chaos causes excitation of the crystalline field around Pr^{3+} ions in both positions that unevenly expands the lines of $f-f$ -transitions even at low temperature.

3.2. Transfer of energy $\text{Pr}^{3+} \rightarrow \text{Gd}^{3+}$ in process of up-conversion in Gd-containing compounds

As it was shown in a very limited number of papers (see for instance [8,12,24]), in Gd-containing matrices doped with Pr^{3+} ions, it is possible to observe UV-UCL of Gd^{3+} ions under laser double-stage excitation of Pr^{3+} ions in the visible spectral range with wavelength of 450 nm. Interconfiguration transitions $4f^2 \rightarrow 4f^15d^1$ in Pr^{3+} overlap

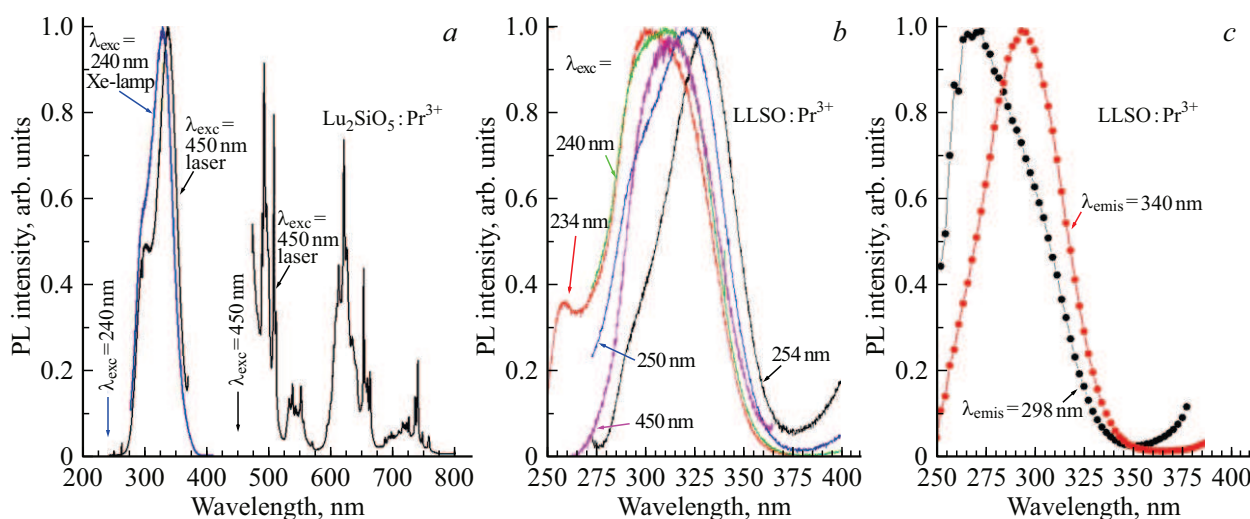


Figure 4. (a) Nanocrystal $\text{Lu}_2\text{SiO}_5:\text{Pr}^{3+}$ (1 mol.%): spectrum of Stokes PL (280–420 nm) at $\lambda_{\text{exc}} = 240$ nm, spectra of UV-UCL and $f-f$ -emission at laser excitation of $\lambda_{\text{exc}} = 450$ nm; (b) LLSO: Pr^{3+} (1% Pr): spectra of Stokes PL when excited by photons with different wavelength (λ_{exc}) and UV-UCL spectrum at $\lambda_{\text{exc}} = 450$ nm, (c) PL excitation spectra.

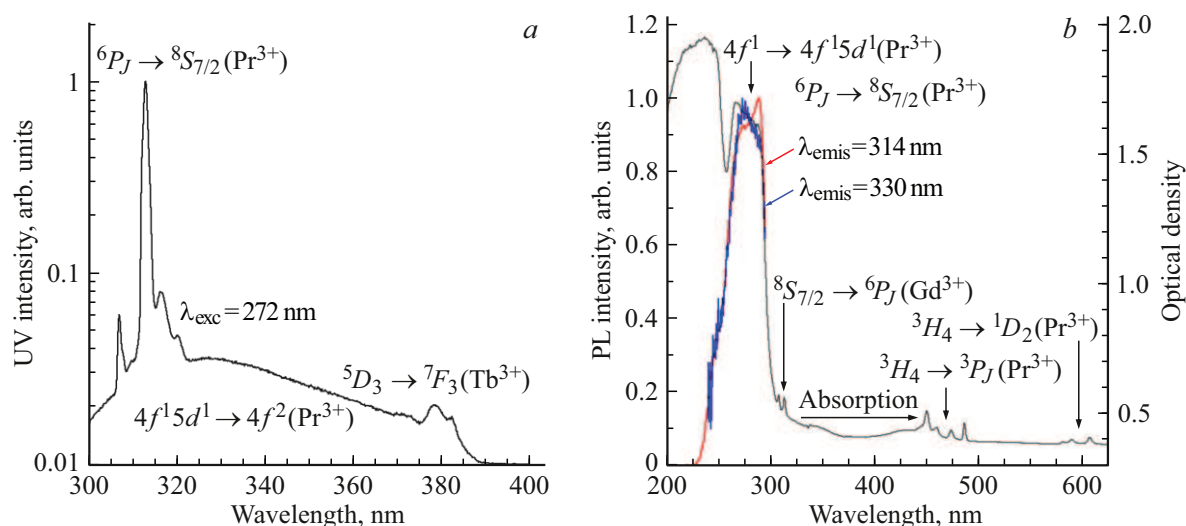


Figure 5. (a) $\text{Gd}_1\text{Y}_2\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Pr}_{0.01}$: fragment of Stokes PL spectrum at $\lambda_{\text{exc}} = 272$ nm; (b) spectra of PL absorption and excitation ($\lambda_{\text{emis}} = 330$ nm).

with electron transitions $^8S_{7/2} \rightarrow ^6I_J$, ^6D_J in Gd^{3+} , which may cause efficient resonant transfer of energy. Therefore, $f-f$ -PL of Gd^{3+} ions excited with visible light in process of up-conversion may be observed.

Ceramics $\text{Gd}_1\text{Y}_2\text{Al}_2\text{Ga}_3\text{O}_{12}$ doped with Pr^{3+} ions

To study the efficiency of $\text{Pr}^{3+} \rightarrow \text{Gd}^{3+}$ energy transfer in process of up-conversion, the samples of quaternary ceramics $\text{Gd}_1\text{Y}_2\text{Al}_2\text{Ga}_3\text{O}_{12}$ with garnet structure were chosen doped with Pr^{3+} ions. The synthesis, the method of transparent ceramics production, certification of samples, the data of X-ray diffraction analysis are described in papers [25–28]. The results of the study of Stokes luminescence at various types of excitation are also presented

here, high efficiency of energy transfer between RE ions is proven, and it is shown how to apply this scintillatory ceramics to detect X-ray, gamma- and neutron radiation.

Fig. 5, a shows a fragment of the spectrum of Stokes UV–PL at the intracenter excitation of Gd^{3+} ions by photons with $\lambda_{\text{exc}} = 272$ nm (transitions $^8S_{7/2} \rightarrow ^6I_J$). The PL spectrum contains the main narrow intense line 314 nm (transition $^6P_{7/2} \rightarrow ^8S_{7/2}$ in Gd^{3+}) against a weak wide band centered in the region of 330 nm. This band corresponds to radiative interconfiguration transitions from the region of mixed electron configuration to the main state of Pr^{3+} $4f^15d^1 \rightarrow 4f^2$ ion. Indeed, the PL excitation spectra compared to the absorption spectra show that the line of 314 nm, as well as the wide band of 330 nm, are excited

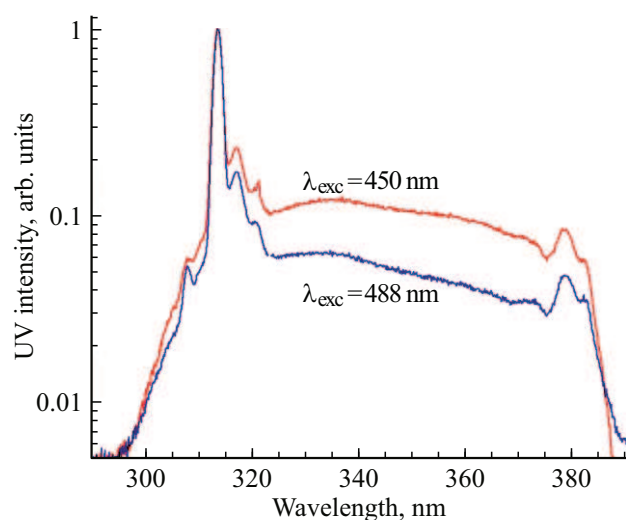


Figure 6. UV-UCL spectra $\text{Gd}_1\text{Y}_2\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Pr}_{0.01}$ under two-photon excitation with a laser diode of 450 or 488 nm.

exclusively in the area of electron transitions $4f^2 \rightarrow 4f^15d^1$ (Pr^{3+}) (Fig. 5, *b*). In the visible spectral range the PL spectrum at $\lambda_{\text{exc}} = 272$ nm (not shown in the figure) contains a typical group of narrow lines corresponding to the radiative transitions from ^3P_J -, $^1D_2$ -states of Pr^{3+} ion. The absorption spectrum (Fig. 5, *b*) shows the presence of intraconfiguration $f-f$ -transitions in Pr^{3+} ions (region of 600 nm and 450–490 nm), in Gd^{3+} ions (region of 310 nm), their position fully corresponds to the available Dicke diagram. Intense absorption in the region of 290 nm is related to interconfiguration $f-d$ -transitions in Pr^{3+} ions. The observed electron transitions are shown in the figure.

Fig. 6 shows UV-UCL spectra of $\text{Gd}_1\text{Y}_2\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Pr}_{0.01}$ when excited by a laser diode with wavelengths of 450 or 488 nm. As in the spectrum of Stokes PL, in the UV-UCL spectrum the intense line of 314 nm dominates, which corresponds to electron transitions $^6P_{7/2} \rightarrow ^8S_{7/2}$ in Gd^{3+} ions. This is the result of energy transfer from $4f^15d^1$ -states of Pr^{3+} ion to excited ^6I_J -, ^6D_J -states of Gd^{3+} ion. The schematic diagram of energy levels of these ions and corresponding electron transitions in absorption and emission are shown in Fig. 7.

It should be noted that UV-UCL yield depends on the gadolinium concentration within the matrix. The highest yield is achieved at the ratio of $\text{Gd}/\text{Y} = 1/2$. It is important that the same result is observed at the direct intracenter excitation of $4f^15d^1$ (Pr^{3+}) states by photons with $\lambda_{\text{exc}} = 272$ nm ($^8S_{7/2} \rightarrow ^6I_J$ -transition to Gd^{3+}), when 314 nm Stokes emission is recorded, or even in the X-ray luminescence spectra. Therefore, the UV-UCL yield depends not only on the energy transfer between RE ions, but on the probability of radiative electron transitions $^6P_{7/2} \rightarrow ^8S_{7/2}$ (Gd^{3+}).

The intense 314 nm line in the UV-UCL spectrum is observed against a weak wide band, which corresponds to interconfiguration $4f^15d^1 \rightarrow 4f^2$ -transitions in Pr^{3+} ion.

Apart from this wide band, both in the spectrum of Stokes PL and in the UV-UCL spectrum, there is a 380 nm line, its position along the wavelength absolutely corresponds to the radiative transitions $^5D_3 \rightarrow ^7F_6$ in Tb^{3+} ions present as uncontrolled impurity in the initial components (precursors) at synthesis of ceramics. Energy transfer $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+}$ is investigated well in the studied ceramics, and its high efficiency is confirmed [25–27]. Therefore, to study the role of coactivators in process of up-conversion, the dependence of UV-UCL yield was studied using the example of the samples doped with Ce^{3+} or Tb^{3+} ions. The concentration of coactivators was permanent ($\text{Ce}^{3+} = 0.01$, $\text{Tb}^{3+} = 0.1$ formula units (f.u.)), and concentration of Pr^{3+} varied. In samples with low content of ions Pr^{3+} (10^{-3} – 10^{-2} f.u.) no UV-UCL was observed. UV-UCL (314 nm line) with a very low yield was observed only when the concentration Pr^{3+} increased to 0.1 f.u. Therefore, when coactivators were added, the UV-UCL yield was either totally unavailable or dropped sharply. This is related to high efficiency of energy transfer of $\text{Gd}^{3+} \rightarrow (\text{Tb}^{3+}, \text{Ce}^{3+})$ in the studied ceramics, as it is shown in the study of Stokes luminescence [16]. Therefore, in case of laser excitation 450 nm in process of up-conversion a serial energy transfer between RE ions is implemented: $\text{Pr}^{3+} \rightarrow \text{Gd}^{3+} \rightarrow \text{Tb}^{3+}, \text{Ce}^{3+}$. I. e. in the presence of the coactivator, an alternative channel of excited states ^3P_J (Pr^{3+}) relaxation arises. At the same time it seems there is a simpler mechanism that exists to quench UV-UCL with the introduction of a codopant. It consists in the fact that the emission of 450 nm laser is absorbed directly by Ce^{3+} or Tb^{3+} ions (intracenter $f-d$ - or $f-f$ -transitions, accordingly). They have the absorption bands in this region [29], therefore, the efficiency of $4f^15d^1$ (Pr^{3+}) state population drops.

Ratio of intensity of 314 nm line and wide UV-band depends on the wavelength of excitation with 450 or 488 nm laser of the same capacity (Fig. 6). When excited by 488 nm laser, the integral yield of the wide PL band measured in the range of 315–378 nm, is 1.7 times lower than when excited with 450 nm laser. Absorption of 450 nm corresponds to the electron transition $4f^2 \rightarrow ^3P_2$, and then relaxation appears by $^3P_0$ -states, and when the second photon is absorbed, the ESA-mechanism of the up-conversion process, as shown in the diagram of electron states of ions Pr^{3+} and Gd^{3+} (Fig. 7). 488 nm absorption corresponds to the electron transition $4f^2 \rightarrow ^3P_0$, and when the second photon is absorbed, the ESA-mechanism of the up-conversion process is being implemented. Besides, you may not exclude the participation of the excited levels $^1D_2$ (Pr^{3+}) in process of up-conversion, and such possibility is available in [15]. In any case two-photon excitation provides for occupation of electron states of the $4f^15d^1$ -region of mixed electron configuration, which follows from the observed UV-UCL spectra and additionally from the spectra of Stokes PL excitation (Fig. 5, *b*). But at excitation of 488 nm contrary to 450 nm excitation, the lower states of $4f^15d^1$ -zone are populated. This changes the probability of electron relaxation from excited states $4f^15d^1$ along three competing channels:

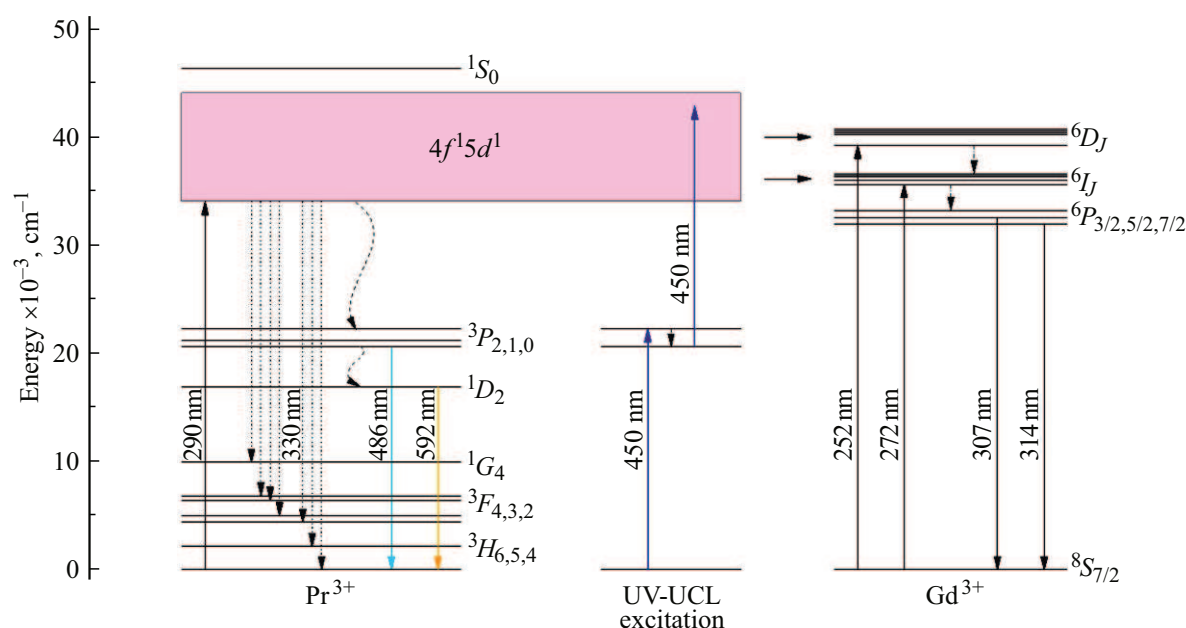


Figure 7. Schematic diagram of electron states of Pr^{3+} and Gd^{3+} ions and corresponding electron transitions in absorption and emission.

resonant energy transfer $4f^15d^1$ (Pr^{3+}) to excited states Gd^{3+} , interconfiguration $4f^15d^1 \rightarrow 4f^2$ UV-luminescence and multi-phonon relaxation $4f^15d^1 \rightarrow {}^3P_0 \rightarrow {}^1D_2$ with subsequent Stokes $f-f$ -emission in the visible spectral range. Excitation spectra of 314 nm line and wide band in the region of 330 nm compared to the absorption spectrum are shown in Fig. 5, *b*. A clear correlation of these spectra is observed. I.e. both emission bands are excited exclusively in the region of interconfiguration $4f^2 \rightarrow 4f^15d^1$ -transitions. This proves that Stokes PL of Gd^{3+} and emission of Gd^{3+} as a result of the process of up-conversion are the result of energy transfer $4f^15d^1$ (Pr^{3+}) $\rightarrow {}^6P_J, {}^6I_J, {}^6D_J$ (Gd^{3+}).

Further we measured the dependence of the UV-UCL on the laser excitation wavelength. At the same power of the laser, UV-UCL yield at $\lambda_{\text{exc}} = 450$ or 488 nm is practically same, whereas at $\lambda_{\text{exc}} = 405$ nm it is below 1%, at $\lambda_{\text{exc}} = 505$ nm — less than 0.1%, and at $\lambda_{\text{exc}} = 512$ nm UV-UCL not observed. Compared to the absorption spectrum (Fig. 5, *b*) it indicates that the occupation of excited states $4f^15d^1$ (Pr^{3+}) happens exclusively via levels ${}^3P_J$ (Pr^{3+}) (electron transitions ${}^3H_4 \rightarrow {}^3P_J$).

Ratio between intensity of UV-UCL at 314 nm wavelength and pumping power of the laser with $\lambda_{\text{exc}} = 450$ nm as shown in Fig. 8. The estimated value of inclination $n = 2.05 \pm 0.07$ ($R^2 = 0.999$), this means that two photons participate in the process of up-conversion. At the same time for Stokes $f-f$ (Pr^{3+})-luminescence (transition ${}^1D_2 \rightarrow {}^3H_4$) the value is $n = 1.03 \pm 0.07$ ($R^2 = 0.999$), which corresponds to linear single-photon process of Stokes PL excitation.

Crystals of fluorides, oxides, phosphates The up-conversion process is efficient in fluoride matrices doped

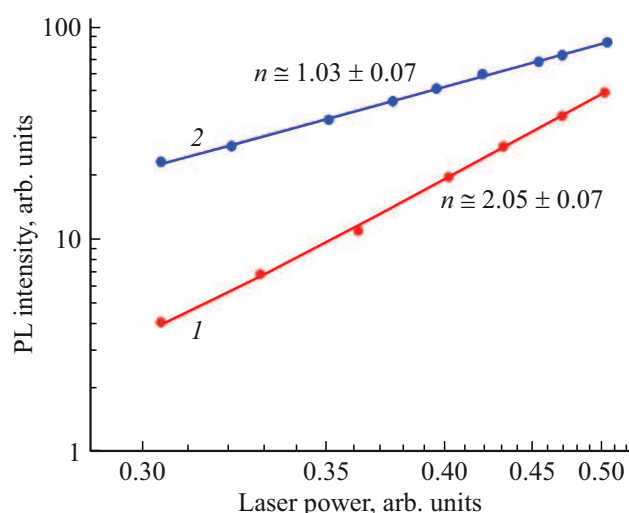


Figure 8. Dependences of UV-UCL yields (314 nm) (curve 1) and Stokes PL (transition ${}^1D_2 \rightarrow {}^3H_4$) (2) on power of excitation with laser 450 nm in $\text{Gd}_1\text{Y}_2\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Pr}_{0.01}$.

with Pr^{3+} [12,13] ions. For the example to study UCL in fluorides, a microcrystalline $\text{CsGd}_2\text{F}_7:\text{Pr}^{3+}$ (2% Pr) was chosen. Spectroscopic properties, dosimetric characteristics at various concentrations Pr^{3+} are studied by us well in [30,31]. And here the method of synthesis, crystalline structure are described, the results of the website-selective $f-f$ -luminescent spectroscopy. The spectrum of Stokes PL when excited by a laser with $\lambda_{\text{exc}} = 450$ nm is characterized by a set of narrow lines corresponding to intraconfiguration $f-f$ -transitions from ${}^3P_0$ - and ${}^1D_2$ -states Pr^{3+} . In the UV-UCL spectrum a 314 nm line appears, which corresponds to electron transitions ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ in Gd^{3+} . I. e. there is

energy transfer $4f^15d^1 (\text{Pr}^{3+}) \rightarrow {}^6P_{7/2} (\text{Gd}^{3+})$ observed. However, the UV-UCL yield is very low relative to Stokes $f-f$ -luminescence. It may be presumed that two-photon 450 nm laser absorption excites only the lowest states of $4f^15d^1$ -region, the efficiency of energy transfer between RE ions is low against efficient relaxation of $4f^15d^1 (\text{Pr}^{3+}) \rightarrow {}^3P_0, {}^1D_2$ with subsequent $f-f$ -emission. Indeed, as shown in [32], the beginning of the band of $4f^2 \rightarrow 4f^15d^1$ -transitions in the spectrum of $\text{CsGd}_2\text{F}_7:\text{Pr}^{3+}$ fluoride absorption is located near 220 nm, therefore in the PL spectrum there are only transitions ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ in Gd^{3+} ions, while the interconfiguration transitions are unavailable [32]. This is confirmed by the studies of UCL and in fluoride $\text{K}_2\text{GdF}_5:\text{Pr}^{3+}$. We found no UCL in this compound. Indeed, as the studies of „quantum-cutting“ [33] show, the region of states $4f^15d^1 (\text{Pr}^{3+})$ in $\text{K}_2\text{GdF}_5:\text{Pr}^{3+}$ is in a shorter-wavelength region — below 230 nm.

Thorough search for UV-UCL was carried out in some other wide band compounds doped with Pr^{3+} ions.

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) single crystal was selected from oxides. This is a known scintillatory crystal, its optical properties are well-studied [34,35]. The $\text{BGO}:\text{Pr}^{3+}$ crystals at $\lambda_{\text{exc}} = 450$ nm clearly show the specific $f-f$ -luminescence, the spectra of the measured Stokes PL of Pr^{3+} ions correspond to the data of paper [36], however, we found no UV-UCL. Absorption spectra show that $4f^15d^1$ -region of states of mixed electron configuration in BGO is above the energy of interregional transitions ($E_g = 4.8$ eV at room temperature [35]), i.e. is in the conduction band. Evidently, such situation is typical for other oxides with relatively low energy E_g .

Data of PL spectroscopy of SrF_2 crystals doped with RE ions are known well [37,38]. We conducted search for UV-UCL in SrF_2 crystals codoped with 0.1% Pr and 0.01% Gd, grown using the method [37,38]. At $\lambda_{\text{exc}} = 290$ nm (intracenter $f-d$ -absorption in Pr^{3+}) Stokes $d-f$ -PL, intense $f-f$ -emission Pr^{3+} , and also a weak line of 313 nm from Stokes PL of Gd^{3+} . However, we found no UV-UCL under laser excitation of 450 nm. We can presume that the efficient relaxation channel $4f^15d^1 (\text{Pr}^{3+}) \rightarrow {}^3P_0, {}^1D_2$ prevails, and $d-f$ -luminescence may have yellow yield.

Search for UV-UCL was conducted in some phosphates — $\text{K}_3\text{Lu}(\text{PO}_4)_2$, KLuP_2O_7 , LiSrPO_4 , doped with Pr^{3+} . These compounds show intense $d-f$ -radio luminescence in the UV-region with the quenching time 10–20 ns, and they are promising as scintillatory materials and effective radiation converters. The spectroscopic data, synthesis and characteristics of these compounds are described in [39–41]. However, UV-UCL was not found at laser excitation of 405 or 450 nm. Based on the studied $d-f$ -PL excitation spectra, it should be concluded that in these phosphates the wavelength of laser excitation is not sufficient to populate the area of excited $4f^15d^1$ -states.

4. Conclusion

The results of the study of interconfiguration $d-f$ -luminescence in the UV-region of the spectrum when excited by a laser diode (450 or 488 nm) in process of up-conversion in the wide-band compounds doped with Pr^{3+} ions show that the process of two-photon absorption is being implemented. Such process is most efficient in crystals with the garnet structure, somewhat less efficient in crystals with the apatite, orthosilicate structure or in lanthanum beryllate. In Gd-containing matrices (in ceramics $\text{Gd}_1\text{Y}_2\text{Al}_2\text{Ga}_3\text{O}_{12}$ and fluorides doped with Pr^{3+}) ions at laser two-photon excitation (450 or 488 nm) a resonant energy transfer is observed between excited states of RE ions $4f^15d^1 (\text{Pr}^{3+}) \rightarrow {}^6P_{7/2} (\text{Gd}^{3+})$ with subsequent UV-radiation 314 nm (transition ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ in Gd^{3+}). Such resonance energy transfer $4f^15d^1 (\text{Pr}^{3+}) \rightarrow {}^6P_{7/2} (\text{Gd}^{3+})$, interconfiguration $d-f$ -PL and multi-phonon relaxation of excited states $4f^15d^1 \rightarrow {}^3P_J$ with subsequent Stokes $f-f$ -emission in the visible spectra range are competing channels of electron relaxation from the region of excited states $4f^15d^1 (\text{Pr}^{3+})$. The process of up-conversion is most effective with energy transfer in ceramics $\text{Gd}_1\text{Y}_2\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Pr}^{3+}$, which is of interest for real practical applications.

Search for UV-UCL in certain oxides, fluorides, phosphates (sometimes with a negative result) shows that the necessary condition for observation of UV-UCL is the energy position of the area of excited states $4f^15d^1 (\text{Pr}^{3+})$ below the conductance band not exceeding double energy of ${}^3H_4 \rightarrow {}^3P_J (\text{Pr}^{3+})$ -transitions, and also low efficiency of multi-phonon relaxation $4f^15d^1 \rightarrow {}^3P_J, {}^1D_2$ and transfer of energy to defects of crystalline structure.

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Conflict of interest

The authors declare no conflict of interest.

References

- [1] F. Auzel. Chem. Rev., **104**, 139 (2004). DOI: 10.1021/cr020357g
- [2] P.P. Feofilov, V.V. Ovsyankin. Appl. Opt., **6** (11), 1828 (1967). DOI: 10.1364/ao.6.001828

- [3] A. Shalav, B.S. Richards, T. Trupke, K.W. Krämer, H.U. Güdel. Appl. Phys. Lett., **86**, 013505 (2005). DOI: 10.1063/1.1844592
- [4] A.M. Srivastava. J. Lumin., **169**, 445 (2016). DOI: 10.1016/j.jlumin.2015.07.001
- [5] E. Aleksanyan, V. Harutunyan, M. Kink, M. Kirm, Yu. Maksimov, V.N. Makhov, T.V. Ouharova. Opt. Commun., **283**, 49 (2010). DOI: 10.1016/j.optcom.2009.09.067
- [6] J. Ganem, W.M. Dennis, W.M. Yen. J. Lumin., **54** (2), 79. DOI: 10.1016/0022-2313(92)90250-D
- [7] C.L. Sun, J.F. Li, C.H. Hu, H.M. Jiang, Z.K. Jiang. Eur. Phys. J. D, **39** (2), 303. DOI: 10.1140/epjd/e2006-00102-7
- [8] D. Yu, H. Li, D. Zhang, Q. Zhang, A. Meijerink, M. Suta. Light: Sci. Appl., **10**, 236 (2021). DOI: 10.1038/s41377-021-00677-5
- [9] S.L. Cates, E.L. Cates, M. Cho, J.-H. Kim. Environ. Sci. Technol., **48** (4), 2290 (2014). DOI: 10.1021/es405229p
- [10] L. Li, L. Zi, F. Yang, S. Feng, C. Wang, Y. Yang. Adv. Phys. Res., **4** (2), 2400097 (2025). DOI: 10.1002/apxr.202400097
- [11] M.D. Dramićanin, M.G. Brik, Ž. Antić, R. Bănică, C. Mosoarca, T. Dramićanin, Z. Ristić, G.D. Dima, T. Förster, M. Suta. Nanomaterials, **15** (7), 562 (2025). DOI: 10.3390/nano15070562
- [12] Y. Sun, Y. Wang, C. Hu, X. Zhou, J. Hao, W. Li, H. Li. Mater., **15** (21), 7680 (2022). DOI: 10.3390/ma15217680
- [13] N. Rebrova, P. Zdeb, K. Lemaški, B. Macalik, O. Bezkrvnyi, P.J. Dereñ. Inorg. Chem., **63** (6), 3028 (2024). DOI: 10.1021/acs.inorgchem.3c03821
- [14] N. Rebrova, P. Zdeb, P.J. Dereñ. J. Phys. Chem. C, **128** (22), 9090 (2024). DOI: 10.1021/acs.jpcc.3c08163
- [15] P. Zdeb, N. Rebrova, P.J. Dereñ. J. Phys. Chem. Lett., **15** (37), 9356 (2024). DOI: 10.1021/acs.jpclett.4c02053
- [16] A.A. Kaminskii, T. Ngoc, S.E. Sarkisov, V.N. Matrosov, M.I. Timoshechkin. Phys. Status Solidi A, **59** (1), 121 (1980). DOI: 10.1002/pssa.2210590117
- [17] J.B. Czirr, M. Berrondo. United States Patent 5483062. (09.01.1996). (Mapleton, Orem, UT).
- [18] V.A. Pustovarov, I.N. Ogorodnikov. J. Surf. Investig., **10** (1), 48 (2016). DOI: 10.1134/S1027451015060178
- [19] M. Pollnau, D.R. Gamelin, S.R. Lüthi, H.U. Güdel. Phys. Rev. B, **61** (5), 3337 (2000). DOI: 10.1103/PhysRevB.61.3337
- [20] P. Pues, M. Laube, S. Fischer, F. Schröder, S. Schwung, D. Rytz, T. Fiebler, U. Wittrock, T. Jüstel. J. Lumin., **234**, 117987 (2021). DOI: 10.1016/j.jlumin.2021.117987
- [21] M. Trevisani, K.V. Ivanovskikh, N. Grillet, F. Piccinelli, M. Bettinelli. Chem. Phys. Lett., **565**, 80 (2013). DOI: 10.1016/j.cplett.2013.02.031
- [22] K.V. Ivanovskikh, Q. Shi, M. Bettinelli, V.A. Pustovarov. Opt. Mater., **79**, 108 (2018). DOI: 10.1016/j.optmat.2018.03.006
- [23] V.A. Pustovarov, A.A. Vasin, M.G. Zuev. Opt. Mater. X, **15**, 100186 (2022). DOI: 10.1016/j.omx.2022.100186
- [24] S. Yan, F. Liu, J. Zhang, X.-J. Wang, Y. Liu. Phys. Rev. Appl., **13**, 044051 (2020). DOI: 10.1103/PhysRevApplied.13.044051
- [25] M. Korzhik, V. Retivov, A. Bondarau, G. Dosovitskiy, V. Dubov, I. Kamenskikh, P. Karpuk, D. Kuznetsova, V. Smyslova, V. Mechinsky, V. Pustovarov, D. Tavrurinov, E. Tishchenko, A. Vasiliev. Crystals, **12** (9), 1196 (2022). DOI: 10.3390/cryst12091196
- [26] M. Korzhik, P. Karpuk, A. Bondarau, A. Ilyushin, I. Kamenskikh, D. Lelekova, V. Pustovarov, V. Retivov, V. Smyslova, D. Tavrurinov, A. Vasiliev. J. Lumin., **265**, 120226 (2024). DOI: 10.1016/j.jlumin.2023.120226
- [27] V. Dubov, A. Bondarau, D. Lelekova, I. Komendo, G. Malashkevich, V. Kouhar, V. Pustovarov, D. Tavrurinov, M. Korzhik. J. Appl. Phys., **135**, 053104 (2024). DOI: 10.1063/5.0186860
- [28] M.V. Korzhik, V.M. Retivov, V.V. Dubov, L.V. Ermakova, V.K. Ivanov, P.V. Karpuk, I.A. Lagutsky, O.Yu. Koval, I.Yu. Komendo, D.E. Lelekova, V.A. Mechinsky, V.A. Pustovarov, V.G. Smyslova, P.S. Sokolov, D.A. Tavrurinov, A.A. Fedorov. ZhTF, **94** (12), 2145 (2024) (in Russian). DOI: 10.61011/JTF.2024.12.59276.271-24
- [29] V.A. Pustovarov, D.A. Tavrurinov, I.Yu. Komendo, V.G. Smyslova, M.V. Korzhik. Opt. Mater., **167**, 117302 (2025). DOI: 10.1016/j.optmat.2025.117302
- [30] M. Yin, V.N. Makhov, N.M. Khaidukov, J.C. Krupa. J. Lumin., **94–95**, 97 (2001). DOI: 10.1016/S0022-2313(01)00254-X
- [31] N. Kristianpoller, D. Weiss, R. Chen, N. Nariyama, N. Khaidukov. Radiat. Prot. Dosim., **100** (1-4), 207 (2002). DOI: 10.1093/oxfordjournals.rpd.a005848
- [32] P. Dorenbos, R. Visser, C. W. E. van Eijk, N. M. Khaidukov, M. V. Korzhik. IEEE Trans. Nucl. Sci., **40** (4), 388 (1993). DOI: 10.1109/23.256586
- [33] T.-J. Lee, L.-Y. Luo, B.-M. Cheng, W.-G. Diao, T.-M. Chen. Appl. Phys. Lett., **92**, 081106 (2008). DOI: 10.1063/1.2884690
- [34] R. Moncorge, B. Jacquier, G. Boulon, F. Gaume-Mahn, J. Janin. J. Lumin., **12–13**, 467 (1976). DOI: 10.1016/0022-2313(76)90124-1
- [35] V.Y. Ivanov, A.V. Kruzhlov, V.A. Pustovarov, V.L. Petrov. Nucl. Instrum. Methods Phys. Res. A, **261** (1-2), 150 (1987). DOI: 10.1016/0168-9002(87)90585-7
- [36] J. Xu, Y. Guyot, K. Lebbou, X. Xu, J. Liu, J. Xu, R. Moncorge. J. Lumin., **260**, 119882 (2023). DOI: 10.1016/j.jlumin.2023.119882
- [37] K.V. Ivanovskikh, V.A. Pustovarov, M. Kirm, B.V. Shulgin. J. Lumin., **122–123**, 28 (2007). DOI: 10.1016/j.jlumin.2006.01.072
- [38] K.V. Ivanovskikh, V.A. Pustovarov, A. Smirnov, B.V. Shulgin. J. Alloys Compd., **451**, 65 (2008). DOI: 10.1016/j.jallcom.2007.04.095
- [39] K.V. Ivanovskikh, V.A. Pustovarov, S. Omelkov, M. Kirm, F. Piccinelli, M. Bettinelli. J. Lumin., **230**, 117749 (2021). DOI: 10.1016/j.jlumin.2020.117749
- [40] V.A. Pustovarov, K.V. Ivanovskikh, S.A. Kiselev, E.S. Trofimova, S. Omelkov, M. Bettinelli. Opt. Mater., **108**, 110234 (2020). DOI: 10.1016/j.optmat.2020.110234
- [41] E. Trofimova, S. Omelkov, I. Romet, M. Kirm, V. Pustovarov, F. Piccinelli. J. Lumin., **240**, 118455 (2021). DOI: 10.1016/j.jlumin.2021.118455

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