Up-conversion white emission and other luminescence properties of a YAG:Yb2O3·Tm2O3·Ho2O3@SiO2 glass-nanocomposite†

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We report on a glass-nanocomposite material consisting of yttrium aluminum garnet (Y3Al5O12, YAG) nanocrystals co-doped with Yb3+, Tm3+ and Ho3+ ions as well as entrapped into a SiO2 xerogel. This nanocomposite material has been prepared by sol–gel procedure. Its structure and morphology has been characterized by means of X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques as well as energy dispersive X-ray (EDX), X-ray photoelectron (XPS) and luminescence spectroscopies. The luminescent glass-nanocomposite exhibited an up-conversion effect under λexc = 980 nm and emission when excited under 355 nm in steady-state conditions. Then time-resolved luminescence emission was observed, when the sample was excited at 290 and 355 nm by a pulse laser. Average decay times for the SiO2 matrix and for some transitions of the Tm3+ and Ho3+ dopants present in the YAG:YbTmHo@SiO2 nanocomposite material have been evaluated. The luminescent nanocomposite when excited under 290 or 355 nm wavelengths in both conditions emits blue light. However, the nanocomposite is promising as a single-source white-light phosphor owing to its up-conversion luminescence under 980 nm excitation. Such optical features make the studied material an alternative phosphor.

Introduction

Up-conversion is an anti-Stokes process in which a near infrared photon is converted into visible or even ultraviolet light owing to multi-photon action. Among various near infrared excitation lasers, the 980 nm one is the most commonly used excitation source generating up-conversion emission.1 Actually there are many up-conversion processes with widely different conversion efficiencies. The processes require energy levels which are resonant with the incoming or outgoing radiation. Lanthanide(m) ions (Ln3+) are very suitable as the emitting centers owing to their numerous electronic levels and narrow emission bands. Among the Ln(m) ions Ho3+ can be applied to obtain red and green up-conversion luminescence and Tm3+ acts as a blue emitting activator under infrared (980 nm) excitation. While, Yb3+ can act as the sensitizer enhancing the emission efficiency due to appropriate structure of energy levels and longer decay lifetime of the excited states.2

The efficiency of the system depends strongly on the choice of the host matrix. It is known that oxides are less suitable than fluorides, since lifetimes in the former are shorter than in the latter due to stronger interaction between the luminescent ion and its coordination environment. Since in the up-conversion oxide material co-doped, e.g., with Yb3+ and Er3+, the lifetime of the intermediary 4I11/2 (Er3+) is shorter, in consequence the total efficiency of the up-conversion process will be lower, in contrast to fluoride material.3 Irrespective of this fact there are many papers devoted to up-conversion in oxide materials, among them also works considering yttrium aluminum garnet (e.g. ref. 2 and 4–11).

Yttrium aluminum garnet (YAG) is a prominent crystalline material of the garnet group. The choice of YAG relies on this material exhibiting exceptional optical transparency, having a cubic crystallographic structure that can well accommodate such dopants as lanthanide ions.12,13 YAG nanocrystals doped with Ln3+ ions were prepared using many different methods.7,14,15

A nanocomposite is defined as a material consisting of at least two different solid phases. In our case glassy silica as the
host phase of larger extent plays a matrix role. Then the nanosized YAG guest phase doped with Ln(n) ions is dispersed into the matrix. Obviously, the constituent phases of the composite are separated by distinct interface. In the nanocomposites, the guest nanoparticles have dimension in the range 1–100 nm. In this type of nanocomposite materials glass is an excellent host owing to its several inherent superior properties compared to those of other encapsulating hosts. There are many types of glass-nanocomposites depending on the compositions, sizes and shapes of the nano-guests as well as processing parameters.  

One of the encapsulating methods used in nanocomposite preparation is sol-gel processing. This method involves the generation of colloidal suspensions (sols) which are subsequently converted to viscous gels and then to rigid xerogels. Thus, by sol–gel procedure crystalline particles can be immobilized in a solid xerogel. Wide range of inorganic and hybrid organic–inorganic composite materials share this common preparation procedure. In contrast to bulk materials prepared by the melting method, sol–gel materials can be obtained as thin films and coatings. If these materials are transparent, then they gain a competitive advantage with respect to bulk glasses and crystals. It is important especially in glass-nanocomposite luminescent materials doped with such luminescent species as Ln3+ ions, where the nanosize of the Ln3+ doped crystals is crucial to avoid light scattering. The nanocrystals play important role, when activated by lanthanide ions. The presence of the crystalline environment around the lanthanide ion allows high absorption and emission cross sections as well as tailoring of the ion–ion interaction by the control of the lanthanide ion partition. This last point is crucial and still an object of intense experimental and theoretical studies.  

The integration of luminescent nanocrystals into vitreous matrix can lead to new optical nanocomposites. There is growing interest to integrate up-conversion nanocrystals with an optical matrix. Not only glass matrices but also rigid vitreous xerogels can serve as indispensable optical matrix materials owing to their high optical transparency, thermomechanical strength and the ability (especially in the case of xerogels) to be shaped into an almost optical transparency, thermomechanical strength and the ability to be shaped into an almost transparent and identical glassy xerogel structure as a blank silica xerogel. Aim of the study is to compare luminescence of the glass nanocomposite excited in different conditions, viz. in steady-state ($\lambda_{\text{exc}} = 355 \text{ and } 980 \text{ nm}$) or by pulse laser ($\lambda_{\text{exc}} = 290 \text{ and } 355 \text{ nm}$) spectroscopy.

### Experimental

#### Synthetic procedures

Pure $\text{Y}_2\text{Al}_2\text{O}_5$ (YAG) and co-doped $94\text{Y}_2\text{Al}_2\text{O}_12\cdot 6\text{Ln}_2\text{O}_3$ (in mol%) materials (abbr. YAG:Ln, where Ln = Yb, Tm and Ho), were synthesized by glycol modification of the sol–gel procedure after Veith et al. The pure YAG as well as doubly co-doped 94YAG:5Yb2O3:1Ho2O3 (abbr. YAG:YbHo) and triply co-doped 94YAG:5Yb2O3:0.8Tm2O3:0.2Ho2O3 (abbr. YAG:YbTmHo) agglomerated crystals were powdered in an agate mortar and then pulverized in methanol slurry to nanosize particles by an ultrasonic technique for 3 h. The chemicals for the doped YAG synthesis such as yttrium trioxide ($\text{Y}_2\text{O}_3$), aluminum nitrate [$\text{Al(NO}_3\text{)}_3\cdot 5\text{H}_2\text{O}$] and appropriate lanthanide salts Ln(NO3)$_3\cdot 5\text{H}_2\text{O}$ (where Ln = Yb, Tm and Ho) of p.a. grade were purchased from Aldrich Co. While acetic acid (CH$_3$COOH), methanol (CH$_3$OH) and 1,2-ethanediol (glycol, HOCH$_2$CH$_2$OH) of p.a. grade were from Polish Chemical Reagents.

The co-doped YAG:YbHo and YAG:YbTmHo nanopowders were immobilized into silica xerogel by sol–gel processing in a one-pot method. 2.5 cm$^3$ of tetramethoxysilane (TMOS) was dissolved in 5 cm$^3$ of methanol and 1 cm$^3$ of water was added. The mixture was stirred and 1.2 cm$^3$ of NH$_3$(aq) catalyst dropwise was added. After that the MeOH sol consisting of the co-doped YAG nanoparticles together with the sol–gel mixture was stirred for 15 min. The molar ratio of TMOS : $\text{H}_2\text{O}$ : MeOH was established as 1 : 4 : 8. After two days, the co-doped YAG nanocrystals YAG:YbHo@SiO$_2$ and YAG:YbTmHo@SiO$_2$ incorporated into rigid wet gels with the materials were obtained. The nanocomposites were dried at 200 °C, then crushed and sieved (0.25–0.50 mm). After that they were calcined at 200, 600, 800 and 1000 °C for 3 hours. The chemicals for the silica matrix preparation such as tetramethoxysilane (TMOS) was purchased from Aldrich Co. but methanol (CH$_3$OH) and ammonia NH$_3$(aq) were from Polish Chemical Reagents.

#### Apparatus

The ultrasonic equipment for the crystals crushing to nanoparticles was Sonorex Super RK 103H. After straining and drying at 120 °C the nanocrystals were thermally treated at 200 °C in a programmable oven equipped with an SM-946 temperature controller.
Powder X-ray diffraction (XRD) analysis of the YAG, doped and co-doped YAG:Ln nanocrystals as well as YAG:Ln@SiO₂ nanocomposites was made using a Bruker D2 Phaser model employing CuKα radiation operated at 30 kV and 0.2 mA. The XRD patterns were collected using scanning steps of 0.02 deg. and counting time 0.4 s per step. The average crystalline size as well as percentage of crystallinity were calculated using Diff. EVA software provided by Bruker.

The topography of the samples was characterized using scanning electron microscope SEM S-3400N (Hitachi, Japan), equipped with a tungsten source. A secondary electron (SE) detector was used and analysis was performed under 20 kV accelerating voltage.

Chemical composition of the investigated materials was examined by means of energy dispersive X-ray spectroscopy (EDX) equipped with Thermo Fisher Scientific detector attached to (SEM) and X-ray photoelectron spectroscopy (XPS) fitted with Thermo Fisher Scientific: Escalab 250Xi utilizing monochromatic Al-Kα source with charge neutralization implemented by means of flood gun. High-resolution XPS spectra were recorded at energy step size of 0.1 eV at pass energy 10 eV. In order to normalize the spectroscopic measurements, the X axis (binding energy) from XPS spectrum was calibrated for the peak characteristics for neutral carbon C1s (284.6 eV). Data analysis was performed using Avantage software provided by the manufacturer.

Photoluminescence spectra were recorded using a monochromators SPM2 produced by Carl Zeiss Jena for excitation and emission. An excitation source in this system was Osram 250 W ozone-free Xenon lamp and laser produced by Optoelectronics Tech. Co., Ltd. MDL-III-980L-1000 mW. Fluorescence intensity was measured using a Hamamatsu R928 Side-on photomultiplier. All spectra were recorded at 300 K.

To follow the luminescence kinetics, we used a system consisting of a YAG:Nd (PL 2143 A/SS) laser and system OPG (optical paramagnetic generators). This system can generate 30 ps laser pulses, with the frequency of 10 Hz with wavelengths ranging 290 and 355 nm. The emission signal was analyzed by a Bruker Optics 2501S spectrometer and the Hamamatsu Streak Camera model C4334-01 with a Hamamatsu R928 Side-on photomultiplier. All spectra were recorded at 300 K.

In order to normalize the spectroscopic measurements, the X axis (binding energy) from XPS spectrum was calibrated for the peak characteristics for neutral carbon C1s (284.6 eV). Data analysis was performed using Avantage software provided by the manufacturer.

Results and discussion

XRD patterns

XRD patterns of the pure YAG (curve a), YAG doped with 6 mol% Yb³⁺ (YAG:Yb, curve b) and YAG triply co-doped with Yb³⁺, Tm³⁺ and Ho³⁺ (YAG:YbTmHo, curve c) dried at 200 °C are presented in Fig. S1.⁷ All the patterns are consistent with the standard data corresponding to cubic Y₃Al₅O₁₂ nanocrystals (PDF 01-082-3500), i.e. no secondary crystalline phase is observed and presence of the dopants did not change the crystalline structure. The calculated by the Scherrer formula average size of the nanocrystals was equal to 27 ± 4 nm.

XRD patterns of the thermally treated YAG:YbTmHo@SiO₂ nanocomposite is shown in Fig. S2.⁷ The sample was dried at 200 °C and then calcined at 600, 800 and 1000 °C. As previously, the XRD patterns are in accordance with the YAG standard data. The average crystallite sizes of the triply co-doped YAG nanoparticles in the nanocomposite collected in Table S1 are within experimental error close to the crystallite size of the un-doped, doubly and triply co-doped YAG nanoparticles. The crystallinity percentage of the samples was estimated. Its values change a little with temperature of the thermal treatment (see Table S1†).

SEM images

SEM micrographs of the pure YAG and doped YAG:Yb powder samples presented in Fig. 3S[a and b,†] respectively exhibit agglomerated crystals. Then in images of greater enlargement in insets are shown nanoparticles which average size could be estimated to ca. 30 nm. It is within experimental error close to the size calculated by the Scherrer formula (vide supra). On the other hand, SEM image of the YAG:YbTmHo@SiO₂ nanocomposite powder thermally treated at 600 °C shows agglomerates (Fig. S4†). Image of greater enlargement in inset shows the sphere-like nanoparticles consisted of the doped YAG nanocrystals capped with amorphous SiO₂. Size of the nanoparticles is near two-fold greater than size of the YAG and YAG:Yb nanocrystals.

EDS and XPS measurements

EDS measurement confirm the composition of the YAG and Yb-doped YAG nanocrystals (Fig. S5,† inset). Whereas high-resolution XPS spectra of the YAG and YAG:Yb demonstrated in Fig. S6† allow to calculate the Y/Al/O ratio for both the samples. The results give a close match to Y₃Al₅O₁₂ (3.0/6.4/11.6 and 3.0/6.1/11.9 for YAG and YAG:Yb samples, respectively) proving their high purity (see Table S2†).

Luminescence spectroscopy

Steady-state emission spectra.

The normalized up-conversion emission spectra recorded at room temperature under near infrared (NIR) excitation at 980 nm for the co-doped YAG nanocrystals and the glass-nanocomposites with silica are compared in Fig. 1(A and B). In general, the emission spectra of the co-doped YAG:YbHo and YAG:YbTmHo nanocrystals (curves a) did not change after their incorporation into silica xerogel (compare with curves b, i.e. the YAG:YbHo@SiO₂ and YAG:YbTmHo@SiO₂ nanocomposite spectra, respectively).

The up-conversion emissions shown in Fig. 1A are generated by two- and three-photon processes such as energy transfer (ET) and excited state absorption (ESA) illustrated in the known schematic energy level diagrams presented in Fig. 2 for Ho³⁺ ions. In the first step Yb³⁺ sensitizer is excited under 980 nm from the ground state 2F⁵/₂ to the 2F⁵/₂ one. Then, occurs the Yb³⁺:2F⁵/₂ → Ho³⁺:5I₄ transfer. In this situation either the non-radiative transition Ho³⁺:5I₄ → 5I₂ takes place and subsequently by step (2) the Ho³⁺ is excited to the 5F₄ state or directly occurs the Ho³⁺:5I₄ → 5F₄ transition by two-photon process (step 2) from Yb³⁺.

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Fig. 1  Up-conversion emission spectra of the samples: (A) YAG:YbHo nanocrystals (curve a) and YAG:YbHo@SiO2 glass nanocomposite (curve b) as well as (B) YAG:YbTmHo nanocrystals (curve a) and YAG:YbTmHo@SiO2 glass nanocomposite (curve b). The samples dried at 200 °C were excited under $\lambda_{\text{exc}} = 980$ nm by the laser in steady-state condition.

Fig. 2  Scheme of energy levels of Yb$^{3+}$ (sensitizer) as well as Tm$^{3+}$ and Ho$^{3+}$ (activators) in YAG:YbTmHo@SiO2 nanocomposite. The scheme demonstrates up-conversion mechanisms of the emissions under 980 nm laser excitation. GSA means ground state absorption, ESA – excited state absorption. ET – energy transfer and NRT – non-radiative transition. After ref. 22 and 28.

former case the red emission about 670 nm (14 870 cm$^{-1}$) corresponds to the $^5F_5 \rightarrow ^1I_8$ transition. Whereas in the latter case can be present two transitions, viz. $^5F_4, ^5S_2 \rightarrow ^1I_8$ and $^5F_4, ^5S_2 \rightarrow ^1I_7$. Owing these transitions are observed such emission bands as green one at about 550 nm (18 180 cm$^{-1}$) and near-infra red (NIR) band centered at 764 nm (13 004 cm$^{-1}$), respectively. However, after the $^5F_5 \rightarrow ^1I_8$ non-radiative decay three-photon process (step 3) takes place the $^5G_4 \rightarrow ^5K_2$ transition. The $^5G_4, ^5K_2 \rightarrow ^3I_6$ relaxation generates an emission band peaked at ca. 650 nm (15 380 cm$^{-1}$).22

Emission spectra shown in Fig. 1B are superpositions of spectra consisting of lines assigned to transitions of Ho$^{3+}$ and Tm$^{3+}$ dopants in YAG:YbTmHo and its glass nanocomposite counterpart YAG:YbTmHo@SiO2. The observed emission bands of Tm$^{3+}$ are due to two-, three- and four-photon up-conversion processes. As previously, the up-conversion mechanism starts when the excited Yb$^{3+}$ ion transfers its energy to the Tm$^{3+}$ and the latter ion reaches the excited $^3H_4$ level. As in the case of Ho$^{3+}$ it is a phonon assisted energy transfer because there is energy difference between the excited state of Yb$^{3+}$ and the excited $^3H_5$ level of Tm$^{3+}$ (see left part of the energy diagram in Fig. 7). Then after the non-radiative relaxation Tm$^{3+}:^3H_5 \rightarrow ^3H_4$ takes place ET from the Yb$^{3+}$ (step 2) that causes the $^5F_4 \rightarrow ^5F_2,3$ transition of Tm$^{3+}$. From this energy level the Tm$^{3+}$ ions can firstly non-radiatively relax to $^3H_4$ and then radiatively relax to the ground state ($^1H_6$). The latter transition generates the NIR emission band centered at 826 nm (11 990 cm$^{-1}$) in the spectra shown in Fig. 1B. Step (3) allows to excite Tm$^{3+}$ to the $^3G_4$ state. From this level start three emission transitions of Tm$^{3+}$, viz. $^1G_4 \rightarrow ^3H_5, ^1G_4 \rightarrow ^3F_4$ and $^1G_4 \rightarrow ^3H_6$ which correspond to bands at 810 nm (12 250 cm$^{-1}$), 637 nm (15 635 cm$^{-1}$) and 484 nm (20 640 cm$^{-1}$), respectively. After the next ESA (step 4) the Tm$^{3+}$ ions are transferred to the $^1D_2$ state from which they can relax by photon emissions of wavelengths of 792 nm (12 540 cm$^{-1}$) and 470 nm (21 220 cm$^{-1}$). In this case the emission lines are related to $^1D_2 \rightarrow ^3F_{2,3}$ and $^1D_2 \rightarrow ^3F_4$ transitions, respectively.22

The up-conversion mechanism in the triply co-doped nanocrystals and nanocomposite could be more complicated because such pairs of energy levels as (Ho$^{3+}:^3I_1$ and Tm$^{3+}:^3F_4$), Ho$^{3+}:^5I_6$ and Tm$^{3+}:^5H_5$, Ho$^{3+}:^5F_5$ and Tm$^{3+}:^5F_3,3$ as well as Ho$^{3+}:^5F_4$ and Tm$^{3+}:^5G_4$ possessing small energy differences between them (compare in Fig. 2). Thus, a quasi-resonant ET Ho$^{3+} \rightarrow$ Tm$^{3+}$, e.g. Ho$^{3+}:^5F_3 \rightarrow$ Tm$^{3+}:^5F_{2,3}$ and next multiphonon non-radiative transitions (NRTs) to the Ho$^{3+}:^5I_1$ and Tm$^{3+}:^5H_4$: levels could be taken into account (see right part of the diagram in Fig. 2). In this case population of the Tm$^{3+}:^3G_4$ state can be reached in the three-photon processes as follows: Yb$^{3+}:^2F_{7/2} \rightarrow$ GSA Yb$^{3+}:^2F_{5/2} \rightarrow$ ESA Ho$^{3+}:^5I_6 \rightarrow$ NRT Ho$^{3+}:^5I_1 \rightarrow$ ESA Ho$^{3+}:^5F_5 \rightarrow$ ET Tm$^{3+}:^5F_{2,3} \rightarrow$ NRT Tm$^{3+}:^5H_4 \rightarrow$ ESA Tm$^{3+}:^3G_4$. The other observed bands are assigned to the same Ho$^{3+}$ electronic transitions as in the doubly co-doped samples YAG:YbHo and YAG:YbHo@SiO2 (Fig. 1A).28

The material consisting of the triply co-doped YAG nanocrystals (YAG:YbTmHo) embedded into silica (YAG:YbTmHo@SiO2) was excited under 355 nm, i.e. the excitation wavelength typical for Tm$^{3+}$, Ho$^{3+}$ ions and additionally for silica matrix (see Fig. 3). The appropriate emission spectra of the YAG:YbTmHo@SiO2 phosphor dried at 200 °C and then calcined at 600, 800 and 1000 °C are demonstrated in Fig. 3. Characteristic feature of the spectra is a band wing penetrated deeply from UV into the visible range. This wing is the long wavelength part of the spectrum (Fig. 3, inset) attributed to...
Electronic transitions between structural defect levels of amorphous SiO₂. Emission lines of Tm³⁺ and Ho³⁺ are observed against the wing background. The distinct Ho³⁺ bands attributed to S₂, F₄ → I₈ (peaked at 541 nm, 18 484 cm⁻¹) and G₄ → I₈ (at 585 nm, 17 094 cm⁻¹) transitions are present only in the spectra of the material thermally treated in the 200–800 °C range (curves a–c). While the Ho³⁺ bands centered at 466 nm (21 459 cm⁻¹) and 771 nm (12 970 cm⁻¹) ascribed to K₈ → I₈ and S₃₁, F₄ → I₁ transitions, respectively, are present also after calcination at 1000 °C (curve d). The Tm³⁺ bands corresponding to D₂ → F₄ (466 nm, 21 459 cm⁻¹), G₄ → H₆ (491, 20 367), G₄ → F₄ (608, 16 447) and H₄ → H₆ (832, 12 019) transitions are also present in all the spectra (a–d). One can assume that the faint red emission related to the S₂, F₄ → I₁ transition of Ho³⁺ is present by additional population for the (S₂, F₄) levels by energy transfer from Tm³⁺ to Ho³⁺ ions. However, the Ho³⁺ band quenching in range between 530 and 600 nm signifies that the Tm³⁺ → Ho³⁺ energy transfer in the material thermally treated at 1000 °C did not exist in this case. The set of the emission lines of Tm³⁺ and Ho³⁺ bands. When the sample is excited under 290 nm (see curve a), among the lines there are four most intensive bands, viz. the resultant emission band peaked at 371 nm (26 963 cm⁻¹) attributed to Tm³⁺:1D₂ → 3H₄ and Ho³⁺:3H₆ → 3I₈ transitions. The next band placed at 466 nm (21 459 cm⁻¹) is a result of overlapping three bands related to both transitions of Tm³⁺:1D₂ → 3F₄ and 1G₄ → 3H₆ as well as the Ho³⁺:3K₈ → 3I₈ transition. Whereas lines centered at 652 (15 337 cm⁻¹) and 736 nm (13 592 cm⁻¹) are owing to the 1G₄ → 3F₄ transition of Tm³⁺ and the S₂, F₄ → I₁ transitions of Ho³⁺, respectively.

**Time-resolved luminescence**

To obtain time-resolved spectra, the YAG:Yb:Tm:Ho@SiO₂ nanocomposite was excited using of a YAG:Nd laser and system OPG (see Apparatus). The apparatus allows to integrate luminescence in the 0–200 µs time interval. The spectra are collected in Fig. 5. Obviously, they are superpositions consisting of Tm³⁺ and Ho³⁺ bands. When the sample is excited under 290 nm (see curve a), among the lines there are four most intensive bands, viz. the resultant emission band peaked at 371 nm (26 963 cm⁻¹) attributed to Tm³⁺:1D₂ → 3H₄ and Ho³⁺:3H₆ → 3I₈ transitions. The next band placed at 466 nm (21 459 cm⁻¹) is a result of overlapping three bands related to both transitions of Tm³⁺:1D₂ → 3F₄ and 1G₄ → 3H₆ as well as the Ho³⁺:3K₈ → 3I₈ transition. Whereas lines centered at 652 (15 337 cm⁻¹) and 736 nm (13 592 cm⁻¹) are owing to the 1G₄ → 3F₄ transition of Tm³⁺ and the S₂, F₄ → I₁ transitions of Ho³⁺, respectively.

Fig. 3 Steady-state emission spectra of the YAG:Yb:Tm:Ho@SiO₂ nanocomposite excited under 355 nm after drying at (a) 200 °C and calcined at: (b) 600, (c) 800 and (d) 1000 °C for 3 h. Inset presents emission spectrum of SiO₂ xerogel dried at 200 °C and excited under 355 nm.

Fig. 4 Excitation spectrum of the YAG:Yb:Tm:Ho@SiO₂ nanocomposite monitored at 466 nm. The nanocomposite was calcined at 600 °C for 3 h. The inset demonstrates excitation spectrum of pure SiO₂ glass monitored at 440 nm. The arrows indicate the excitation wavelengths (290 and 355 nm) used in steady-state condition.

Fig. 5 Time-resolved emission spectra of the YAG:Yb:Tm:Ho@SiO₂ calcined at 600 °C for 3 h. The material was excited by the pulse laser under: (a) 290 and (b) 355 nm and the luminescence was integrated for the time interval 0–200 µs.
Similar bands or their traces are present in the emission spectrum excited under 355 nm (see Fig. 5, curve b). However, mutual intensity ratios of the bands are quite other and two lines centered at ca. 615 nm (16,345 cm\(^{-1}\)) are absent in comparison to the spectrum excited under 290 nm (curve a). Moreover, the spectrum (curve b) differs from the emission spectrum excited under the same wavelength but in steady-state condition (see Fig. 3, curve b).

Photoluminescence lifetime measurements for YAG:Yb,Tm,Ho@SiO\(_2\) were performed by the pulsed laser under excitation at 290 nm (see decay curves in Fig. 6). The average lifetime values for electronic transitions related to the four most intense lines mentioned above (see Fig. 5) are presented in Table 1. The average decay times \(\tau_{av}\) were evaluated using the equation:

\[
\tau_{av} = \frac{\int I(t)dt}{\int I(t)dt}
\]  

where \(I(t)\) is the emission intensity at time \(t\).

Calculated average decay times \(\tau_{av}\) of the above mentioned transitions are listed in Table 1 for \(\lambda_{exc} = 290\) and 355 nm. One notes that independently on the excitation wavelength the decay times demonstrate approximate values for the observed transitions in both lanthanide dopants of YAG nanoparticles incorporated into silica matrix.

In much shorter time interval (0–50 ns) and under 290 nm excitation was observed for the YAG:Yb,Tm,Ho@SiO\(_2\) only a time-resolved spectrum of the vitreous silica matrix (Fig. 7). The spectrum consists of a strong and broad emission band centered at ca. 440 nm (22,738 cm\(^{-1}\)). Its origin is attributed to photon recombinations from numerous defects (as dangling bonds) in the amorphous silica.\(^\text{29,30}\)

The measured decay profile of the silica luminescence under excitation by the pulse laser at 290 nm is shown in Fig. 8. The curve allows to estimate average emission decay time value for silica equal to 5.6 ± 0.6 ns.

### Table 1

<table>
<thead>
<tr>
<th>Ln(^{3+})</th>
<th>Transition</th>
<th>(\lambda_{exc}/\text{nm})</th>
<th>Average decay time (\tau_{av}/\mu\text{s})</th>
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<tbody>
<tr>
<td>Tm(^{3+})</td>
<td>(1\text{D}_2 \rightarrow 1\text{H}_6)</td>
<td>290</td>
<td>41 ± 3</td>
</tr>
<tr>
<td>Tm(^{3+})</td>
<td>(1\text{G}_4 \rightarrow 1\text{I}_6)</td>
<td>355</td>
<td>30 ± 2</td>
</tr>
<tr>
<td>Ho(^{3+})</td>
<td>(4\text{G}_4 \rightarrow 4\text{I}_5)</td>
<td>290</td>
<td>33 ± 2</td>
</tr>
<tr>
<td>Ho(^{3+})</td>
<td>(5\text{S}_2, 5\text{F}_4 \rightarrow 5\text{I}_7)</td>
<td>355</td>
<td>36 ± 3</td>
</tr>
</tbody>
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Fig. 7 Time-resolved emission spectrum of the YAG:Yb,Tm,Ho@SiO\(_2\) nano-composite calcined at 600 °C for 3 h and excited at 290 nm by the pulse laser. The luminescence was integrated in the time interval 0–50 ns.

**Chromaticity**

The emission spectra of the YAG:Yb,Tm,Ho@SiO\(_2\) glass-nanocomposite under different excitation wavelengths and luminescence techniques (such as the steady state and pulse laser measurements) are demonstrated in Fig. 9. Under the 355 nm excitation (curve a) in the steady-state condition, the nanocomposite material emits simultaneously reddish, green...
and blue (RGB) luminescent light (see Fig. 3 curve b). The emissions are ascribed to the transitions of $\text{Tm}^{3+}$ and $\text{Ho}^{3+}$ ions, while blue emission is especially intense due to electronic transition in silica (see Fig. 3, inset). The up-conversion spectrum (curve b) obtained under 980 nm excitation by the laser in steady-state condition supply with red, green and bluish green light owing to the transitions of $\text{Tm}^{3+}$ and $\text{Ho}^{3+}$ ions (compare Fig. 1B). On the other hand, under excitations 355 and 290 nm by the pulse laser (curves c and d, respectively) also the both lanthanide ions are responsible for the emission in visible range. However, the 355 nm excitations delivers only red and blue emission (Fig. 5, curve b), while under 290 nm excitation is observed light consisting of emissions of primary colours (RGB) (Fig. 5, curve a).

The CIE chromaticity coordinates and diagram of YAG:YbTmHo@SiO$_2$ under the different excitation wavelengths and luminescent techniques are presented in Table 2 and Fig. 10, respectively. The luminescent nanocomposite emits cold white light with bluish tone (point A), when excited by 355 nm in steady-state condition. In this case the correlated colour temperature ($T_{cc}$) is rather high (ca. 8100 K). Whereas the up-conversion emission (point B) excited at 980 nm in the same condition is white and its $T_{cc}$ = 4800 K is in between temperatures of mean noon sunlight and household tungsten-filament light bulb (100 W). Both the emissions excited under 290 and 355 nm by pulse laser emitted blue light which $T_{cc}$ values in the former case (point D) is equal to 14 000 K but in the latter case (point C) $T_{cc}$ is too high to evaluate them.

### Conclusions

The glass nanocomposite, i.e. nanocrystalline YAG co-doped with $\text{Yb}^{3+}$, $\text{Tm}^{3+}$ and $\text{Ho}^{3+}$ entrapped in glassy silica (YAG:YbTmHo@SiO$_2$), was successively prepared by sol–gel method. Presence of the specific lanthanide ions such as $\text{Yb}^{3+}$, $\text{Tm}^{3+}$ and $\text{Ho}^{3+}$ in the nanocomposite allows to observe up-conversion effect, when the composite sample was excited under 980 nm in steady-state condition. Other steady-state emission was also recorded, when $\lambda_{\text{exc}}$ = 355 nm. The nanocomposite material excited by pulse laser shows dissimilar time-resolved luminescence spectra for different excitation wavelengths ($\lambda_{\text{exc}}$ = 290 and 355 nm). Luminescence property based on up-conversion effect of the glass-nanocomposite excited under 980 nm in steady-state condition allows to recognize the material as a white phosphor candidate.

### Conflicts of interest

There are no conflicts to declare.

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**Table 2** The CIE coordinates of the YAG:YbTmHo@SiO$_2$ glass-nanocomposite calcined at 600 °C for 3 h

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X$</th>
<th>$Y$</th>
<th>$T_{cc}$ K</th>
<th>$\lambda_{\text{exc}}$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.300</td>
<td>0.307</td>
<td>8100</td>
<td>355</td>
</tr>
<tr>
<td>B</td>
<td>0.359</td>
<td>0.351</td>
<td>4800</td>
<td>980</td>
</tr>
<tr>
<td>C</td>
<td>0.194</td>
<td>0.191</td>
<td>$-$</td>
<td>$355^b$</td>
</tr>
<tr>
<td>D</td>
<td>0.260</td>
<td>0.282</td>
<td>14 000</td>
<td>290$^b$</td>
</tr>
</tbody>
</table>

$^a$ Impossible to evaluate due to high $T_{cc}$. $^b$ Excited by the pulse laser.
References