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ARTICLE

Up-conversion white emission and other luminescence properties of a YAG:Yb_2O_3·Tm_2O_3·Ho_2O_3@SiO_2 glass-nanocomposite

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S1. Results and discussion

XRD patterns

In Fig. S1 are collected XRD patterns of the studied materials. The diffraction peaks of the pure YAG (curve a), YAG doped with 6 mol.% Yb^{3+} (YAG:Yb, curve b) and YAG triply co-doped with Yb^{3+}, Tm^{3+} and Ho^{3+} (YAG:YbTmHo, curve c) dried at 200 °C. The peak appearing at the angle 50.35° is an instrument error. The average crystallite size was calculated using the Scherrer formula: $D_{hkl} = K \cdot \lambda / (\beta \cdot \cos\vartheta)$, where K is a constant equal to 0.89, λ - X-ray wavelength equal to 0.15405 nm, β is the full-width at half-peak maximum, ϑ - the diffraction angle and D_{hkl} is the crystallite size along [hkl] direction. The nanocrystal size (D) was calculated mainly from the XRD peaks related to (420), (422) and (532) planes at 2θ = 33.52, 36.75 and 46.77°, respectively. The average size of the nanocrystals was equal to 27±4 nm.

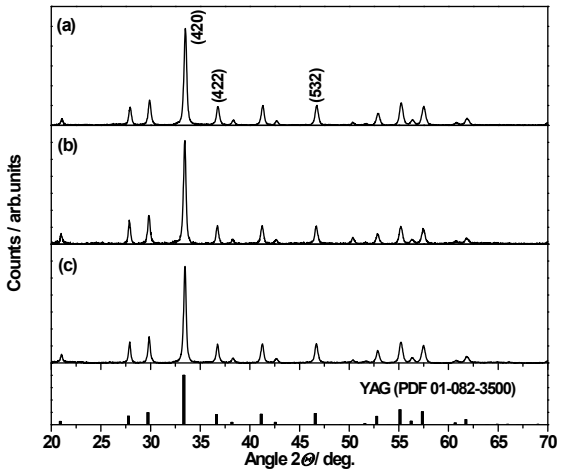

Fig. S1 XRD patterns of: (a) YAG, (b) YAG:Yb and (c) YAG:YbTmHo dried at 200 °C. Small peak at 50.35° is an instrument error.

XRD pattern of the YAG:YbTmHo@SiO_2 nanocomposite firstly dried at 200 °C and then calcined at 600, 800 and 1000 °C are shown in Fig. S2. The patterns are in accordance with YAG standard data.

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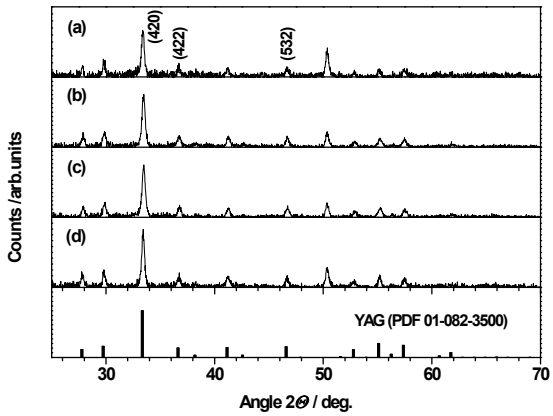

Fig. S2 XRD patterns of the triply co-doped YAG:YbTmHo@SiO_2 dried at (a) 200 °C and calcined at (b) 600, 800 and 1000 °C. Peak at 50.35° is an instrument error.

Tab. S1 Size of the triply co-doped YAG:YbTmHo nanocrystals incorporated into the silica matrix as well as crystallinity of this YAG:YbTmHo@SiO_2 nanocomposite (in per cent) after thermal treatment

Characteristics of samples	Thermal treatment temperature / °C			
	200	600	800	1000
Crystallite size *D* / nm	31±5	26±4	27±4	28±4
Crystallinity *C* / %	54	65	64	53

As previously the (420), (422) and (532) crystal planes were used to calculate size (*D*) of the thermally treated YAG:YbTmHo nanocrystals immobilized in SiO_2 matrix. The average crystallite sizes of the triply co-doped YAG nanoparticles in the thermally treated nanocomposite are collected in Tab. S1. The sizes within experimental error are close to the crystallite size of the guest (un-doped), doubly and triply co-doped YAG nanoparticles. Besides the crystallinity percentage of the samples was calculated using simple method based on the comparison of the areas of diffraction peaks and background in the collected diffraction patterns. Since the calculated areas are a function of several factors, the obtained values (see Tab. S1) serve only as estimated ones.

SEM images

Fig. S3 shows SEM micrographs registered for the pure YAG (image a) and doped YAG:Yb (image b) samples. The images of lower enlargements show agglomerates consisting of grains. Then size of the nanocrystalline grains can be estimated in inserts (images of greater magnification) to be *ca*. 30 nm.

The YAG nanocrystals co-doped with Yb^{3+}, Tm^{3+} and Ho^{3+} ions as well as capped by SiO_2 xerogel layer as the YAG:YbTmHo@SiO_2 nanocomposite demonstrate in the SEM image of lower magnification (Fig. S4) powder consisting of agglomerated sphere-like particles. However, the greater enlargement image exhibits that in the agglomerates are present sphere-like nanoparticles of above two-fold greater size than size of the YAG nanocrystals (see Fig. S3).

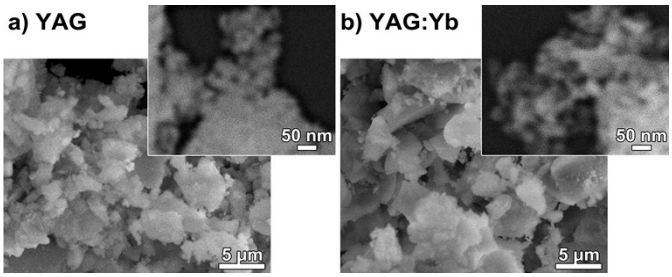

Fig. S3 SEM micrographs of: (a) YAG and (b) YAG:Yb grains. The samples dried at 200°C.

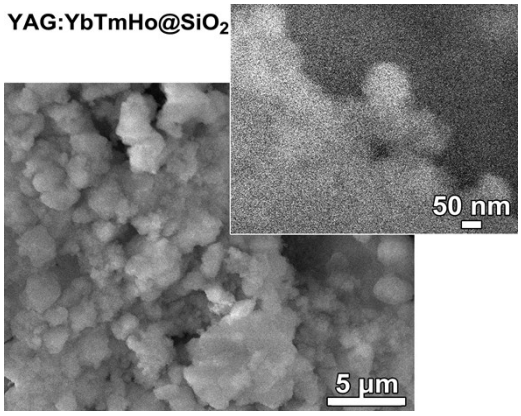

Fig. S4. SEM image of the YAG:YbTmHo@SiO_2 glass nanocomposite calcined at 600°C.

EDS and XPS measurements

The EDS spectra of the un-doped YAG and YAG:Yb samples are illustrated in Fig. S5. In the plot (a) are present all of the as-designed elements Y, Al and O evidently noticed for the un-doped (host) sample. While the spectrum (b) of the YAG:Yb clearly exhibits the anticipated presence of the Yb. The EDS spectra did not detect any other impurities in the samples. Besides this spectroscopy also allows to approximate the reciprocal atomic ratios (see inserts in Fig. S5).

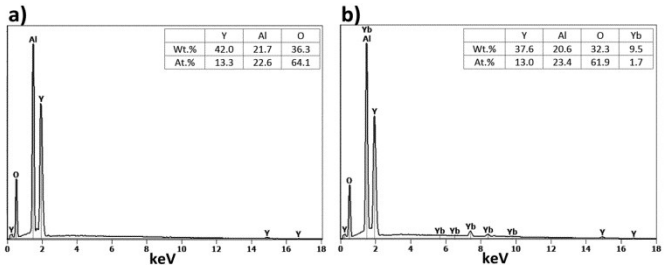

Fig. S5. The EDS spectra of: (a) YAG host and YAG:Yb nanocrystalline samples dried at 200°C.

High-resolution XPS results of the pure YAG and YAG:Yb samples in the energy range of Y 3d, Yb 4d, Al 2p and O 1s region are presented on Fig. S6. Each investigated sample has been analysed after 50 s of ion beam etching to remove the carbon and oxygen contamination present due to exposure of samples to atmospheric air as well as to represent the investigated sample as closely as possible and The location of yttrium, aluminum and oxygen peaks corroborate with the literature data available for YAG.[1-3] Their location and contribution values in the spectra are collected in Tab. S2. The Y 3d and Al 2p spectra are composed of one peak doublet, while two separate chemical states were observed for O 1s spectra. Then the peak located at 530.1 eV corresponds to yttrium aluminum perovskite $YAlO_3$ and the second, smaller peak at 531.5 eV is ascribed to oxidized Y or Al, usually in a form of Al_2O_3 or $Y(OH)_3$. High-resolution analysis in the energy range of ytterbium revealed Yb $4d_{5/2}$ peak at the energy range 184.9 eV that originates from Yb^{3+}.[3] Its share is relatively low (~0.2 at.%). The Y/Al/O ratio calculated for both samples are listed in Tab. S2.

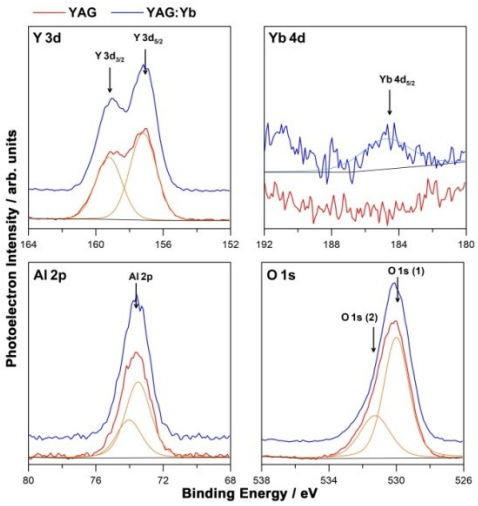

Fig. S5 High-resolution XPS spectra recorded for Y 3d, Yb 4d, Al 2p and O 1s energy range for: YAG (red line) and YAG:Yb (blue line). The samples were dried at 200°C.

Tab. S2 Contribution of elements in the pure YAG and YAG:Yb nanocrystals calculated by high-resolution XPS analysis**.** The samples dried at 200°C.

Sample	Y $3d_{5/2}$	Al $2p_{3/2}$	O 1s (1)	O 1s (2)	Yb $4d_{5/2}$
YAG / atom.%	14.3	30.3	38.8	16.6	---
YAG:Yb / atom. %	14.3	28.9	45.2	11.4	0.2

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