Structural, optical and magnetic properties of $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$ (0<x<0.20) nanocrystals: effect of Yb content

Izabela Kamińska[1], Dawid Jankowski[2], Bożena Sikora[1], Przemysław Kowalik[1], Roman Minikayev[1], Tomasz Wojciechowski[1,3], Michał Chojnacki[1], Kamil Sobczak[4], Jarosław Rybusiński[5], Jacek Szczytko[5], Karolina Zajdel[6], Andrzej Suchocki[1,7], Wojciech Paszkowicz[1], Małgorzata Frontczak-Baniewicz[6] and Krzysztof Fronc[1]

[1]Institute of Physics Polish Academy of Sciences, al. Lotników 32/46, Warsaw 02-668, Poland
[2]Research Foundation Baltic Institute of Technology, al. Zwycięstwa 96/98, 81-451 Gdynia, Poland
[3]International Research Centre MagTop, al. Lotników 32/46, Warsaw 02-668, Poland
[4]University ofWarsaw Biological and Chemical Research Centre, Żwirki iWigury 101,Warsaw 02-089, Poland
[5]Institute of Experimental Physics, Faculty of Physics, University of Warsaw, Warsaw, Poland
[6]Mossakowski Medical Research Centre Polish Academy of Sciences, Pawińskiego 5, Warsaw 02-106, Poland
[7] Institute of Physics, Kazimierz Wielki University, Weyssenhoffa 11, 85-072, Bydgoszcz, Poland
emial: ikaminska@ifpan.edu.pl

INTRODUCTION

The paramagnetic $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$ (x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20) nanocrystals (NCs) were synthesized by the microwave-induced solution combustion method. The XRD, TEM and SEM techniques were applied to determine the NCs' structures and sizes. The XRD patterns confirmed that the NCs have for the most part a regular structure of the Y_3Al_5O12 (YAG) phase. The changes of the distance between donor Yb^{3+} (sensitizer) and acceptor Er^{3+} (activator) were realized by changing the donor's concentration with a constant amount of acceptor. Under 980 nm excitation, at room temperature, the NCs exhibited strong red emission near 660 and 675 nm, and green upconversion emission at 550 nm, corresponding to the intra 4f transitions of Er^{3+} ($^4F_{9/2}$, $^2H_{11/2}$, $^4S_{3/2}$)→Er3+ ($^4I_{15/2}$). The strongest emission was observed in a sample containing 18% Yb^{3+} ions. The red and green emission intensities are respectively about 5 and 12 times higher as compared to NCs doped with 2% of Yb^{3+} . In order to prove that the main factor responsible for the increase of the upconversion luminescence efficiency is reduction of the distance between Yb^{3+} and Er^{3+}, we examined, for the first time the influence of hydrostatic pressure on luminescence and luminescence decay time of the radiative transitions inside donor ion. The decrease of both luminescence intensity and luminescence decay times, with increasing hydrostatic pressure was observed. After applying hydrostatic pressure to samples with e.g. 2% and 6% Yb^{3+}, the distance between the donor and acceptor decreases. However, for higher concentrations of the donor, this distance is smaller, and this leads to the effective energy transfer to Er^{3+} ions. With increasing pressure, the maximum intensity of near infrared emission is observed at 1029, 1038 and 1047 nm, what corresponds to $^2F_{5/2}$→$^2F_{7/2}$ transition of Yb^{3+} [1].

[1] I. Kamińska , D. Jankowski, B. Sikora, P. Kowalik, R. Minikayev, T. Wojciechowski, M. Chojnacki, K.Sobczak, J. Rybusiński, J. Szczytko, K. Zajdel, A. Suchocki, W. Paszkowicz, M. Frontczak-Baniewicz, K. Fronc, Structural, optical and magnetic properties of $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$ (0<x<0.20) nanocrystals: effect of Yb content, *Nanotechnology* 31 (2020) 225711 (14pp).

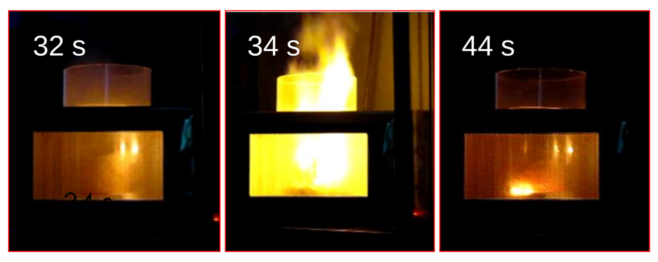
NANOPARTICLE SYNTHESIS

MICROWAVE SOLUTION COMBUSTION

REDUCER	OXIDANTS
$CO(NH_2)_2$	$Y(NO_3)_3 \cdot 6H_2O$ $Al(NO_3)_3 \cdot 9H_2O$ $Er(NO_3)_3 \cdot 5H_2O$ $Yb(NO_3)_3 \cdot 5H_2O$

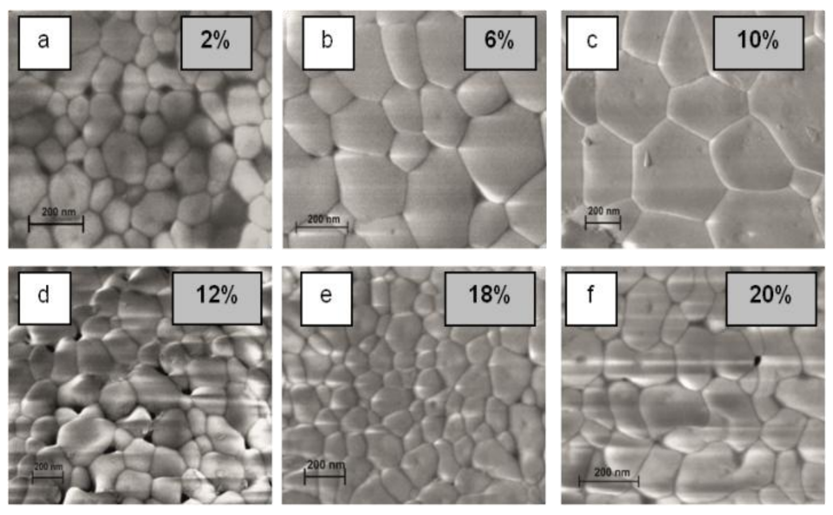
$$3Y(NO_3)_3 + 5Al(NO_3)_3 + 20CO(NH_2)_2 = Y_3Al_5O_{12} + 20CO_2 + 40\,H_2O + 32\,N_2$$

Reaction: about 10 minutes,
700°C- spontaneous combustion of the mixture- 30s
Reaction temperature - 1500 °C

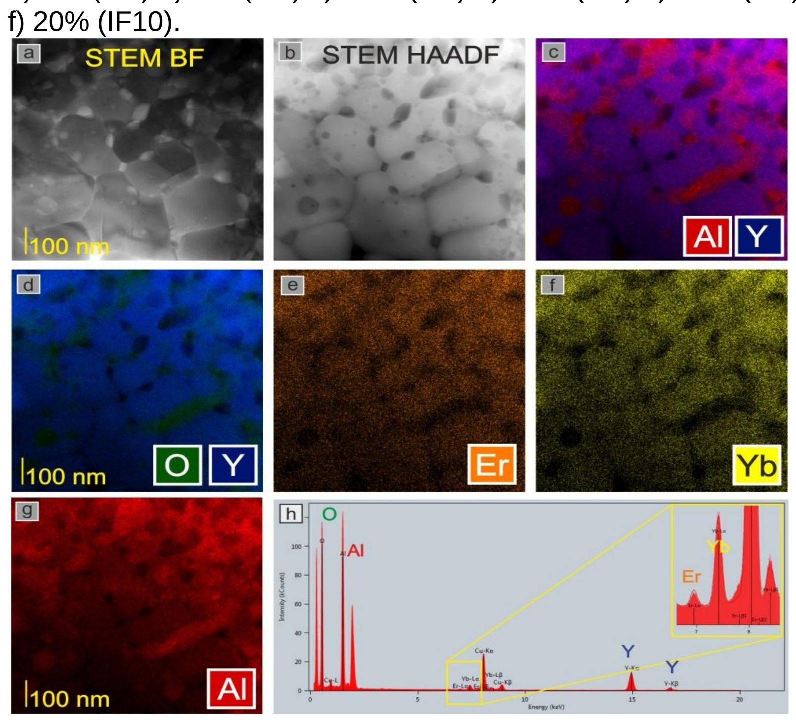


Combustion synthesis in a microwave oven over time: 32s, 34s, 44s.

NANOPARTICLE SIZE BY SCANNING and TRANSMISSION ELECTRON MICROSCOPY

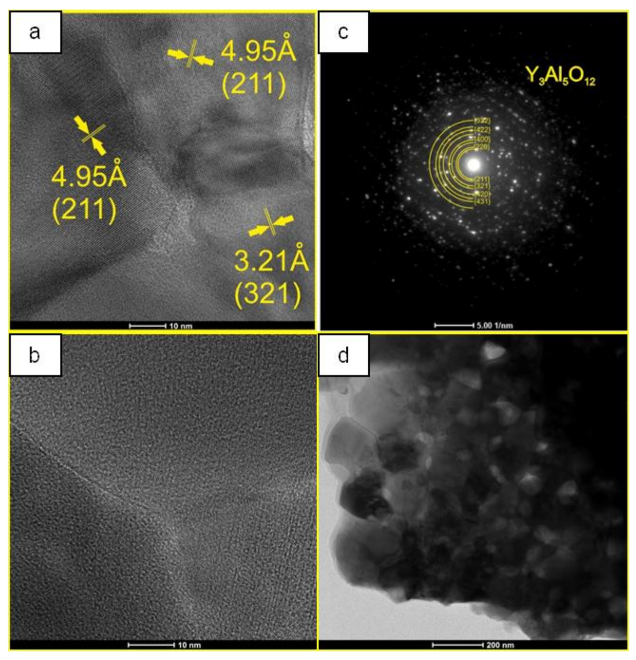


The SEM images of $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$ (x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20) with different concentration of Yb^{3+} ions: a) 2% (IF5) b) 6% (IF6) c) 10% (IF7) d) 12% (IF8) e) 18% (IF9) f) 20% (IF10).



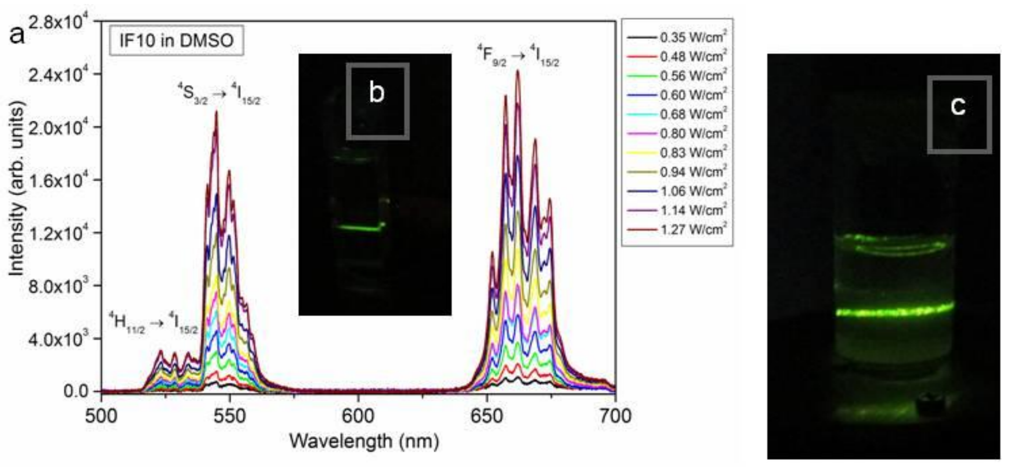
STEM images (a) in bright field and (b) in HAADF of $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$, x = 0.20 (IF10) NCs. The element mappings of (c) Al and Y (d) O and Y (e) Er (f) Yb and (g) Al of the NCs. (h) Confirmed presence of Er^{3+} and Yb^{3+} ions in the EDX spectra of the NCs matrix.

HRTEM

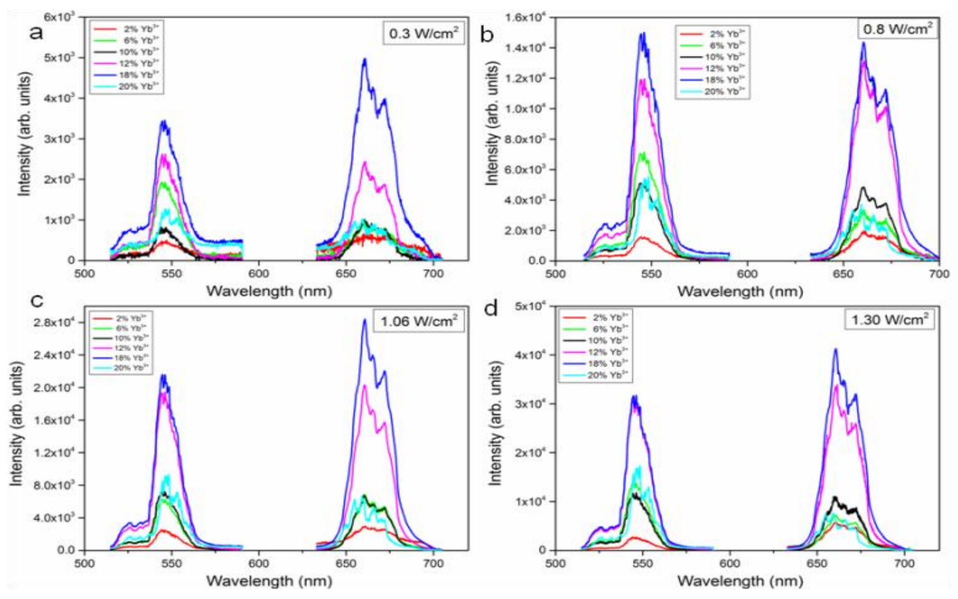


(a, b) HRTEM images of $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$, x = 0.20 (IF10) NCs and (c) electron diffraction pattern corresponding to the cubic crystal structure of the nanostructures. d) TEM image of the NCs.

PHOTOLUMINESCENCE OF NPs SUSPENDED IN DMSO AND POWDER FORM

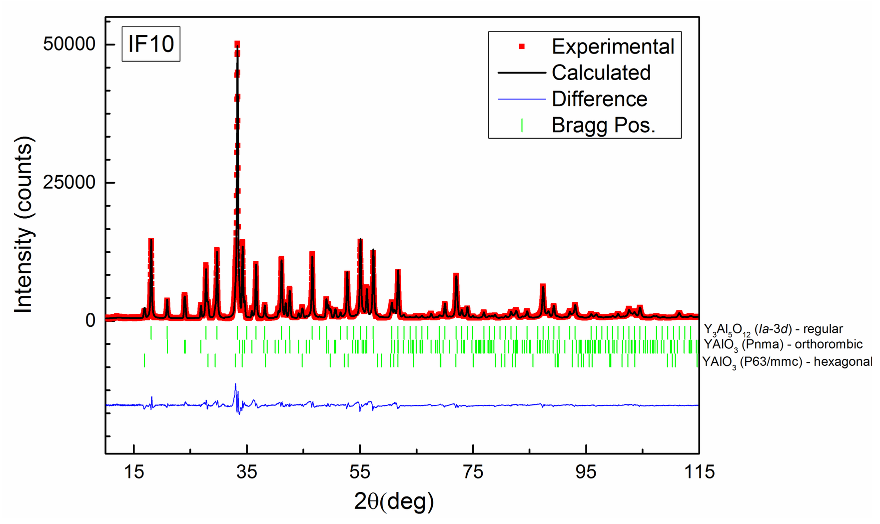


(a) Upconversion luminescence spectra of $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$, x = 0.20 (IF10) NCs in the DMSO solution as a function of the power densities. Insets: (b-c) Green-emitting UCNCs in DMSO solution when excited with a 980 nm diode laser (CW) (laser power density ~1.3 $W \cdot cm^{-2}$). The concentration of the NCs was 2 $mg \cdot ml^{-1}$.



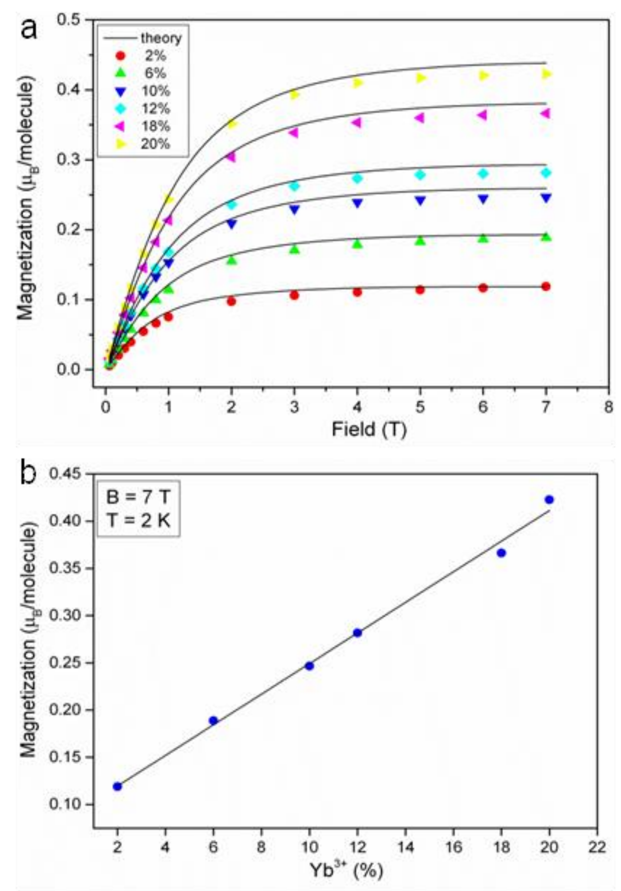
The upconversion spectra of six $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$ (x = 0.02, 0.06, 0.10, 0.12, 0.18, 0.20) samples (in powder form) under the 980 nm laser excitation for four selected laser power densities (CW): a) 0.30 $W \cdot cm^{-2}$ b) 0.80 $W \cdot cm^{-2}$ c) 1.06 $W \cdot cm^{-2}$ and d) 1.30 $W \cdot cm^{-2}$.

X-RAY DIFFRACTION

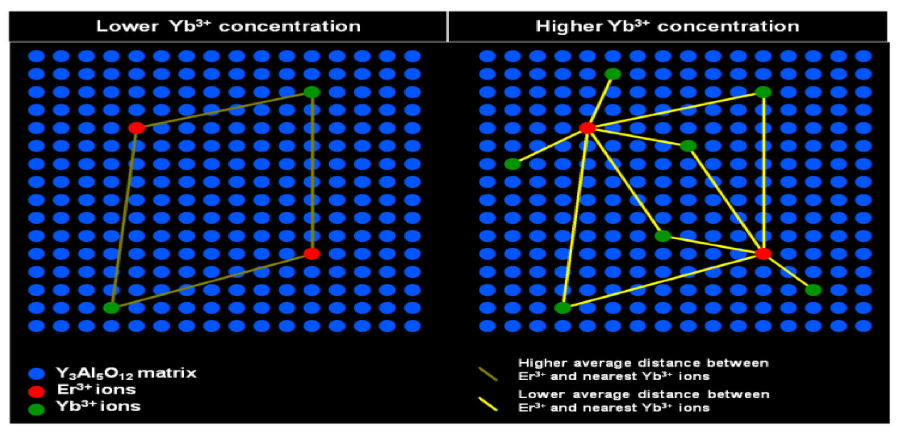


Rietveld refinement for $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$ (0<x<0.20) NCs with different Yb^{3+} concentrations a) 20% (IF10)

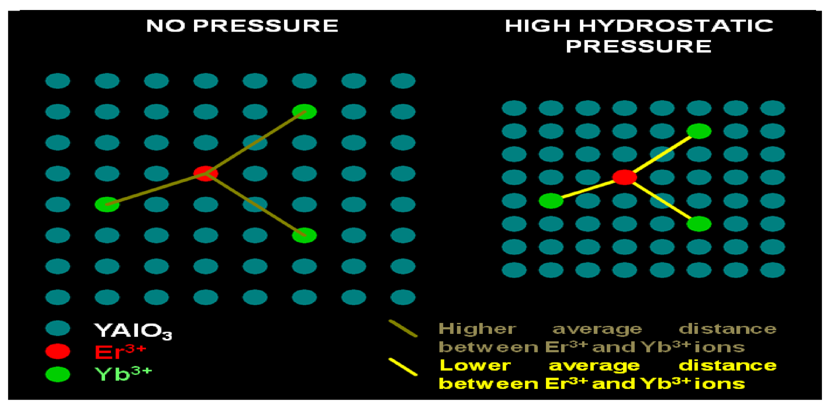
MAGNETIC PROPERTIES OF $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$ (0<x<0.20) NCs



(a) Magnetization at T = 2.0 K as a function of magnetic field for different ytterbium concentrations. Theoretical magnetization curves are marked with the line. (b) Magnetization at T = 2.0 K, B = 7.0 T as a function of concentration of Yb^{3+} dopant.

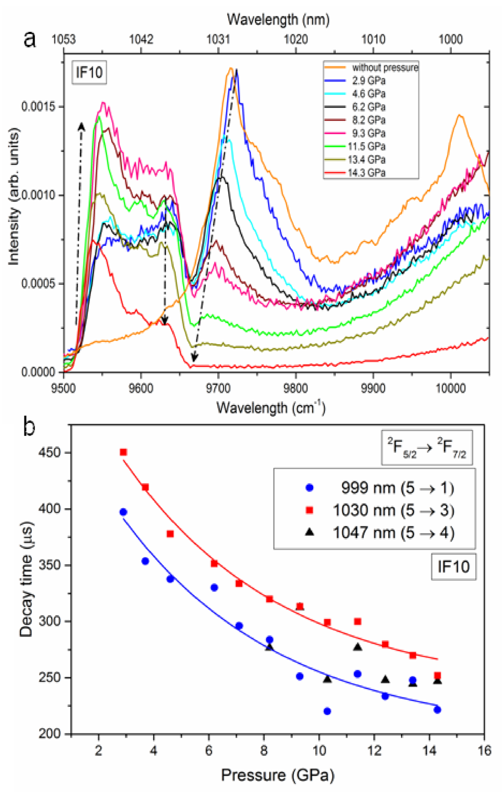


The effect of increasing the Yb^{3+} concentration on the reduction of the average distance between Er^{3+} and Yb^{3+} ions.

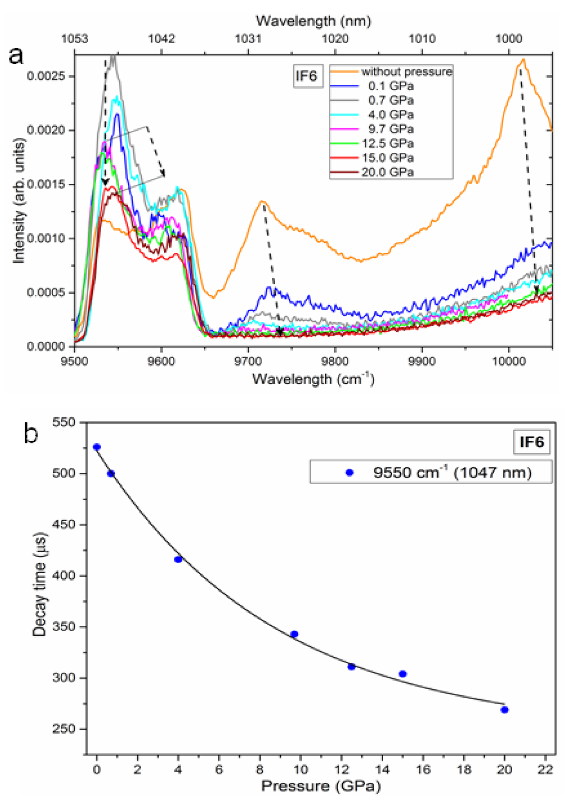


The influence of the hydrostatic pressure on the average distance between Yb^{3+}- Er^{3+} ions.

HIGH-PRESSURE LUMINESCENCE



(a) Pressure dependence of $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$, x = 0.2 (IF10) nanostructures on emission spectra at room temperature. (b) Pressure dependence of the luminescence decay times of Yb^{3+} ions in the NCs. The nanostructures were excited by the 940 nm diode pumped solid state *laser, continuous mode, P_{out}>100 mW.* The argon was used as a pressure-transmitting medium.



(a) Pressure dependence of emission spectra at room temperature for 6% Yb^{3+} doped $Y_{3-0.02-x}Er_{0.02}Yb_xAl_5O_{12}$, x =0.06 (IF6) nanostructures.
(b) Pressure dependence of the luminescence decay times of Yb^{3+} ions in the NCs. The nanostructures excited by the 940 nm diode pumped solid state laser, continuous mode, *P_{out}>100 mW.* The oil was used as a pressure-transmitting medium.

CONCLUSIONS

The YAG NCs are a good candidate for nanoscintillators and lasers. The material is ideal host for the Er^{3+} and Yb^{3+} doping.

The NCs exhibited the visible luminescence at 530 nm ($^2H_{11/2}/^4S_{3/2} \rightarrow {}^4I_{15/2}$) and 660 nm ($^4I_{11/2} \rightarrow {}^4I_{15/2}$) in the organic environment.

We observed a 12-fold (550 nm) and a 9.5-fold (660 nm) increase of luminescence intensity in the NCs, compared to the lowest concentration of Yb^{3+} ions for the continuous wave laser excitation at 980 nm (1.27 $W \cdot cm^{-2}$ and 1.06 $W \cdot cm^{-2}$), respectively.

This emission arose from a two-photon upconversion process.

The average distance between Yb^{3+}-Er^{3+} for the optimum Yb^{3+} doping concentration (18%) in the NCs is 3.6766Å. The study confirm that the main factor responsible for the enhancement of the efficiency of the upconversion luminescence is reducing the Yb^{3+}-Er^{3+} distance.

The effects of the hydrostatic pressure on the decay time of emitting $^2F_{5/2}$ level for the x = 0.20 has been observed. It has shortened from 397 ± 4 μs to 221 ± 2 μs (999 nm) and from 450 ± 2 μs to 252 ± 1 μs (1030 nm) (at the pressure of about 14 GPa).

At the same time, as the pressure increases, we observe a drop of the intensity of the luminescence of the Yb^{3+} ions. Both these facts suggest the increase of the non-radiative processes with the increase of the hydrostatic pressure and thus decrease of the inter-ionic distances.

Thru analogy with the experiments with increasing the Yb^{3+} dopant concentration, where decrease of the average distances between ions leads to the increase of energy transfer between Yb^{3+} (donor) and Er^{3+} (acceptor) we can postulate, that the increase of the non-radiative processes caused by the pressure have the same mechanism.

Magnetization of examined up-converting NCs increases linearly with Yb^{3+} dopant concentration, as expected for a paramagnetic system, where ion-ion interaction can be neglected.

Acknowledgements

The research was partially financed by the project Sonata from the National Science Centre, UMO-2014/15/D/ST5/02604.The study was carried out at the Biological and Chemical Research Centre, University of Warsaw, established within the project co-financed by European Union from the European Regional Development Fund under the Operational Programme Innovative Economy, 2007 – 2013, Panda2 nr 501-D312-56-0000002 and Miniatura 2017/01/X/ST3/01380. This work has been done in the NanoFun laboratories co-financed by the European Regional Development Fund within the Innovation Economy Operational Program, the Project No. POIG.02.02.00-00-025/09/.