Optica Applicata, Vol. XLI, No. 2, 2011

Spectroscopic investigations of rare-earth materials for luminescent solar concentrators

Anna KOZŁOWSKA[1*], Magdalena NAKIELSKA[1], Jerzy SARNECKI[1], Ludwika LIPIŃSKA[1], Olgierd JEREMIASZ[2], Dariusz PODNIESIŃSKI[3], Andrzej MALĄG[1]

[1] Institute of Electronic Materials Technology, Wólczyńska 133, 09-919 Warsaw, Poland

[2] Abraxas, Piaskowa 27, 44-300 Wodzisław Śląski, Poland

[3] Institute of Optoelectronics, Military University of Technology,
Kaliskiego 2, 00-908 Warsaw, Poland

[*] Corresponding author: Anna.Kozlowska@itme.edu.pl

The spectroscopic analysis of materials for luminescent solar concentrators (LSC) is presented. The samples of polymethyl mathacrylate (PMMA) polymer matrix containing nanocrystals Nd,Yb:$Y_3Al_5O_{12}$ (Nd,Yb:YAG), Nd,Yb:$Gd_3Ga_5O_{12}$ (Nd,Yb:GGG) and Nd,Yb:Y_2O_3 (Nd,Yb:YO) were prepared. The nanocrystals were obtained via the (Pechini) modified sol–gel method. Spectroscopic investigations were performed for the nanocrystals before and after incorporating them in LSC plates. In the experiment, two diode lasers (DL) were used as excitation sources: DL operating at 808 nm to excite Nd^{3+} ions and DL operating at 976 nm for direct excitation of Yb^{3+} ions. Strong fluorescence signal from Yb^{3+} ions by 808 nm excitation proved an efficient energy transfer from Nd^{3+} to Yb^{3+} ions. The spectroscopic results indicate the successful incorporation of nanosized crystals into PMMA matrix. The best effects were obtained for Nd,Yb:YAG and Nd,Yb:GGG nanocrystals. Presented results show that polymer materials with nanocrystals doped by rare earth ions are promising solution for photovoltaic applications offering stability and emission in the spectral range matched to the maximum sensitivity of a silicon solar cell.

Keywords: solar concentrator, photovoltaics, solar cell, luminescent materials, rare earth ions.

1. Introduction

Luminescent solar concentrators (LSC) gained a considerable interest during last years as a low cost alternative to large area solar cells used in standard photovoltaic panels. LSC typically consists of a polymer plate doped with a luminescent material, *e.g.*, fluorescent organic dye [1]. This material absorbs sunlight incident on the surface of LSC. Subsequently, light is reemitted at a longer wavelength and by total internal reflection is transported to the edge of the plate, where a small solar cell is placed (Fig. 1).

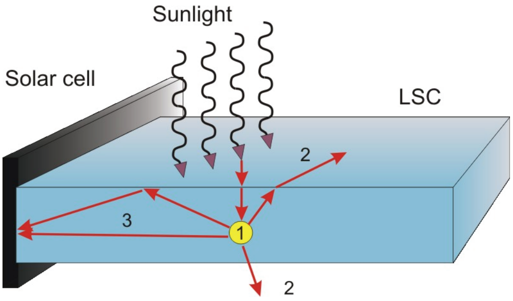

Fig. 1. Schematic of a luminescent solar concentrator. 1 – nanopowder Nd,Yb:YAG, Nb,Yb:GGG or Nd,Yb:YO that absorbs and emits photons; 2 – photons emitted outside the region of total internal reflection (losses); 3 – photons transported to the solar cell.

The performance of LSC is mainly limited by absorption spectrum of available organic dyes (typically to 600 nm), leaving significant portion (40%) of incident solar energy unabsorbed. The alternative approach is the application of quantum dots (QD) $A^{II}B^{VI}$. At the moment, however, state-of-the-art quantum dots are not photostable although are effective from the point of view of absorption and emission properties.

The efficiency of a silicon solar cell with LSC is expected to be the best when luminescent centers absorb sunlight up to the wavelength of about 900 nm and subsequently emit within the range 950–1100 nm, corresponding to the maximum spectral sensitivity of silicon. This requirement can be fulfilled with the use of oxide nanocrystals doped with rare earth (RE) ions. In present work, this solution is explored and luminescent nanocrystals containing RE ions are incorporated in polymer plates.

2. Sample preparation

The nanocrystals of $Y_3Al_5O_{12}$ (YAG), $Gd_3Ga_5O_{12}$ (GGG) and Y_2O_3 (YO) compounds were prepared via the (Pechini) modified sol–gel method. Mentioned oxides were codoped by 3% Nd and 15% Yb rare ions. For preparation of GGG, firstly gallium oxide was dissolved in nitric acid. The dissolvent was evaporated and deionized water was added. Gadolinium and neodymium oxides were dissolved in solution of acetic acid. The solutions were mixed together and ethylene glycol as cross-linking agent was added. The obtained mixture was evaporated slowly, dried and then grinded in an agate mortar to fine powder. This powder was calcined in air at 1100 °C. The synthesis of YAG or YO is very similar and less complicated because all starting oxides easily dissolve in acetic acid. The temperatures of YAG and YO calcination were respectively: 1000 °C and 700 °C.

The crystal structures of samples were characterized by X-ray diffraction (XRD) using a Siemens D-500 diffractometer with CuK_{α} radiation at 1.548 Å. According to the characterization results, all samples were single phase. The mean size of the crystallites was evaluated using Scherrer's formula. It varied from 10 to 70 nm.

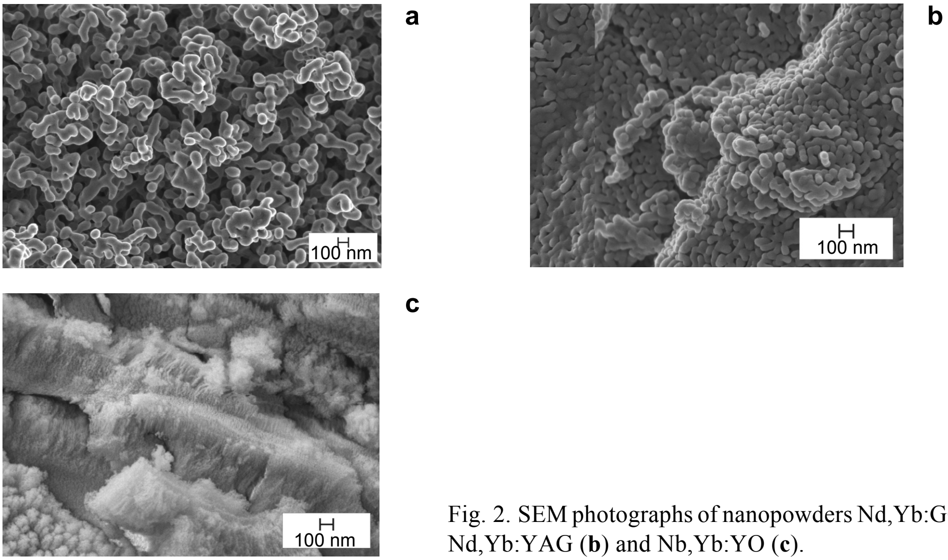

Fig. 2. SEM photographs of nanopowders Nd,Yb:GGG (**a**), Nd,Yb:YAG (**b**) and Nb,Yb:YO (**c**).

The size and morphology of nanopowders were analyzed by high resolution scanning electron microscopy (HRSEM). Exemplary SEM photographs of Nd,Yb:GGG, Nd,Yb:YAG and Nb,Yb:YO nanopowders are shown in Fig. 2.

In order to prepare LSC plates, in the first step Nd,Yb:YAG, Nd,Yb:GGG and Nd,Yb:YO nanocrystallite powders were deagglomerated using ultrasounds in the presence of commercial surface active agents directly in methyl methacrylate monomer (MMA) or in tetrahydrofuran (THF). Two options for sample preparation were chosen: polymerization of MMA (option 1) and dissolving commercial PMMA pallets in THF, then drying (option 2). Successfully disperged MMA samples were added with 1% of UV polymerization activator Irgacure 1700 (Ciba) and put into Petry's dishes, closed and irradiated by UV for 48 hours. PMMA (PLEXIGLAS® 7N from Degussa) pellets were added into THF samples and dissolved by a magnetic stirrer. Solutions were put into Petry's dishes and dried in room conditions for 48 hours, then baked in an oven at 60 °C for 24 hours. Samples have thickness 200–300 μm.

3. Spectroscopic characterization

3.1. Experimental setup

In the experiment, two diode lasers (DL) were used: DL operating at $\lambda = 808$ nm to excite Nd^{3+} ions and LD operating at $\lambda = 976$ nm for direct excitation of Yb^{3+} ions. The luminescence spectra were measured with the use of the monochromators: Spectra Pro 2300i (Princeton Instruments/Acton) equipped with the thermoelectrically cooled InGaAs detector and HR 460 (Jobin–Yvon) with the photomultiplier R5509-72

(Hamamatsu) for IR range. The emission decays were recorded with the oscilloscope TDS 2022B (Tektronix).

3.2. Results and discussion

The results of spectroscopic characterization are presented in Figs. 3–6. The properties of nanopowders before and after incorporation into the polymeric plates are compared. Figure 3 shows the emission spectra under 808 nm excitation for Nd,Yb:GGG and Nd,Yb:YAG powders as well as PMMA plates. All spectra reveal $^2F_{5/2} \to {}^2F_{7/2}$ transition of Yb^{3+} which proves an efficient energy transfer $\mathrm{Nd}^{3+} \to \mathrm{Yb}^{3+}$ ion. Only a weak contribution is related to $^4F_{3/2} \to {}^4I_{11/2}$ of Nd^{3+}.

Emission spectra obtained under 976 nm excitation for nanopowders and plates are presented in Fig. 4. Again, a dominant $^2F_{5/2} \to {}^2F_{7/2}$ transition of Yb^{3+} with

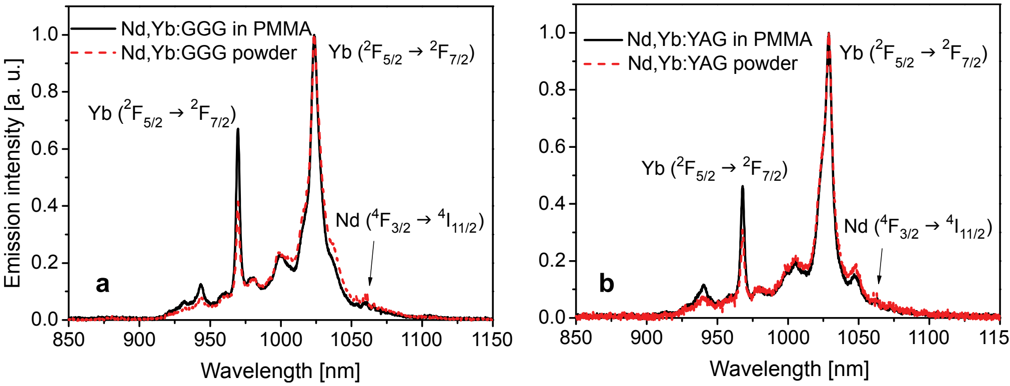

Fig. 3. Emission spectra of Nd,Yb:GGG (**a**) and Nd,Yb:YAG (**b**) powders as well as PMMA plate measured under 808 nm excitation.

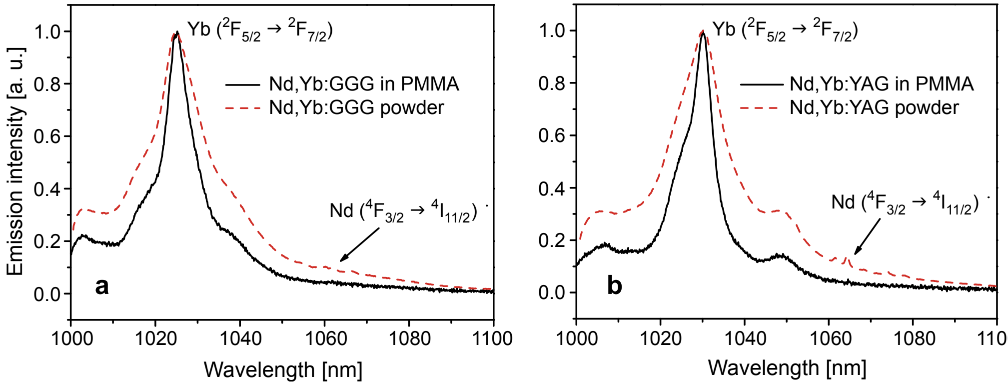

Fig. 4. Emission spectra of Nd,Yb:GGG (**a**) and Nd,Yb:YAG (**b**) powders as well as PMMA plate measured under 976 nm excitation.

a weak contribution of ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ of Nd^{3+} can be observed. Emission lines of both Nd,Yb:GGG and Nd,Yb:YAG nanocrystals are narrowed after incorporation into a polymer plate which can be a result of deagglomeration of the powder and surface related effects.

Apart from the IR emission, a relatively weak, up-converted green emission for YAG and GGG under 976 nm excitation was observed (Fig. 5). This anti-Stokes emission is related to the ${}^2G_{7/2} \rightarrow {}^4I_{9/2}$ transition of Nd^{3+}. The visible "hot" emission following the intense 976 nm cw excitation of Yb^{3+} in Nd,Yb:YAG nanocrystalline ceramics was extensively studied in Ref. [2]. Alike behaviour of co-doped Yb^{3+} and Nd^{3+} YAG epitaxial layers was observed and discussed more in detail in [3].

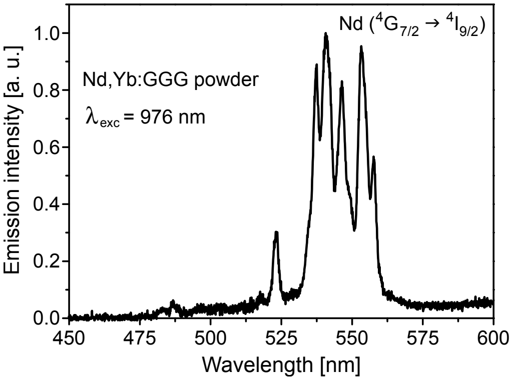

Fig. 5. Up-conversion fluorescence spectra of Nd,Yb:GGG excited at 976 nm.

Emission spectra for Nd,Yb:YO powder measured under 808 nm and 976 nm excitation (Fig. 6) reveal typical Yb^{3+} and Nd^{3+} transitions in YO matrix [4, 5]. However, the obtained fluorescence signal was weak and therefore this material was not used in further investigations.

Room temperature emission decays measured for Nd,Yb:YAG and Nd,Yb:GGG under 976 nm excitation are shown in Fig. 7. The decays are related to ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$

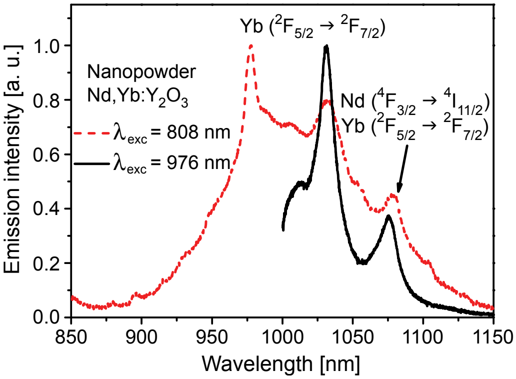

Fig. 6. Emission spectra of Nd,Yb:YO powder obtained under 808 nm and 976 nm excitation.

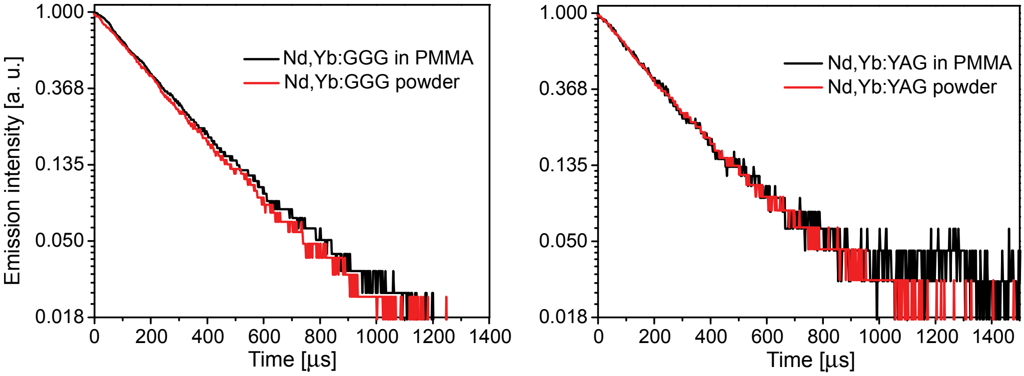

Fig. 7. Room temperature emission decays of Nd,Yb:GGG (**a**) and Nd,Yb:YAG (**b**) powders as well as PMMA plate measured under 976 nm excitation.

transition in Yb^{3+} ions. All decay characteristics are almost identical regardless of the type of the matrix. The observed shortening of the lifetimes compared to single crystal doped only by Yb^{3+} ions (from ~1 ms to ~220 µs) is caused most probably by energy transfer from Yb^{3+} to Nd^{3+}.

4. Conclusions

The results of spectroscopic characterization of PMMA polymer plates containing Nd,Yb:YAG; Nd,Yb:GGG and Nd,Yb:YO nanocrystals for luminescent solar concentrators (LSC) were presented. The results indicate the successful incorporation of nanosized crystals into PMMA matrix. Most promising results were obtained for Nd,Yb:YAG and Nd,Yb:GGG nanocrystals.

The results show that investigated polymer materials with Nd, Yb doped oxide nanopowders are an interesting solution for photovoltaic applications offering stability and emission in the spectral range matched to the maximum sensitivity of a silicon solar cell.

Acknowledgements – The authors gratefully acknowledge Dr. Artur Wnuk for the help in obtaining presented results. This work was supported by the National Centre for Research and Development under the research project NR 15-0030-04 and partly ITME Statute Project No. 07-1-1022-0.

References

[1] Rowan B.C., Wilson L.R., Richards B.S., *Advanced material concepts for luminescent solar concentrators*, IEEE Journal of Selected Topics in Quantum Electronics **14**(5), 2008, pp. 1312–1322.
[2] Bednarkiewicz A., Stręk W., *Laser-induced hot emission in* Nd^{3+}/Yb^{3+}*:YAG nanocrystallite ceramics*, Journal of Physics D: Applied Physics **35**(20), 2002, pp. 2503–2507.

[3] WNUK A., SARNECKI J., MALINOWSKI M., MŁYŃCZAK J., MIERCZYK Z., *Interaction between* Nd^{3+} *and* Yb^{3+} *ions in epitaxial YAG laser waveguide*, CLEO'2005, Europhysics Conference Abstracts, Munich–Germany, 29B, 2005, CE6-1.

[4] WALSH B.M., MCMAHON J.M., EDWARDS W.C., BARNES N.P., EQUALL R.W., HUTCHESON R.L., *Spectroscopic characterization of* $Nd{:}Y_2O_3$*: application toward a differential absorption lidar system for remote sensing of ozone*, Journal of the Optical Society of America B **19**(12), 2002, pp. 2893–2903.

[5] SHIRAKAWA A., TAKAICHI K., YAGI H., BISSON J., LU J., MUSHA M., UEDA K., YANAGITANI T., PETROV T., KAMINSKII A., *Diode-pumped mode-locked* $Yb^{3+}{:}Y_2O_3$ *ceramic laser*, Optics Express **11**(22), 2003, pp. 2911–2916.

Received September 25, 2010