

Upconversion luminescence properties of nanocrystallite MgAl_2O_4 spinel doped with Ho^{3+} and Yb^{3+} ions

A. Watras, P.J. Dereń*, R. Pązik, K. Maleszka-Bagińska

Institute for Low Temperature and Structure Research of Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland

ARTICLE INFO

Article history:

Available online 6 April 2012

Keywords:

Nanocrystallite
 MgAl_2O_4
 Spinel
 Upconversion
 Ho^{3+}
 Yb^{3+}

ABSTRACT

The upconversion luminescence spectra of nanocrystallite MgAl_2O_4 doped with 1% of Ho^{3+} and 5% of Yb^{3+} ions after excitation at 980 nm were measured. Influence of excitation regime either continuous or pulse on upconversion mechanisms was shown. For continuous wave (CW) laser excitation upconversion process is due to phonon assisted Excited State Absorption (ESA). For pulse laser excitation upconversion emission is due to Energy Transfer Upconversion (ETU).

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

There are many papers on upconversion emission in materials doped with Ho^{3+} and Yb^{3+} ions [1–5]. One of potential application for such phosphors is using them for enhancing efficiency of GaAs photovoltaic cells. These photovoltaic cells are effective for red and green light, but equipped with such phosphor will convert into electricity also the IR part of Solar radiation [6].

MgAl_2O_4 spinel was chosen as a host for holmium and ytterbium ions. Their physical and mechanical properties are well known. Spinel has high melting point (2135 °C), good thermal shock resistance and mechanical strength [7]. The synthetic nanocrystallite MgAl_2O_4 was already obtained by the Pechini method [8].

In this work we present for the first time (to our knowledge) preliminary studies of upconversion luminescence of nanocrystallite MgAl_2O_4 spinel doped with Ho^{3+} and Yb^{3+} ions. The upconversion phenomenon was investigated for continuous wave (CW) and pulse laser excitation.

2. Experimental

Sample was prepared by modified Pechini method. As the starting materials $\text{Mg}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, Ho_2O_3 (Alfa Aesar 99.99%) and Yb_2O_3 (Alfa Aesar 99.99%) were chosen. Citric acid and

ethylene glycol were added as a chelating and polymerization agents, respectively.

Stoichiometric amounts of lanthanides oxides were dissolved in dilute HNO_3 to transfer them into soluble in water nitrate salts and the excess of acid was evaporated at 90 °C. Afterwards all substrates were dissolved in deionized water and mixed with the solution of ethylene glycol and citric acid. The fixed molar ratio of citric acid and ethylene glycol to total chelated metal cations was 5:1. After that final homogeneous solution was placed into plastic containers and kept into dryer at 80 °C until brown resin was obtained. Subsequently the resin was sintered at 1100 °C for 8 h in air atmosphere with 10 °C/min temperature rise step. Structure studies of the obtained nanocrystallite powder were characterized using XRD powder diffraction.

The XRD were measured on Panalytical X'pert equipped with $\text{Cu K}\alpha$ lamp. For CW excitation and power dependence measurements we have used fiber coupled 975 nm laser diode with 4 W output power. The end of the fiber was at 0.5 cm distance from sample, no lens was used and estimated spot diameter was 2.5 mm, accordingly when laser diode was set at 4 W (at its maximum) the power density was 82 W/cm². For pulse excitation we have used 980 nm line from tunable Ti:Sapphire laser pumped by second harmonic Nd:YAG. Laser light was focused to a 2 mm diameter spot at the sample by a 4 cm focal length lens. Laser pulse energy was set to 2 mJ and pulse duration was 10 ns, the repetition rate was 10 Hz. The emission was analyzed by Jobin Yvon THR1000 monochromator equipped with Hamamatsu R928 photomultiplier and CCD camera. To measure emission decay profiles we used digital oscilloscope LeCroy WaveSurfer 400.

* Corresponding author.

E-mail address: P.Deren@int.pan.wroc.pl (P.J. Dereń).

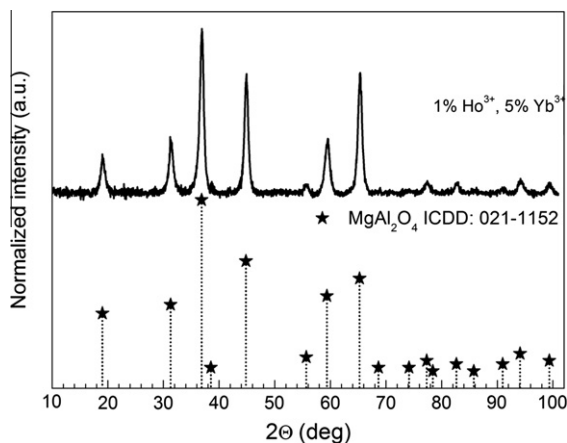


Fig. 1. XRD spectrum of nanocrystallite MgAl_2O_4 spinel doped with 1% of Ho^{3+} and 5% of Yb^{3+} ions.

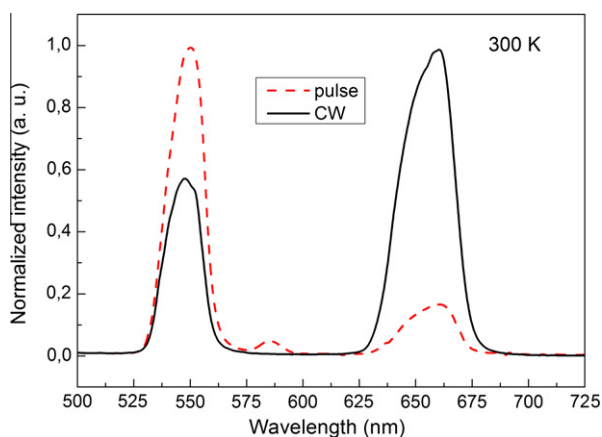


Fig. 2. Upconversion emission spectra of MgAl_2O_4 doped with 1% of Ho^{3+} and 5% of Yb^{3+} ions at 300 K.

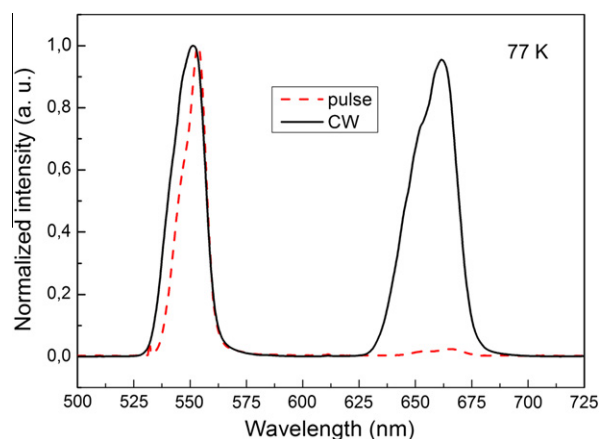


Fig. 3. Upconversion emission spectra of MgAl_2O_4 doped with 1% of Ho^{3+} and 5% of Yb^{3+} ions at 77 K.

3. Results and discussion

The XRD spectrum of MgAl_2O_4 doped with 1% of Ho^{3+} ions and 5% of Yb^{3+} ions is presented in Fig. 1. It can be seen that sample has

structure without any additional phases. The average grain size estimated with Williamson–Hall method is 11 nm.

The upconversion luminescence spectrum measured at 300 K is presented in Fig. 2. The sample was excited at 980 nm by CW and pulsed laser. Solid line shows in Fig. 2 emission obtained after CW excitation and dashed after pulse excitation. One can see that for CW excitation there are only two emission bands; one green centered at 550 nm assigned to the $(^5\text{F}_4, ^5\text{S}_2) \rightarrow ^5\text{I}_8$ transition and second red centered at 660 nm and assigned to the $^5\text{F}_5 \rightarrow ^5\text{I}_8$ transition. For pulse excitation there is additional band with maximum at 585 nm, which corresponds to the $(^3\text{K}_7, ^5\text{G}_4) \rightarrow ^5\text{I}_6$ transition. One can expect to observe transitions from the $^5\text{G}_4$ level to the ground and first excited level, the $^5\text{I}_8$ and the $^5\text{I}_7$, respectively. But we did not observe them, because they are very weak. Taking into account Squared Reduced Matrix Elements and Omega parameters obtained for other oxides doped with $\text{Ho}(\text{III})$ [9], it was possible to calculate the so called transition strengths of above mentioned transitions. After that we can formulate a rule of thumb, that the $^5\text{G}_4 \rightarrow ^5\text{I}_6$ transition is much stronger than the $^5\text{G}_4 \rightarrow ^5\text{I}_8$ and the $^5\text{G}_4 \rightarrow ^5\text{I}_7$ one. By the way the latter was covered by second harmonic of the excitation line, therefore not seen. We have to stress that spectra of the sample excited by pulse laser differ significantly from those excited by CW radiation, although in both cases the samples were excited at the same wavelength. The low temperature make this difference even more striking (see Fig. 3), the small band at 585 nm disappears and the red band become almost invisible for pulse excitation.

It is evident from the experimental data, that the mechanisms of upconversion emission for CW and pulse excitation are different. The processes that occur with CW excitation will be discussed first. Excitation wavelength match well the absorption of Yb^{3+} ions therefore due to high absorption cross-section of Yb^{3+} in spinel incident photons are well absorbed. Then the energy is transferred to the $^5\text{I}_5$ and $^5\text{I}_6$ levels of Ho^{3+} ions (see Fig. 4). The $^5\text{I}_7$ level is populated by nonradiative transitions from the $^5\text{I}_6$ one.

The emitting $(^5\text{F}_4, ^5\text{S}_2)$ and $^5\text{F}_5$ levels are populated by excited state absorption (ESA) from the $^5\text{I}_6$ and $^5\text{I}_7$ levels, respectively. At 300 K the red emission is approximately two times more intense than green one, but at 77 K green emission has the same intensity as the red one (see Fig. 3). This can be explained by very efficient at 300 K multi-phonon energy transfer from the $^5\text{I}_6$ and the $^5\text{S}_2$ level. Transfer from the $^5\text{I}_6$ level populates the $^5\text{I}_7$ one and thus the $^5\text{I}_7 \rightarrow ^5\text{F}_5$ ESA becomes more effective. Second mentioned above transfer feeds directly the $^5\text{F}_5$ level. At 77 K multiphonon transfer is much less efficient and therefore the green emission becomes relatively stronger.

For pulse excitation the upconversion mechanism is different, the emission is observed due to so called energy transfer upconversion (ETU). Pump energy excites mainly the green emission (see Fig. 2). Incident photons are also well absorbed by the Yb^{3+} ions then energy is transferred directly to the $^5\text{I}_5$, $^5\text{F}_4$ and $^3\text{H}_6 + ^3\text{D}_2$ levels, which is indicated in Fig. 5 by W_{YH1} , W_{YH2} and W_{YH3} arrows, respectively. The emitting levels are populated via multiphonon nonradiative transitions. The $^5\text{F}_5$ level is populated with assistance of cross relaxation process: $(^5\text{S}_2, ^5\text{I}_8) \rightarrow (^5\text{I}_4, ^5\text{I}_7)$ (dotted arrows in Fig. 5.), which populates $^5\text{I}_7$ and makes the ESA process possible.

The cross relaxation as well as last energy transfer step: W_{YH3} must be phonon assisted because at 77 K emission from the $^5\text{G}_4$ quintet is not observed and the red emission from $^5\text{F}_5$ level is barely seen.

Dependence of intensity of upconversion emission on excitation power (CW regime) in $\text{MgAl}_2\text{O}_4:(\text{Ho}^{3+}, \text{Yb}^{3+})$ is plotted in log–log scale in Fig. 6. For the green emission two different slopes can be seen for low and high pump power. For low pump power (from

Download English Version:

<https://daneshyari.com/en/article/1495241>

Download Persian Version:

<https://daneshyari.com/article/1495241>

[Daneshyari.com](https://daneshyari.com)