

## Governing of down-shifting processes in $\text{LiLaP}_4\text{O}_{12}:\text{Tb}^{3+},\text{Yb}^{3+}$ for enhancement of its near-infrared emission

K. Grzeszkiewicz\*, L. Marciniak, D. Hreniak

(Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław 50-422, Poland)

Received 22 March 2016; revised 25 April 2016

**Abstract:** Downshifting behavior of the  $\text{Tb}^{3+}$ - $\text{Yb}^{3+}$  co-doped nanocrystalline  $\text{LiLaP}_4\text{O}_{12}$  powders synthesized by co-precipitation method was presented and discussed. The structural phase purity of obtained material was confirmed by X-ray diffraction (XRD) measurements. Strong enhancement of ytterbium  ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$  emission intensity was observed with decreasing  $\text{Tb}^{3+}$  concentration under UV excitation. Dependence of efficiency of energy transfer between dopants on pumping wavelength was investigated due to better understanding of down-shifting mechanism. It was found that luminescence intensity of  $\text{Yb}^{3+}$  decreased above 10 mol.% dopant content, what was caused by concentration quenching. The power dependence measurements were carried out at 77 and 300 K. The resulting slopes had the same value of 1, what indicated the existence of linear down-shifting process, independent of the temperature.

**Keywords:** downshifting;  $\text{LiLaP}_4\text{O}_{12}$ ;  $\text{Tb}^{3+}$ ;  $\text{Yb}^{3+}$ ; rare earths

The energy conversion mechanisms are crucial for further development of such technologies as third-generation photovoltaic cells, e.g., multi junction solar cells based on thin film of CdS/CdTe. To this day the largest energy losses in this type of photovoltaic panels are caused by strong absorption of UV and blue photons by front CdS layer with band gap energy of 2.4 eV ( $\sim 510$  nm)<sup>[1]</sup>. Down-shifting layer capable of converting these photons into longer wavelengths photons, so called luminescent solar concentrator, may greatly minimize the spectral losses<sup>[1]</sup>. This feature would also be beneficial in the case of Si photovoltaic panels. The lanthanide ions are very suitable to this purpose due to their down-conversion/down-shifting properties reported in some crystal lattices<sup>[2,3]</sup>.

The idea of down-conversion has been formed as an extension of quantum cutting (QC) phenomena, involving splitting the energy of UV photon into two visible photons. QC was first observed in  $\text{YF}_4$  doped with  $\text{Pr}^{3+}$  ions<sup>[4,5]</sup>. Due to high losses accompanying the process it has been concluded that efficient quantum cutter cannot be found if material is doped only with single rare earth ion. It has been shown that it is possible to achieve higher efficiency by using energy transfer between two different RE ions<sup>[6]</sup>. This mechanism, called down-conversion, is intensively studied in variety of pairs of lanthanide ions. One of the promising  $\text{Ln}^{3+}$  ions pair, in which that phenomenon occurs is  $\text{Tb}^{3+}$ - $\text{Yb}^{3+}$ <sup>[7-12]</sup>.

$\text{LiLaP}_4\text{O}_{12}$  is a material, that belongs to family of polyphosphate compounds, which are widely studied in lit-

eratures. It crystallizes in the  $\text{LiNdP}_4\text{O}_{12}$  structure with space group  $C2/c$  (monoclinic symmetry)<sup>[13]</sup>. The site symmetry of the  $\text{Nd}^{3+}$  ion is  $C_1$ . Polyphosphates acquire the most interesting spectroscopic features, when doped with RE ions. For example, laser properties have been reported for high doping level of  $\text{Nd}^{3+}$ <sup>[14]</sup>. Also there are papers dealing with  $\text{Ce}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Pr}^{3+}$  ions as dopants<sup>[15]</sup>, and even reporting temperature dependence of  $\text{Pr}^{3+}$  luminescence from the  ${}^1\text{S}_0$  and  $4f^15d^1$  states for photon cascade emission (PCE) study<sup>[16]</sup>. On the other hand, relatively small number of studies is devoted to down-conversion/ down-shifting properties of RE ions in this crystal lattice.

In this work we investigated down-shifting properties of  $\text{LiLaP}_4\text{O}_{12}$  nanopowders co-doped with  $\text{Tb}^{3+}$  and  $\text{Yb}^{3+}$ . Energy transfer between dopants was confirmed and strong  $\text{Yb}^{3+}$  emission after UV  $\text{Tb}^{3+}$  excitation was observed. The optimal concentration of dopant ions was determined to reduce concentration quenching as well as to ensure efficient energy transfer to  $\text{Yb}^{3+}$ .

## 1 Experimental

$\text{LiLaP}_4\text{O}_{12}:\text{Tb}^{3+},\text{Yb}^{3+}$  powders were successfully prepared by co-precipitation method<sup>[17,18]</sup>. The stoichiometric amounts of lanthanum, terbium and ytterbium oxides as well as lithium carbonate of high purity were dissolved in diluted nitric acid to obtain nitrates soluble in water. Afterwards the nitrates were mixed together. Obtained solution was mixed with ammonium diphosphate

\* Corresponding author: K. Grzeszkiewicz (E-mail: [k.grzeszkiewicz@int.pan.wroc.pl](mailto:k.grzeszkiewicz@int.pan.wroc.pl); Tel.: +48 71 3954 169)

and then it was dried at 70 °C for one day. Finally, obtained material was heat treated at 450 °C for 8 h.

The powder diffraction studies were carried out on a PANalytical X'Pert Pro diffractometer using Ni-filtered Cu K $\alpha$  radiation ( $V=40$  kV,  $I=30$  mA). Emission spectra were recorded with 0.01 nm resolution under 266 nm Nd:YAG laser excitation using a JobinYvon THR1000 monochromator with exchangeable gratings detectors. Power dependence measurements were performed using laser diode 266nm as excitation and laser beam power meter Coherent-Field Master LM-2 (0.4–1.1  $\mu$ m spectral range,  $P_{\max}=50$  mW).

## 2 Results and discussion

XRD patterns for the samples of LiLaP $_4$ O $_{12}$  doped with 1% Tb $^{3+}$ ,  $x\%$  Yb $^{3+}$  are presented in Fig. 1. The phase purity of the samples was confirmed by comparison with the reference data (ICSD 184917 for LiNdP $_4$ O $_{12}$ ). Slight shift (with maximum value 0.4°) of all peaks of measured XRD pattern to higher angles of  $2\theta$  is observed. It is associated with doping with Tb $^{3+}$  and Yb $^{3+}$  instead of Nd $^{3+}$  ions. They are coordinated by 8 oxygen atoms in this structure, hence their ionic radii are equal to 0.104, 0.0985 and 0.1109 nm, respectively. Also, substituting by smaller ions affects the unit cell parameters and results in constant offset of all diffraction peaks.

Luminescence spectra of LiLaP $_4$ O $_{12}$ :Tb $^{3+}$ , Yb $^{3+}$  with fixed 20% Yb $^{3+}$  concentration are presented in Fig. 2.

Characteristic Tb $^{3+}$  emission peaks at 489, 543, 587 and 620 nm assigned to  $^5D_4 \rightarrow ^7F_J$  ( $J=6, 5, 4, 3$ ) transitions are clearly visible for sample with high Tb $^{3+}$  concentration ( $\geq 10\%$ ). Their intensities strongly decrease with lowering Tb $^{3+}$  concentration. At the same time strong enhancement of ytterbium  $^2F_{5/2} \rightarrow ^2F_{7/2}$  emission is observed. The emission spectra have been normalized to the most intense transition to show relative changes in intensities of Tb $^{3+}$  and Yb $^{3+}$  luminescence. Obtained results indicate a presence of energy transfer processes between dopants with higher efficiency for a lower sensi-

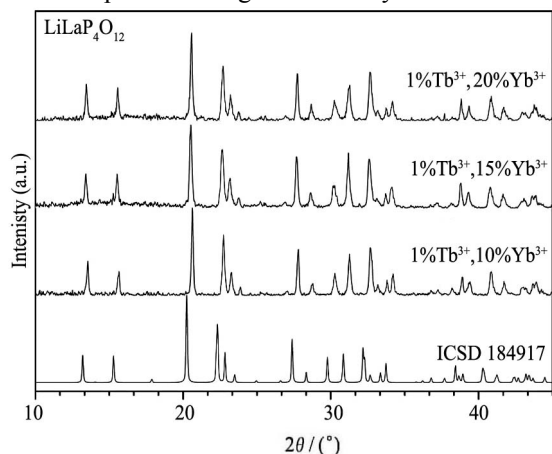


Fig. 1 XRD pattern of LiLaP $_4$ O $_{12}$ :1%Tb $^{3+}$ ,  $x\%$ Yb $^{3+}$  with standard peaks (ICSD 184917) included

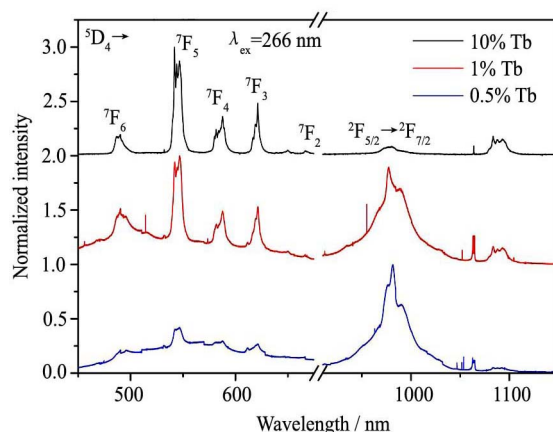


Fig. 2 Visible and NIR luminescence spectra of LiLaP $_4$ O $_{12}$ :  $x\%$ Tb $^{3+}$ , 20%Yb $^{3+}$  under 266 nm excitation

tizer concentration. Strong reduction of Tb $^{3+}$  emission in favor of Yb $^{3+}$  is even more clearly visible, if ratios of observed Tb $^{3+}$  and Yb $^{3+}$  transitions to  $^5D_4 \rightarrow ^7F_6$  (radiative relaxation to the ground state of terbium) are presented. Fig. 3 shows these ratios in function of Tb $^{3+}$  concentration.

Terbium  $^5D_4 \rightarrow ^7F_5$  transition cannot participate in possible a down-conversion mechanism, because the energy of this transition is not resonant with a double energy of excited  $^2F_{5/2}$  ytterbium state. On the other hand the energy of  $^5D_4 \rightarrow ^7F_6$  transition is resonant and it could eventually assist in DC. Comparing changes in their emission intensities provides information about a type of energy conversion process. Thus, it enables a distinguishing between down-shifting and down-conversion mechanisms. One can see that for a low doping level (below 2% Tb $^{3+}$ ) the ratio between  $^5D_4 \rightarrow ^7F_5$  and  $^5D_4 \rightarrow ^7F_6$  transitions decreases (red curve in Fig. 3). In the same time Yb $^{3+}$  emission is greatly enhanced (black curve). That result suggests decreasing contribution of  $^5D_4 \rightarrow ^7F_5$  radiative transition for the benefit of efficient energy trans-

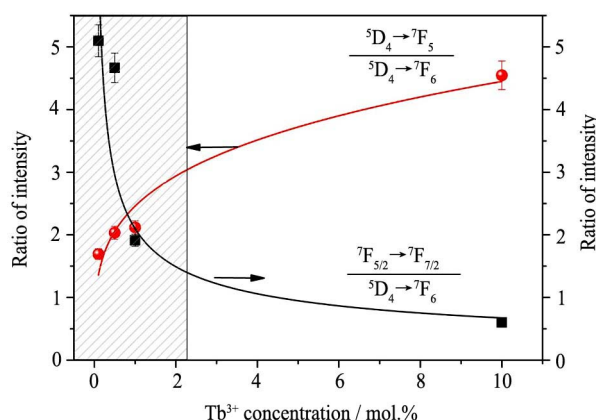


Fig. 3 Correlated ratios of  $^5D_4 \rightarrow ^7F_5$  (Tb $^{3+}$ ) and  $^7F_{5/2} \rightarrow ^7F_{7/2}$  (Yb $^{3+}$ ) emission intensities to  $^5D_4 \rightarrow ^7F_6$  (radiative relaxation to ground state) as a function of terbium concentration (The hatched area approximates the concentration range, in which one can expect occurrence of efficient down-shifting process)

Download English Version:

<https://daneshyari.com/en/article/1258858>

Download Persian Version:

<https://daneshyari.com/article/1258858>

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