This article was published in an Elsevier journal. The attached copy is furnished to the author for non-commercial research and education use, including for instruction at the author's institution, sharing with colleagues and providing to institution administration.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>

Synthesis and up-converted luminescence of $\text{Y}_3\text{NbO}_7\text{:Er}$

Adam Walasek^a, Jian Zhang^b, Shiwei Wang^b, Eugeniusz Zych^{a,*}

^a Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie, 50-383 Wrocław, Poland

^b Shanghai Institute of Ceramics, CAS, 1295 Dingxi Road, 200050 Shanghai, PR China

Available online 19 December 2006

Abstract

Synthesis of cubic $\text{Y}_3\text{NbO}_7\text{:Er}$ using Li_2SO_4 flux is reported and spectroscopic properties of the resultant powders are presented. The dopant content has varied in the range of 0.1–15 at.%. Absorption, excitation and emission spectra are characterized by relatively broad structures related to the Er^{3+} ion. The broadening results from some inhomogeneity of the metal surrounding. For diluted samples both photoluminescence and up-converted emission are dominated by a green luminescent band around 550 nm. With an increasing concentration of the dopant a red band located around 665 nm gets systematic enhancement and in up-conversion it finally dominates the spectrum. For low concentrations the up-conversion occurs through excited state absorption mechanism while for higher Er contents energy transfer mechanism dominates.

© 2006 Elsevier B.V. All rights reserved.

PACS: 42.65; 42.70; 71.55

Keywords: Niobates; Erbium; Luminescence; Upconversion

1. Introduction

Y_3NbO_7 crystallizes in cubic structure ($a = 5.25 \text{ \AA}$) [1,2]. An exceptional feature of the system – which may be derived from the fluorite structure – is that all metal ions ($3 \times \text{Y}$ and $1 \times \text{Nb}$) randomly occupy one metal site offered by the host lattice. The system is O-deficient and the O-vacancy is randomly distributed within the coordination sphere of the metal [3,4]. Because of such structure we considered Y_3NbO_7 especially attractive for up-converted luminescence (UCL), where resonant or quasi-resonant conditions between the involved levels of an activator and the energy of excitation photons must be fulfilled to raise an electron to a high energy excited state [5] either through excited-state-absorption (ESA) or energy-transfer (ET) mechanism [6]. Analogously to Er-doped CaGdAlO_4 and $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ researched by Wells [7,8], we expected

that inhomogeneous broadening of absorption bands may help to achieve such resonant conditions.

2. Materials and experiments

For the synthesis of $\text{Y}_3\text{NbO}_7\text{:}x \text{ at.}\% \text{ Er}$ powders ($x = 0.1\text{--}15$) stoichiometric mixture of Nb_2O_5 , Y_2O_3 and Er_2O_3 was combined with Li_2SO_4 flux and placed in an alumina crucible, in which it was heated at 1300°C for 5 h. The product was recovered by washing out the flux with deionized water and filtering. The powders were dried at 200°C .

X-ray diffraction (XRD) patterns were measured with IRYS diffractometer in the range of $2\theta = 10\text{--}120^\circ$ using $\text{Cu K}\alpha$ radiation. Reflection spectra were measured with UV–VIS–NIR CARY 500 Scan spectrophotometer with the resolution of 0.1 nm. The spectra were automatically converted into absorption units by the instrument software. Transmission electron microscopy (TEM) images were taken with JEM-2100F under an operating voltage of 200 kV. Photo excited luminescence (PL) spectra were

* Corresponding author. Tel.: +48 71 375 7248; fax: +48 71 328 2348.
E-mail address: zych@wchuwr.chem.uni.wroc.pl (E. Zych).

recorded using Fluorolog-3 spectrofluorometer equipped with a 450 W Xenon lamp and Hamamatsu R928P photomultiplier. The UCL spectra were recorded with the same system using an optical fiber coupled diode laser tuned to 980 nm as the excitation source. Both PL and UCL spectra were taken at room temperature and were corrected for the spectral response of the measuring system.

3. Results and discussion

In Fig. 1 we present an XRD pattern of Y_3NbO_7 :15%Er, which is fully representative of all powders investigated, and the theoretical pattern for cubic Y_3NbO_7 . We can easily see that the fabricated Y_3NbO_7 :Er crystallizes in cubic structure and, to the level of the instrument sensitivity, the material is crystallographically pure.

In Fig. 2 we present TEM image of the Y_3NbO_7 :5%Er powder, which is fully representative of other samples. The presented image exposes that the particles are only slightly agglomerated and their sizes are in the range of 400–600 nm, which means that the Li_2SO_4 flux does not promote any extensive growth of the grains.

In Fig. 3 we show an absorption spectrum of Y_3NbO_7 :15%Er, which is representative of all other concentrations. Below about 310 nm we can see a very intense component, whose intensity rises rapidly to saturation. Such a characteristic suggests that this band is related to a fundamental absorption of the Y_3NbO_7 host material. All features located at wavelengths longer than about 350 nm can be easily assigned to f–f transitions of the Er^{3+} ion. Due to the structural disorder within the metal site, which we mentioned earlier, the absorption features are much broader than those of typical crystals offering a clearly defined symmetry of the environment. We shall see similar characteristics in emission spectra.

We decided to use the 377 nm excitation for regular PL spectra and 980 nm for UCL. The latter is appropriate to excite the Er^{3+} ion up to the $^4\text{I}_{11/2}$ state, from where the

Fig. 1. An XRD pattern of the Y_3NbO_7 :15%Er powder and a theoretical diffractogram for the cubic Y_3NbO_7 .

Fig. 2. A representative TEM image of the Y_3NbO_7 :Er powders. Note a low level of agglomeration and spheroidal shape of grains.

Fig. 3. Absorption spectrum of Y_3NbO_7 :15%Er. Note a significant broadening of the Er^{3+} f → f absorption features. The strong band below about 310 nm results from the Y_3NbO_7 host lattice (HL) absorption.

electron can possibly be elevated further to the $^4\text{F}_{7/2}$ intercepting the energy of another 980 nm photon [6,9,10].

Now let us compare the PL (Fig. 4a) and the UCL spectra (Fig. 4b) for all tested concentrations. There are generally observed two emission bands located around 545 and 670 nm. Their assignment is given in Fig. 4. Note that all emission features are much broader than those typically observed in emissions of a crystal environment [11–13]. This we ascribe to an inhomogeneous broadening resulting from the specific structure of the host material.

At the very first look the PL and UCL emissions are similar. In both types of spectra intensity of the red emission band near 670 nm rises with increasing Er content, proving that non-radiative relaxation down to the $^4\text{F}_{7/2}$ level becomes more efficient for a heavier doping. Nevertheless, we can easily note a different dependence of PL and UCL spectra on Er content. Most of all, in PL spectra the intensity of the red emission never surpasses the green one. In the case of UCL the situation is to a large extent different. For the lowest concentrations the up-converted

Fig. 4. Concentration dependence of PL (a), and UCL (b) spectra. Note that only in the UCL the red band intensity surpasses the green one for higher Er contents. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

luminescence is purely green like in PL. However, when the Er content reaches 5% the colour changes towards yellow and finally it becomes orange and the band located around 670 nm takes the major part of the total UCL. Clearly, the UCL colour is controlled by Er content. In both types of spectra the $^2H_{11/2} \rightarrow ^4I_{15/2}$ luminescence may be observed. A thermal $^2H_{11/2} \leftarrow ^4S_{3/2}$ back-transfer of the electrons is usually accounted for its appearance.

In Fig. 5 we present how the slopes of the $\log(I) - \log(P)$ relationship (I and P stands for emission intensity and laser beam power, respectively) depend on the Er concentration for the most intense UCL bands: the green $^4S_{3/2} \rightarrow ^4I_{15/2}$ and the red $^4F_{9/2} \rightarrow ^4I_{15/2}$. The behaviour of the slopes of the two transitions is very similar. Note that for the 670 nm UCL the data starts from 0.5% since for the 0.1%

this band was practically absent. For the most diluted systems the slopes are very close to 2. This means that both UCL emissions are created through the same ESA mechanism. The first IR photon excites an electron from the $^4I_{15/2}$, ground state up to the $^4I_{11/2}$ level and the second one kicks the same electron further up to the $^4F_{7/2}$. As the concentration of the dopant increases the slopes of the double-log dependence systematically decrease to finally reach the value of 1 ± 0.1 for 5–15% of Er content. This indicates that the mechanism of UCL changes from ESA into ET. Hence, for higher Er contents the second portion of the energy the electron receives from a neighboring excited Er^{3+} ion rather than directly from the excitation beam.

4. Conclusions

Cubic $Y_3NbO_7:Er$ powders with different doping concentration of Er ions were synthesized using Li_2SO_4 flux. The absorption, PL and UCL spectra revealed a significant broadening of spectral features, which resulted from variation of the activator environment symmetry. By changing the concentration of Er^{3+} ions, the up-conversion luminescent colour of the $Y_3NbO_7:Er$ powders could be gradually tuned from green to light orange.

Acknowledgements

The work was financed by European Community under grants # II-05-106 EC, by European Social Fund within the “Project of Lower Silesia Research Grants for Increasing Innovations for PhD Students” under Grant # Z/2.02/II/2.6/04/04/U/03/05, and co-financed by the Natural Science Foundation of China, Grant # 50372075.

Fig. 5. Variations of the slope of the $\log I - \log P$ dependence with Er concentration for the two main UCL emissions located around 545 nm and 657 nm. The lines were drawn to guide the eye only.

References

- [1] J.G. Allpress, H.J. Rossell, *J. Solid State Chem.* 27 (1979) 105.
- [2] M. Wakeshima, H. Nishimine, Y. Hinatsu, *J. Phys. Condens. Matter* 16 (2004) 4103.
- [3] Y. Yokogawa, M. Yoshimura, S. Somiya, *Solid State Ionics* 28–30 (1988) 1250.
- [4] T. Tanaka, N. Ishizawa, M. Yoshimura, F. Maruno, H. Oyanagi, *J. Solid State Chem.* 114 (1995) 79.
- [5] R. Francini, S. Pietrantoni, M. Zambelli, A. Speghini, M. Bettinelli, *J. Alloy. Compd.* 380 (2004) 34.
- [6] F. Auzel, *Chem. Rev.* 104 (2004) 139.
- [7] M. Yamaga, N. Kodama, T. Yosida, B. Henderson, K. Kindo, *J. Phys.: Condens. Matter* 9 (1997) 9639.
- [8] J.P.R. Wells, T.P.J. Han, M. Yamaga, N. Kodama, H.G. Gallagher, *J. Lumin.* 87–89 (2000) 1093.
- [9] A.M. Pires, O.A. Serra, M.R. Davolos, *J. Alloy. Compd.* 374 (2004) 181.
- [10] A.M. Pires, O.A. Serra, S. Herr, H.U. Güdel, *J. Appl. Phys.* 98 (2005) 063529–063531.
- [11] H. Guo, Y. Li, D. Wang, W. Zhang, M. Yin, L. Lou, S. Xia, *J. Alloy. Compd.* 376 (2004) 23.
- [12] D. Wang, M. Yin, S. Xia, V.N. Makhov, N.M. Khaidukov, J. C. Krupa, *J. Alloy. Compd.* 368 (2004) 337.
- [13] X. Mateos, R. Solé, J. Gavalda, M. Aguiló, F. Díaz, J. Massons, *J. Lumin.* 115 (2005) 131.