

Luminescence of nano- and macrosized LaPO₄:Ce,Tb excited by synchrotron radiation

V. Pankratov^{a,*}, A.I. Popov^a, A. Kotlov^b, C. Feldmann^c

^a Institute of Solid State Physics, University of Latvia, 8 Kengaraga, LV-1063 Riga, Latvia

^b HASYLAB at DESY, Notkestrasse 85, D-22607 Hamburg, Germany

^c Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstrasse 15, D-76131 Karlsruhe, Germany

ARTICLE INFO

Article history:

Received 20 June 2010

Received in revised form 28 November 2010

Accepted 29 December 2010

Available online 2 February 2011

Keywords:

LaPO₄

Ce³⁺

Tb³⁺

Nanocrystals

Luminescence

Synchrotron radiation

ABSTRACT

Comparing the luminescence properties of nanosized and macroscopic LaPO₄:Ce,Tb powders are performed in wide spectral range using synchrotron radiation. In the present study, LaPO₄:Ce,Tb nanopowder was produced by means of a microwave-induced synthesis in ionic liquids, whereas the bulk sample represents a commercial lamp phosphor. Emission and excitation of both, Ce³⁺ and Tb³⁺ luminescence, is observed to be different when comparing bulk and nanosized LaPO₄:Ce,Tb. In particular, it was shown that the fine structure of the Ce³⁺ as well as the Tb³⁺ related emission is poorly resolved for the nanomaterial. It is suggested that the nanoparticles surface plays a key role regarding the perturbation of rare-earth ions and changes their luminescence properties. Furthermore, it is demonstrated that allowed f–d transitions on Tb³⁺ at high energy are significantly suppressed for nanosized LaPO₄:Ce,Tb. Energy transfer is required to initiate Tb³⁺ emission even in the vacuum ultraviolet spectral range.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Lanthanum phosphate (LaPO₄), also known as monazite, has been widely used as a phosphor and proton conductor as well as in sensors, lasers, ceramic materials, catalysts and heat-resistant materials. This is due to its interesting properties such as very low solubility in water, high thermal stability, high index of refraction, and so on [1–5]. Rare earth orthophosphates as host matrices – and LaPO₄ in particular – also exhibit quite a good photochemical and radiation stability. Monazite has been suggested as a waste form for high-level nuclear waste [6]. In particular, LaPO₄ was under active investigation in Japan for the precipitation of actinides from nuclear waste tanks [7].

In recent years, LaPO₄ has been also shown to be a useful host lattice for lanthanide ions to produce phosphors that emit in a broad range of colors [1,5,8–10]. Doping with different types of rare-earth ions (Eu³⁺, Ce³⁺, Tb³⁺, Nd³⁺, Er³⁺, Pr³⁺, Ho³⁺, Yb³⁺, Tm³⁺) in macro- as well as nanosized LaPO₄ have been frequently reported in the literature. Among all these phosphate-type phosphors, trivalent cerium (Ce³⁺) and terbium (Tb³⁺) co-activated LaPO₄ (LaPO₄:Ce,Tb) bulk powder is known as most efficient because of the high-efficiency energy transfer between Ce³⁺ and Tb³⁺ [1,5,8–10]. Bulk LaPO₄:Ce,Tb is also intensely used as an excellent green emitting phosphor for fluorescent lamps [5].

The allowed f–d transition on Tb³⁺ lays in the vacuum ultraviolet (VUV) spectral range in LaPO₄. In order to effectively absorb the relatively low energy ultraviolet (UV) light, consequently, a sensitizer should be used. For LaPO₄:Ce,Tb, Ce³⁺ via its effective 4f–5d absorption serves as the sensitizer, whereas Tb³⁺ acts as the luminescent center. Thus, LaPO₄:Ce,Tb bulk powders exhibit high-efficiency green emission at around 545 nm under UV irradiation since the energy transfer from Ce³⁺ to Tb³⁺ is designated by an excellent efficiency, too.

Recently, we reported on the time-resolved luminescence characteristics of nanosized LaPO₄:Ce,Tb using the fourth harmonic of a YAG:Nd pulsed laser (excitation at 266 nm) in a wide temperature range. Several models were proposed for the energy transfer process from Ce³⁺ to Tb³⁺ via host lattice states in nanosized LaPO₄ [11]. Note that LaPO₄ belongs to the class of wide band-gap materials and its experimental band gap was reported to be around 8.0 eV [12,13]. To extend the excitation energy range, in this paper we use the pulsed synchrotron radiation, which due to its broad and continuous spectrum is a very useful tool for the investigation of optical and luminescence properties of wide band-gap materials [14–16] that are dominated by UV and VUV excitation.

2. Experimental details

In the present study LaPO₄:Ce,Tb (45 mol% of Ce³⁺, 15 mol% of Tb³⁺) nanopowder was produced via a microwave-accelerated

* Corresponding author. Tel.: +371 2925 9719; fax: +371 6713 2778.

E-mail address: vpank@latnet.lv (V. Pankratov).

synthesis in ionic liquids. This method as well as peculiarities of $\text{LaPO}_4:\text{Ce},\text{Tb}$ nanophosphor were described in detail elsewhere [17–19]. A mean particle diameter of 8–10 nm is obtained for the nanopowder. The commercial bulk $\text{LaPO}_4:\text{Ce},\text{Tb}$ powder phosphor (from Philips) was studied in the present work for comparison. The dopant concentration in the bulk powder was the same as in the nanomaterial and such concentration is quite common for $\text{LaPO}_4:\text{Ce},\text{Tb}$ phosphors. Due to the similar radii of the three-valent rare-earth ions, phase separation does not occur [20,21].

In the present study luminescence properties of $\text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+}$ in the UV–VUV spectral range were studied with pulsed synchrotron radiation from the DORIS III storage ring at DESY (Hamburg, Germany). The Superlumi experimental station of HASYLAB was used for the measurements of emission and excitation spectra [22,23]. The excitation spectra were recorded in the 330–60 nm (3.7–20 eV) spectral range with a spectral resolution of 0.3 nm. Excitation spectra of sodium salicylate were normalized to equal synchrotron radiation intensities impinging onto the sample. Luminescence spectra in the UV and visible/infrared range were recorded with a monochromator (SpectraPro-308i, Acton Research Corporation) equipped with a liquid nitrogen cooled CCD detector (Princeton Instruments) and a photomultiplier (HAMAMATSU R6358P). The spectral resolution of the analyzing monochromator was typically at 11 nm. Emission spectra were corrected for the spectral response of the detection system.

3. Results and discussion

Luminescence spectra of Tb^{3+} emission for both bulk and nanosized samples are pictured in Fig. 1. The spectra were recorded with 250 nm photons which correspond to a $4f^1 \rightarrow 4f^05d^1$ transition on Ce^{3+} . In both samples the characteristic Tb^{3+} lines resulting from $^5\text{D}_4 \rightarrow ^7\text{F}_j$ transitions occur. However, a significant discrepancy between emission spectra is observed if the fine structures of the Tb^{3+} emission lines are considered in details. The comparison of the fine structures of the most intensive line ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) is shown as an inset in Fig. 1. In contrast to the commercial bulk material the fine structure of the Tb^{3+} lines is significantly smoothed in the case of the nanopowder. It is known that the fine structure of the Tb^{3+} lines appears due to crystal-field splitting. Therefore, the strongly smoothed structure of Tb^{3+} lines in the spectrum of nanosized sample could indicate either a low crystallinity of the nanosized sample or a strong perturbation of the crystal field due to the small nanoparticles size. Since X-ray diffraction data clearly demonstrate the crystallinity of the nanosized sample [17–19], we suggest that the nanoparticles surface plays a keyrole with concern to the crystal field perturbation.

A significant discrepancy between commercial and nanosized $\text{LaPO}_4:\text{Ce},\text{Tb}$ could also be seen in the emission spectra of Ce^{3+} in Fig. 2. Firstly, a characteristic duplet structure of the Ce^{3+} emission band in the 300–360 nm range caused by splitting 4f ground level is well resolved in the bulk sample (cf. red line¹ in Fig. 2), whereas this duplet structure is almost absent in the spectrum of the nanopowder (blue line in Fig. 2). Secondly, the Ce^{3+} emission band is slightly shifted to the low energy side. By analogy with the Tb^{3+} emission considered above, the unresolved fine structure of the Ce^{3+} emission band in the nanosized sample could be explained by a perturbed crystal field around the Ce^{3+} ions. Taking into account that the 5d levels are especially sensitive to the Ce^{3+} ion environment, a perturbed crystal field in the nanoparticles could lead to the red shift of the Ce^{3+} emission band.

¹ For interpretation of color in Fig. 2, the reader is referred to the web version of this article.

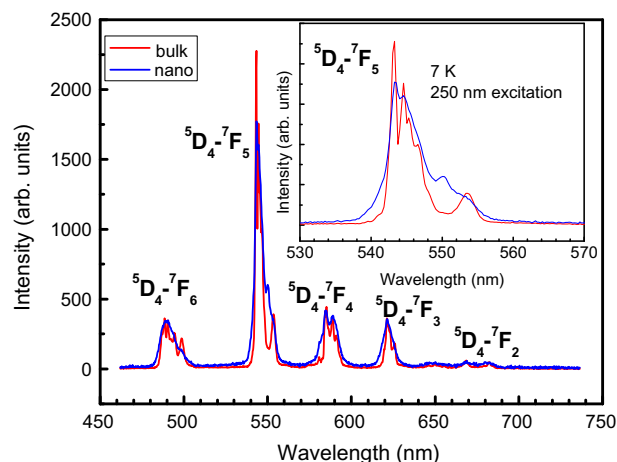


Fig. 1. Emission spectra of Tb^{3+} ions in the macroscopic and nanosized $\text{LaPO}_4:\text{Ce},\text{Tb}$ under excitation in Ce^{3+} absorption band (250 nm) at 7 K. Fine structure of the most intensive line is demonstrated inset in details.

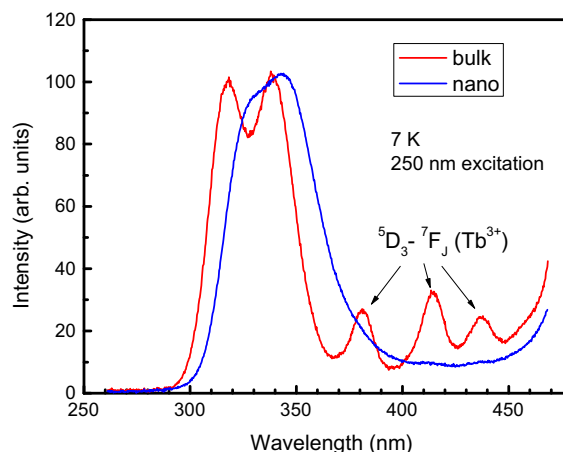


Fig. 2. Emission spectra of Ce^{3+} ions in the macroscopic and nanosized $\text{LaPO}_4:\text{Ce},\text{Tb}$ under excitation in Ce^{3+} absorption band (250 nm) at 7 K.

Less intensive peaks which are well resolved in Fig. 2 for the bulk sample most likely belong to $^5\text{D}_3 \rightarrow ^7\text{F}_j$ transitions on Tb^{3+} . Note that such transitions were not detected for nanosized samples. It is suggested that strong cross-relaxation processes are responsible for degradation of $^5\text{D}_3 \rightarrow ^7\text{F}_j$ emission lines in the nanocrystals. Indeed, a high impurity concentration in relatively small nanoparticles creates favorable conditions for effective cross-relaxation processes.

Excitation spectra of Ce^{3+} and Tb^{3+} are depicted in Figs. 3 and 4 for the bulk and the nanosized samples, respectively. The excitation spectrum of the Ce^{3+} emission in the 4.0–6.5 eV range of the bulk sample (Fig. 3, blue circles) shows $4f \rightarrow 5d$ transition of Ce^{3+} ion in the LaPO_4 matrix. This spectrum is composed of five bands peaking at 4.46, 4.76, 5.2, 5.8 and 6.05 eV, which are due to the transition from the ground state $^2\text{F}_{5/2} (4f^1)$ to the five crystal-field split levels of $^2\text{D} (5d^1)$ excited state in LaPO_4 lattice. These bands are similar to those observed for cerium-doped LaPO_4 and were reported before [24,25]. On the other hand, the bands located in the 6.5–8.0 eV region are related to near-activator exciton bands [25]. The formation and relaxation of near-activator excitons is well-known and established in semiconductors as well as in some ionic crystals [11,26].

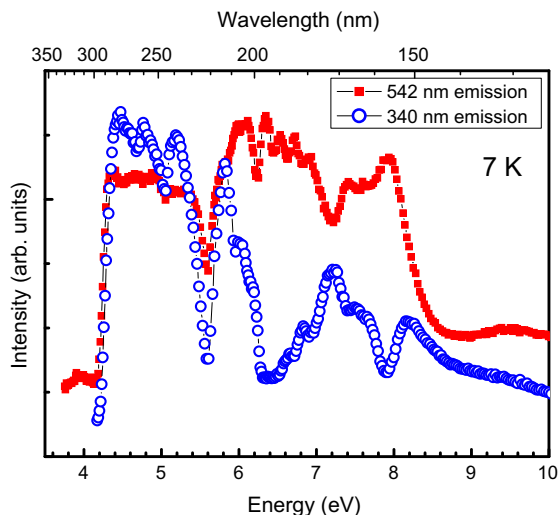


Fig. 3. Excitation spectra of Ce^{3+} (340 nm) and Tb^{3+} (542 nm) emissions in the macroscopic $\text{LaPO}_4:\text{Ce,Tb}$ at 7 K.

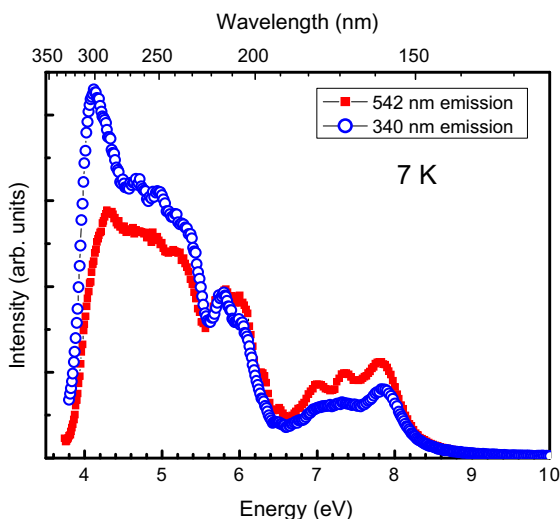


Fig. 4. Excitation spectra of Ce^{3+} (340 nm) and Tb^{3+} (542 nm) emissions in the nanosized $\text{LaPO}_4:\text{Ce,Tb}$ at 7 K.

The excitation spectrum of Tb^{3+} emission for the bulk sample could be visually divided in two ranges: 4.0–5.6 eV and 5.6–7.7 eV. The excitation spectrum of Tb^{3+} emission at energies higher than 5.6 eV represents f–d transitions of the Tb^{3+} ion. The abundant structure of this part of the Tb^{3+} excitation spectrum is explained by the spin-allowed and the spin-forbidden f–d transition from the ground ^7F ($4f^8$) state to the lowest ^7D ($4f^75d$) and to the lowest ^9D ($4f^75d$) terms. In sum, ten bands could be resolved in this spectrum (Fig. 3, red squares) in the 5.6–7.7 eV range which is described in detail in [24] for terbium-doped LaPO_4 . The band peaking at 7.9 eV could be due to near-activator exciton by analogy to the near-activator exciton bands in the Ce^{3+} excitation spectrum. Another part of the excitation spectrum of Tb^{3+} emission in 4.0–5.6 eV is very close to the excitation spectrum of the Ce^{3+} emission (Fig. 3). Taking into account that f–f transitions of Tb^{3+} occur in this spectral range and that these transitions are not effective, the intensive Tb^{3+} excitation band (in 4.0–5.6 eV range) is due to energy transfer from Ce^{3+} to Tb^{3+} .

The excitation spectrum for Ce^{3+} emission in the nanosized sample has intensive bands in the 3.5–6.5 eV spectral range (Fig. 4) which are qualitatively similar to the corresponding

excitation bands obtained for the bulk material in Fig. 3. However, there are several peculiarities in the Ce^{3+} excitation spectrum for the nanopowder. First of all and in contrast to the bulk sample, the fine structure due to the crystal-field splitting is poorly resolved for the nanomaterial. The reason of this poorly resolved structure is similar to the considerations regarding the poorly resolved structure in the Ce^{3+} and Tb^{3+} emission spectra (Figs. 1 and 2). Secondly, the intensive excitation band peaking at 4.0 eV (300 nm) is observed for the nanomaterial (Fig. 4.) and which is absent in the excitation spectrum of bulk $\text{LaPO}_4:\text{Ce,Tb}$ (Fig. 3). The origin of this band is unclear now. However, we can speculate that this excitation band arises due to perturbation of the 5d levels on Ce^{3+} in nanosized $\text{LaPO}_4:\text{Ce,Tb}$. As a result of such perturbation 5d excited state are slightly shifted and, thus, Ce^{3+} excitation and emission spectra of the nanomaterial are shifted to the low energy side as compared to the corresponding spectra of the bulk sample. Note also that the intensity of the excitation band peaking at 4.0 eV of the nanomaterial is higher than the intensity of the other 4f–5d bands. This fact might indicate that the back transfer process is very effective if one excites the lowest Ce^{3+} 4f–5d transition in the nanopowder.

The structure of the excitation spectrum of the Tb^{3+} emission coincides qualitatively with the shape of the excitation spectrum related to Ce^{3+} in nanosized $\text{LaPO}_4:\text{Ce,Tb}$ (Fig. 4). The intensive excitation of Tb^{3+} in 3.5–5.6 eV range is due to energy transfer from Ce^{3+} by analogy with the bulk sample. On the other hand, the part of the excitation spectrum due to f–d transitions on Tb^{3+} (5.6 eV and higher) is significantly suppressed in the nanomaterial. This result is in contradiction to the Tb^{3+} excitation spectrum of the bulk sample where a significant contribution of the f–d transition on Tb^{3+} was detected in the 5.6–7.7 eV range (Fig. 3). It means that Tb^{3+} practically cannot be directly excited in nanosized $\text{LaPO}_4:\text{Ce,Tb}$, but could be excited after energy transfer from Ce^{3+} only. We suggest that due to the small nanoparticle size and a high impurity concentration, Tb^{3+} and Ce^{3+} ions are closely distributed, i.e. no isolated Tb^{3+} ions are present in the nanoparticles. Since the cerium concentration is in three times higher than for terbium, Ce^{3+} ions “shield” Tb^{3+} ions and Ce^{3+} excitation is much more probable.

4. Conclusions

Comparative analysis of luminescence properties of bulk and nanosized $\text{LaPO}_4:\text{Ce,Tb}$ was performed in a wide spectral range including the VUV spectral range. It was demonstrated that the fine structure of both, Ce^{3+} and Tb^{3+} emissions, is significantly smoothed in the case of the nanosized material. It is suggested that a perturbed crystal field is responsible for the luminescence properties changes of Ce^{3+} and Tb^{3+} dopants in the nanosized material. The reason for this crystal field perturbation in the nanopowder is attributed to the nanoparticle’s surface. Significant differences regarding the excitation spectra for bulk- and nano- $\text{LaPO}_4:\text{Ce,Tb}$ were also obtained for Ce^{3+} as well as for Tb^{3+} emission. It is concluded that the Tb^{3+} emission of the nanosized material could not be directly excited under excitation via allowed f–d transitions, and that energy transfer from Ce^{3+} is required for excitation of Tb^{3+} in VUV range.

Acknowledgements

The work of V. Pankratov was granted by ESF Project #2009/0202/1DP/1.1.1.2.0/09/APIA/VIAA/141. The research of A.I. Popov was partially supported by Sadarbības projekts #10.0032. The experiments at DESY leading to these results have received funding from the European Community’s Seventh Framework Programme (FP7/2007–2013) under Grant agreement #226716.

References

- [1] N. Hashimoto, Y. Takada, K. Sato, S. Ibuki, *J. Lumin.* 48–49 (1991) 893.
- [2] T. Norby, N. Christiansen, *Sol. State Ionics* 77 (1995) 240.
- [3] Y. Hikichi, T. Ota, K. Daimon, T. Hattori, M. Mizuno, *J. Am. Ceram. Soc.* 81 (1998) 2216.
- [4] Y. Fang, A. Xu, R. Song, H. Zhang, L. You, J.C. Yu, H. Liu, *J. Am. Chem. Soc.* 125 (2003) 16025.
- [5] C. Feldmann, T. Jüstel, C.R. Ronda, P.J. Schmidt, *Adv. Funct. Mater.* 13 (2003) 511.
- [6] G.J. McCarthy, W.B. White, D.E. Pfoertsch, *Mater. Res. Bull.* 13 (1978) 1239.
- [7] A. Meldrum, L.A. Boatner, R.C. Ewing, *Phys. Rev. B* 56 (1997) 13805.
- [8] K. Riwozki, H. Meysamy, H. Schnablegger, A. Kornowski, M. Haase, *Angew. Chem. Int. Ed.* 40 (2001) 573.
- [9] S. Heer, O. Lehmann, M. Haase, H.U. Güdel, *Angew. Chem. Int. Ed.* 42 (2003) 3179.
- [10] K. Riwozki, H. Meysamy, A. Kornowski, M. Haase, *J. Phys. Chem. B* 104 (2000) 2824.
- [11] V. Pankratov, A.I. Popov, S.A. Chernov, A. Zharkouskaya, C. Feldmann, *Phys. Status Solidi b* 247 (2010) 2252.
- [12] E. Nakazawa, F. Shiga, *J. Lumin.* 15 (1977) 255.
- [13] U. Sasum, M. Kloss, A. Rohmann, L. Schwarz, D. Haberland, *J. Lumin.* 72–74 (1997) 255.
- [14] V. Pankratov, M. Kirm, H. von Seggern, *J. Lumin.* 113 (2005) 143.
- [15] H.H. Rüter, H. von Seggern, R. Reininger, V. Saile, *Phys. Rev. Lett.* 65 (1990) 2438.
- [16] V. Pankratov, L. Grigorjeva, S. Chernov, T. Chudoba, W. Lojkowski, *IEEE Trans. Nucl. Sci.* 55 (2008) 1509.
- [17] G. Bühler, C. Feldmann, *Angew. Chem. Int. Ed.* 45 (2006) 4864.
- [18] G. Bühler, C. Feldmann, *Appl. Phys. A* 87 (2007) 631.
- [19] A. Zharkouskaya, C. Feldmann, K. Trampert, W. Heering, U. Lemmer, *Eur. J. Inorg. Chem.* (2008) 873.
- [20] G. Blasse, B.C. Grabmaier, *Luminescent Materials*, Springer, Berlin, 1994.
- [21] W.M. Yen, S. Shionoya (Eds.), *Phosphor Handbook*, CRC Press, Boca Raton, FL, 1999.
- [22] G. Zimmerer, *J. Lumin.* 119–120 (2006) 1.
- [23] G. Zimmerer, *Rad. Meas.* 42 (2007) 859.
- [24] E. Nakazawa, F. Shiga, *Jpn. J. Appl. Phys.* 42 (2003) 1642.
- [25] G. Stryganyuk, D.M. Trots, A. Voloshinovskii, T. Shalapska, V. Zakordonskiy, V. Vistovskyy, M. Pidzyrailo, G. Zimmerer, *J. Lumin.* 128 (2008) 355.
- [26] A.S. Chernov, L. Trinkler, A.I. Popov, *Rad. Eff. Def. Sol.* 143 (1998) 345.