Journal of Luminescence 142 (2013) 96–102

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

A study of optical properties of Sm^{3+} ions in α-$Na_3Y(VO_4)_2$ single crystals

Marcin Sobczyk*, Damian Szymański

Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

ARTICLE INFO

Article history:
Received 30 January 2013
Received in revised form
19 March 2013
Accepted 29 March 2013
Available online 10 April 2013

Keywords:
Samarium Sm^{3+}
Vanadates
Luminescence
Energy transfer
Crystals
Vibronic transitions

ABSTRACT

Single crystals of α-Sm^{3+}:$Na_3Y(VO_4)_2$ have been grown by the flux growth method. The absorption (300 K) fluorescence (4.2 and 300 K) and excitation (7 and 300 K) spectra as well as the fluorescence dynamics of the Sm^{3+}-doped title crystals are presented and analyzed in detail. The energy transfer between Sm^{3+}–Sm^{3+} as well as from VO_4^{3-} to Sm^{3+} were studied in detail. A Judd–Ofelt intensity analysis of the absorption (300 K) spectrum has been applied for determination of Ω_λ parameters which in turn have been used in calculation of the radiative transition probability factor (A), fluorescence branching ratios (β), natural (radiative) lifetime of the $^4G(4)_{5/2}$ level of Sm^{3+} and emission cross-section (σ_{em}). For the first time very large lifetimes of the Sm^{3+} fluorescence level have been observed.

1. Introduction

Tetraoxovanadates(V) activated by lanthanide ions are of interest due to their useful luminescent properties. Vanadates, except Tb^{3+}, are excellent host lattices for various trivalent lanthanide ions, due to their efficiency energy transfer from the VO_4^{3-} ion to these activator ions leading to intense emission [1]. Absorption bands of the $4f^N \rightarrow 4f^N$ transitions of Ln^{3+} doped tetraoxovanadates (V) are characterized by relatively high values of cross sections allowing an efficient excitation into $^{2S+1}L_J$ levels, using a cheap commercial source of excitation. Eu^{3+}: YVO_4 was an important commercial red phosphor used in color television, cathode ray tubes (CRTs) and high-pressure lamps [2,3]. Europium doped vanadates have been used as phosphors for X-ray intensifying screen and X-ray computed tomography [4]. Nd^{3+}-doped YVO_4 single crystals are very efficient commercial laser materials operating at 1064 nm and pumped by semiconductor laser at 808 nm due to a broad and strong Nd^{3+} absorption bands [5–7]. Neodymium and erbium ions-doped vanadates(V) shows a strong emission under UV excitation due to the efficient energy transfer from the CT state to the $4f^3$ (Nd^{3+}) or $4f^{11}$ (Er^{3+}) electronic states [8,9]. Relatively strong fluorescence at 1064 nm from Nd^{3+} ions was observed also in Nd^{3+}:$KZnLa(VO_4)_2$ under 808 or 354.5 nm excitation to the $^4F_{5/2}$ or CT bands, respectively [9]. Erbium-doped $KCaY(VO_4)_2$ shows a strong green and near infrared emission under UV observed under excitation at 980 and 320 nm, respectively.

In recent years an increasing interest in inorganic samarium(III) compounds: bulk crystals, nanocrystals and glasses has been reported due to high fluorescence quantum yields. Analyzes of absorption and fluorescence spectra, decay kinetics and mechanisms of energy transfer leading to the depopulation of fluorescence level has been presented by many authors. Trivalent samarium ions are widely used as activators characterized by efficient emission from the $^4G(4)_{5/2}$ level to the ^6H_J (J=5/2, 7/2, 9/2, 11/2) states in vis spectral region [10,11]. The color of this emission is usually reddish orange.

Fluorescence of Sm^{3+} ions in the NIR region, which originate from the $^4G(4)_{5/2}$ level to the $^6H_{13/2}$, $^6H_{15/2}$ and ^6F_J (J=1/2, 3/2, 5/2, 7/2, 9/2, 11/2) states, is presented and discussed very rarely. The $^4G(4)_{5/2}$ state shows different quenching emission channels which make the Sm^{3+} ion an interesting case to analyze the energy transfer process. Studies of Sm^{3+}-doped crystals and glasses are mainly focused for the possible application as phosphors of visible light efficiency, which absorb the excitation energy in the UV–VUV and vis regions [12,13]. Earlier studies on optical absorption and emission spectra of Sm^{3+}: $LiNbO_3$ have demonstrated the possibility a laser action with a unique orange wavelength [14]. The scientific literature encountered also a report of NIR to vis upconverted emission for some Sm^{3+} -doped crystals [15,16]. However, among all the trivalent lanthanide ions, except promethium, spectroscopic properties of the Sm^{3+} ion are still little understood and described. It especially concern hosts in which CT transitions are located in the near UV with efficient energy transfer to the $4f^5$ levels of Sm^{3+}, such as e.g. tetraoxovanadates (V) matrices [17].

Earlier spectroscopic studies of Dy^{3+} [18] and Nd^{3+}-doped [19] α-$Na_3Y(VO_4)_2$ shows that α-$Na_3Y(VO_4)_2$ is promising host matrix

* Corresponding author. Tel. +48 71 3757333, +48 71 3757321; fax: +48 71 328 2348.
E-mail address: marcin.sobczyk@chem.uni.wroc.pl (M. Sobczyk).

0022-2313/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jlumin.2013.03.062

for lanthanide ions. The crystal exhibits an efficient energy transfer from VO_4^{3-} to the Dy^{3+} ion [18]. Low energy excitation losses and high emission cross-section of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ laser transition at 1064 nm were observed for α-Nd^{3+}: $Na_3Y(VO_4)_2$ single crystals [19].

The aim of the present study is to investigate the fluorescence properties of Sm^{3+}-doped α-$Na_3Y(VO_4)_2$ single crystals. α-$Na_3Y_{1-x}Sm_x(VO_4)_2$ (where $x=0.01$, 0.1, 0.5, 1.0, 2.0 and 5.0 at%) single crystals with an average size of about 140 μm^3 were grown by flux growth method. The absorption (300 K), excitation (300 K) and fluorescence (4.2 and 300 K) spectra were investigated in detail in the NIR–vis–UV and VUV region along with the electronic structure of Sm^{3+} and energy transfer mechanisms between Sm^{3+}–Sm^{3+}, and Sm^{3+}–VO_4^{3-} ions. The Judd–Ofelt theory has been applied to characterize important emission properties of Sm^{3+} ions. Radiative transition probabilities, fluorescence branching ratios, radiative decay time and emission cross-sections have been calculated. The effect of the Sm^{3+} ion concentration on decay times are discussed.

2. Experimental

The single crystals of α-$Na_3Y_{1-x}Sm_x(VO_4)_2$ (where $x=0.01$, 0.1, 0.5, 1.0, 2.0 and 5.0 at%) were prepared according to the procedure reported for α-Nd^{3+}: $Na_3Y(VO_4)_2$ in Ref. 19. The maximum size of the α-$Na_3Y_{1-x}Sm_x(VO_4)_2$ crystal achieved is about $18 \times 4 \times 2$ μm^3 for the optimum process conditions (1323 K and cooling rate 2 K/h). High purity (99.999%) Na_2CO_3, Y_2O_3, Sm_2O_3 and NH_4VO_3 were used as starting materials.

The electronic absorption spectra were recorded at room temperature on a Cary 500 SCAN NIR–vis–UV spectrophotometer (Varian). Microcrystalline samples in form of compressed and polished disc-shaped pellets (ca. 0.494 mm thick and 12.63 mm diameter) were used in order to obtain high-quality absorption spectra. Previously water from the surface of the pellets, has been removed by heating for a time at 500 °C followed by a slowly cooling to room temperature. Finally they were fixed in the spectrophotometer on a copper holder.

The fluorescence and excitation spectra corrected for the instrument characteristics in the vis–UV region were recorded on Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) equipped with a continuous Xe lamp. The fluorescence signals were detected using a high-resolution HR–4000 Ocean-Optics spectrofluorometer. For low-temperature measurements (fluorescence spectra) a continuous flow helium cryostat (Oxford model CF 1204) equipped with a temperature controller was used.

Fluorescence decay curves were recorded with a GDM-1000 monochromator and a Tektronix model TDS 3052 digital oscilloscope following the selective excitation by a Continuum Surelite I optical parametric oscillator (OPO) pumped by a third harmonic of a Nd:YAG laser and detected by an Hamamatsu R955 photomultiplier with S-20 spectral response.

UV–VUV spectroscopic measurements with synchrotron radiation were undertaken on beamline I of the SUPERLUMI experimental station of the Synchrotronstrahlungslabor HASYLAB at DESY in Hamburg, Germany. VUV eexcitation spectra were corrected for spectral efficiency of the excitation source by using a sodium salicylate standard. A detailed description of this set-up is given elsewhere [20].

3. Results and discussion

3.1. Electronic structure and fluorescence properties

The α-$Na_3Y(VO_4)_2$ crystallizes in the monoclinic space group $P2_1/n$ with $Z=2$ [18,21]. The Sm^{3+} ions replace the single crystallographic position of Y^{3+}. The site symmetry of the Y^{3+} and Sm^{3+} is C_{2v}. Free Sm^{3+} ion has a $4f^5$ configuration with the $^6H_{5/2}$ ground state level.

High-resolution absorption spectrum of the α-$Na_3Y_{0.95}Sm_{0.05}(VO_4)_2$ crystal was measured at 300 K in NIR–vis–UV spectral region and is shows in Fig. 1. In the 5500–25000 cm^{-1} range, relatively sharp and well separated bands of intraconfigurational $4f^5 \rightarrow 4f^5$ transitions from the $^6H_{5/2}$ level were observed, exclusively. The absorption bands of the Sm^{3+} ion can be classified into two groups: the first group in the NIR spectral region, contains transitions up to about 10700 cm–^{1} and the second one is a high–energy group containing transitions in the vis–UV range. The absorption bands observed between 6000–7000 cm^{-1} are ascribed to transitions from the $^6H_{5/2}$ level to the $^6F_{1/2}$, $^6H_{15/2}$ and $^6F_{3/2}$ levels. The $^6H_{5/2} \rightarrow {}^6F_{1/2}$ and $^6H_{5/2} \rightarrow {}^6F_{3/2}$ transitions are characterized by much larger values of matrix elements than the $^6H_{5/2} \rightarrow {}^6H_{15/2}$ transition; we conclude that the most intensive line at 6353 cm^{-1} is a Stark component of the $^6F_{1/2}$ level and the intensive lines at 6816 and 6833 cm^{-1} are crystal-field components of the $^6F_{3/2}$ level. The bands between 7000 and 10700 cm^{-1} and 17500–20000 cm^{-1} are well separated. Their assignment to the corresponding electronic transitions do not cause problems. Bands observed between 20400–20900 cm^{-1} are ascribed to transitions from the $^6H_{5/2}$ to the $^4I(3)_{9/2}$ and $^4M_{15/2}$ states. In the α-Sm^{3+}:$Na_3Y(VO_4)_2$ crystal, $S'L'M_{J'}$ levels higher energies than that of $^4M_{15/2}$ are not observed due to scattering of light by the pressed pellet.

The 4.2 and 300 K fluorescence spectra of the α-Sm^{3+}:$Na_3Y(VO_4)_2$ crystal, pumped by the 405 nm diode laser are shown in Fig. 2 along with emission peaks labeled as shown. The spectra were calibrated for the spectral response of the used monochromator and detector. The 405 nm (24691 cm^{-1}) laser line excites the $4f^5$ electrons from the $^6H_{5/2}$ ground level to the $^6P_{3/2}$ level, and next the $^4G(4)_{5/2}$ level is populated via a non-radiative process. The observed fluorescence lines are found to originate from the $^4G(4)_{5/2}$ level to those of $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{11/2}$ and $^6H_{13/2}$ in the visible range and to the $^6H_{13/2}$, $^6F_{1/2}$, $^6H_{15/2}$ and $^6F_{3/2}$ levels in the near–infrared spectral region. The bands, corresponding to the $^4G(4)_{5/2} \rightarrow {}^6H_{9/2}$ transition with maximum at 15264 cm^{-1} are stronger than the $^4G(4)_{5/2} \rightarrow {}^6H_{7/2}$ transition as well as the other transitions. For Sm^{3+}:YVO_4 the $^4G(4)_{5/2} \rightarrow {}^6H_{7/2}$ transition is dominating [22]. Reddish orange light from the Sm^{3+}:$Na_3Y(VO_4)_2$ is observed by naked eyes and its CIE chromaticity coordinates are calculated to be ($x=0.627$, $y=0.349$) based on the emission spectrum excited by 405 nm at 300 K. Several extra lines, due to vibronics, were detected too. The fine structure of the $^{2S+1}L_J$ multiplets is well manifest in the 4.2 K. At 300 K one observes additional lines with correspond to transitions from the second and third crystal-field component of the $^4G(4)_{5/2}$ level. One may notice also a

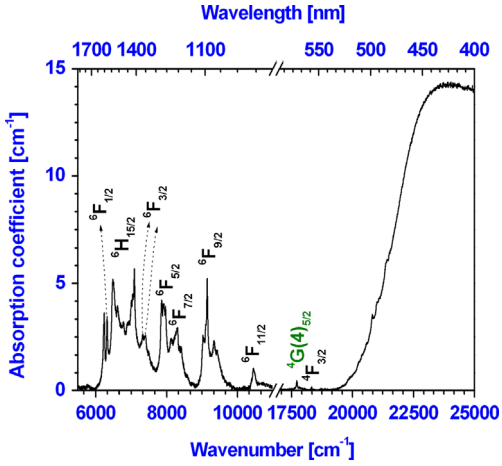

Fig. 1. Absorption spectrum of α-Sm^{3+}: $Na_3Y(VO_4)_2$, recorded at 300 K.