The luminescence properties of dysprosium ions in silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$

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The new material consisting of $Gd_{1.6}Dy_{0.4}(WO_4)_3$ incorporated into silica xerogel was prepared via the coprecipitation method. The luminescence properties of the studied material were analyzed by means of emission and excitation spectra, including the result of luminescence lifetimes of Dy(III) ion. The enhanced yellow emission due to the excitation energy transfer from WO_4^{2-} group to Dy(III) ion upon excitation at $\lambda_{exc} = 240$ nm is the main result of this paper.

1. Introduction

It is well-known that rare earth ions play an important role in such applications as efficient solid-state materials emitting visible light. The essence of photoluminescence spectroscopy of the trivalent rare earth ions is associated with their characteristic narrow emission band arising from the intraconfigurational 4*f*–*f* transitions [1]. Nowadays, the three emission colors: blue, green and red are usually obtained with rare earth ions. Among red phosphors, materials with Eu(III) and Sm(III) ions are the most extensively studied of the various luminescent materials [2–4]. However, green light is obtained by using materials with Tb(III) ion [5]. On the other hand, trivalent dysprosium ions exhibit very interesting luminescence of two primary color phosphors. The energy level of Dy(III) ion offers the possibility of efficient emissions at 480 nm and 575 nm which are due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) transitions, respectively, in the spectral region [6]. Additionally, the emission of Dy(III) ion strongly depends on the kind of host matrix. The $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition is named as hypersensitive and its intensity strongly depends on the host, however,

the $^4F_{9/2} \to {}^6H_{15/2}$ transition is less sensitive. Dysprosium ions are good as a yellow source, because of strong yellow luminescence and it creates the possibility of using them in yellow lasers and for generation of white light emission to be used for optical display systems [7]. The luminescence properties of Dy^{3+} ions as potential candidates for laser host in some crystals [8], glasses [6, 9] and gels [10] have been studied.

Tungstates doped with rare earth ions have been investigated widely for a variety of optical applications. Therefore we focused our attention on the synthesis and luminescence properties of materials consisting of Gd(III) tungstate in the presence of Dy^{3+} ions incorporated into silica xerogels. These xerogels have a wide transmission region, good thermal stability and high nonlinear refractive index. During the last years numerous xerogels matrices were obtained by the sol–gel process [11].

The sol–gel process is an excellent method for preparing inorganic or hybrid organic–inorganic amorphous materials. This method occurs at ambient temperature and allows to obtain various shapes of materials like bulks or thin films for preparing phosphors for luminescent materials [12]. Moreover, this method has the advantage of providing negligible diffusion loss, high quality and purity.

In this study, we present new results for materials consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$, which showed two major emission peaks at 480 and 575 nm. Among them the most intense is a peak placed at about 575 nm.

2. Experiment

2.1. Sample preparation

Material consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$ was prepared via the coprecipitation method. The starting compounds used in these studies were of at least analytical grade. Sodium tungstate was purchased from POCh, Poland; lanthanide (III) nitrates: $Dy(NO_3)_3 \cdot 5H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$ from Aldrich Co.; disodium ethylenediaminetetraacetate (EDTA) from POCh, Poland; polyethylene glycol 400 (PEG 400) and tetramethoxysilane ($Si(OCH_3)_4$, TMOS) from Aldrich Co.

To prepare the material, sodium tungstate was dissolved in warm water (60 °C). The aqueous solutions of gadolinium (III) and dysprosium (III) nitrates were mixed together. Then the solutions of lanthanide (III) nitrates and sodium tungstate in appropriate amounts were mixed. After a while, insoluble white precipitate of $Gd_{1.6}Dy_{0.4}(WO_4)_3$ was obtained. Next, EDTA was added to this mixture to form a stable complex with Ln(III) ions, while WO_4^{2-} groups remained dissolved in the solution. Sodium compounds used during the synthesis procedure have not been eliminated, because they can play a role of a charge compensator. The incorporation of Na^+ ions greatly enhances the luminescence intensity and stabilizes the structure probably due to the influence of charge compensation of alkali metal ion [13]. Polyethylene glycol (PEG) and TMOS were added to homogeneous solution upon continuous stirring and heating; after several hours transparent gel was formed as a result of the sol–gel process. In the last step the product was calcined over the temperature range 600–900 °C for 3 h in the air atmosphere. Finally, we obtained

material in which $Gd_{1.6}Dy_{0.4}(WO_4)_3$ is incorporated into silica xerogel as a white powder.

2.2. Apparatus

The photoluminescence excitation and emission spectra were recorded on a Cary Eclipse spectrofluorometer with a reflection spectra attachment. The emission spectra of the silica xerogel samples doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$ were obtained upon excitation at $\lambda_{exc} = 240$ nm within the absorption band range of the WO_4^{2-} group, at that excitation wavelength acceptors do not absorb. Additionally, the emission spectra of the studied materials were obtained within absorption bands of Dy(III) ion $\lambda_{exc} = 352$ nm. The luminescence kinetics was recorded at room temperature with the pulsed spectrofluorometer described previously in detail [14].

3. Results and discussion

The photoluminescence behavior of Dy(III) ions in the prepared material consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$ was examined regarding their applications as yellow lasers and for the generation of white light emission to be used for optical display systems. For material studied, enhancement of the emission intensity of Dy(III) ions was observed because of the energy transfer. It is evidenced by the results of excitation and emission spectra. Emission spectra were recorded under excitation by $\lambda_{exc} = 352$ nm and $\lambda_{exc} = 240$ nm. The high emission intensity of the material consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$ were obtained upon excitation at 240 nm within the absorption band range of the WO_4^{2-} group, at that excitation wavelength acceptors do not absorb.

The photoluminescence excitation spectrum of material consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$ and annealed at 800 °C is shown in Fig. 1. The spectrum was measured upon the emission wavelength $\lambda = 575$ nm which corresponds to

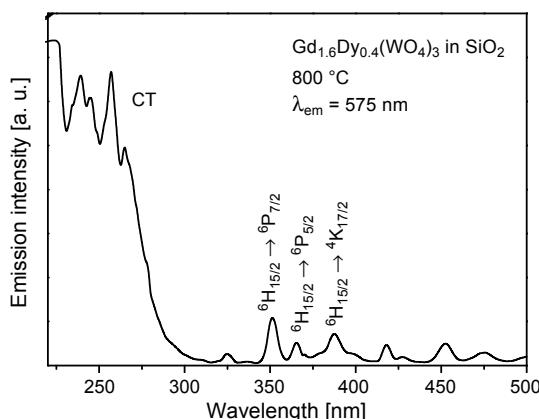Fig. 1. Excitation spectra of material consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$.

the Dy(III) $^4F_{9/2} \to {}^6H_{13/2}$ transition. A broad excitation band centering at about 240 nm with a shoulder at about 250 nm is observed in the UV range. It is attributed to the charge transfer (CT) transition from oxygen to tungsten in WO_4^{2-} group, it means the transition can be assigned to the transition from the ground state $^1A_1$ to the upper state $^1T_1$. However, the shoulder at about 250 nm can correspond to the charge transfer transition between $O^{2-} \to Dy^{3+}$. It indicates that the interactions between Dy^{3+} ions and host lattice are strong. Along this band, it is also possible to observe several narrow bands located between 320 and 500 nm, which are assigned to the appropriate electronic transitions of Dy(III) ion as follows: $^6H_{15/2} \to {}^6P_{7/2}$ (352 nm), $^6H_{15/2} \to$ $\to {}^6P_{5/2}$ (364 nm), $^6H_{15/2} \to {}^4K_{17/2}$ (388 nm), $^6H_{15/2} \to {}^4G_{11/2}$ (429 nm), $^6H_{15/2} \to$ $\to {}^4I_{15/2}$ (452 nm) and $^6H_{15/2} \to {}^4F_{9/2}$ (476 nm). Two of them, $^6H_{15/2} \to {}^6P_{7/2}$ and $^6H_{15/2} \to {}^4K_{17/2}$ transitions, are the most intense.

Figure 2 shows the photoluminescence emission spectra of material consisting of $Gd_{1.6}Dy_{0.4}(WO_4)_3$ incorporated into silica xerogel and annealed at 800 °C under different excitation wavelengths at $\lambda_{exc} = 352$ nm and $\lambda_{exc} = 240$ nm, respectively. Independently of the excitation wavelengths we get sharp emission lines. The shape of the lines is quite similar, however the intensity of the bands is different. The two intense bands are centered at 485 nm and 575 nm with less intense band at 662 nm. The observed luminescence peaks are due to the transitions from excited energy level $^4F_{9/2}$ of the dysprosium ion to $^6H_{15/2}$ (blue), $^6H_{13/2}$ (yellow) and $^6H_{11/2}$ (red), respectively. Additionally, the spectrum *a* consists of a wide intrinsic luminescence band in the region 300–470 nm of the host with the maximum placed at about 420 nm. This band is based on the radiative transition within the tetrahedral $[WO_4^{2-}]$ group [15, 16]. From the literature [16] it is shown that, if the excitation wavelength is longer than 240 nm and shorter than 390 nm, the WO_4^{2-} group cannot be excited directly. Therefore we cannot observe the emission of tungstate group in the spectrum *b*.

Emission intensity enhancement is observed if the Dy(III) ions in silica xerogel are excited with the wavelength corresponding to the CT absorption band, *i.e.*, $\lambda_{exc} =$
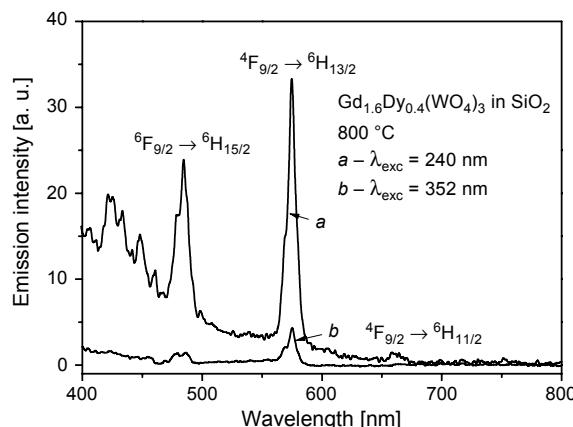

Fig. 2. Emission spectra of material consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$.
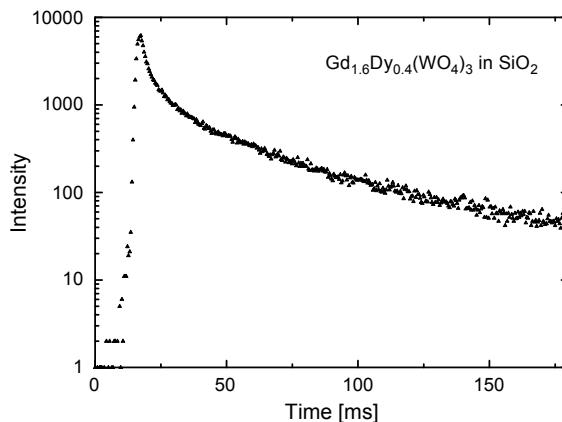
Fig. 3. Luminescence decays for material consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$. Observation wavelength at λ_{obs} = 575 nm; excitation wavelength λ_{exc} = 240 nm.

= 240 nm. In the case of the excitation wavelength λ_{exc} = 352 nm, characteristic of Dy(III) ion, the emission intensity of the band located at 575 nm is about nine times lower. The enhancement effect results from energy transfer from $O^{2-} \to W$ transition in tungstate group to Dy(III) ion.

Moreover, the luminescence decay for the $^4F_{9/2}$ state of dysprosium ion in the studied material was analyzed (Fig. 3). It was found that the luminescence decay curve can be formally described as non-exponential with two components: τ_1 = 33.59 μs (A_1 = 1797.9) and τ_2 = 4.44 μs (A_2 = 158470), where: A_1 and A_2 – denote the amplitudes of respective decay components, τ_1 and τ_2 are fluorescence lifetimes components contributing to the average lifetime. For the purpose of this work, τ_1 and τ_2 are formal fitting parameters used only to obtain the average lifetime τ_{av}. The measured $^4F_{9/2}$ lifetime of Dy(III) ion is equal to τ_{av} = 4.7 μs. The values determined by us are much shorter. In our amorphous silica xerogels, the concentration of OH groups, which decrease lifetime, is higher as compared to glass and crystalline systems. In fact, OH stretching vibrations (3500 cm^{-1}) induce non-radiative relaxation by covering the energy gaps between electronic states with several vibrational quanta.

It is worthy of note that we deal here with only one luminescent center at a given observation wavelength, which decays in a complex way as a result of energy transfer leading to the deviations from single exponential decay [17].

In order to avoid emission quenching of O–H oscillators, the emission intensity of Dy(III) ion has been studied as a function of annealing temperature in material consisting of $Gd_{1.6}Dy_{0.4}(WO_4)_3$ incorporated into silica xerogel. Figure 4 shows that the emission intensity of Dy(III) ion in the studied materials increases with the increase in temperature up to 800 °C. Water molecules come from both silica matrix and coordination sphere of Dy(III) ion. Thus, the removal of O–H groups leads to an increase in the emission intensity. In our previous paper [3], we reported that heating at least up to 1000 °C causes a decrease in of the emission intensity. This is possible,
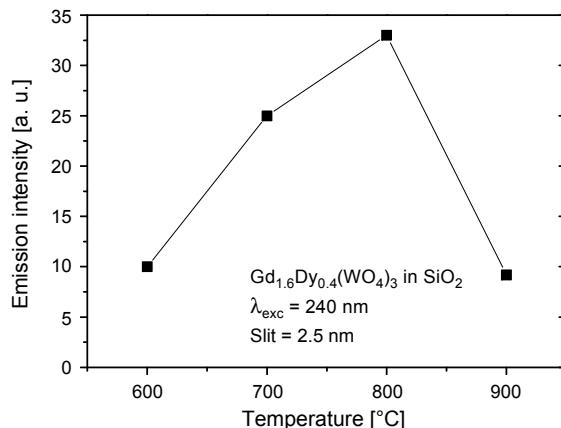
Fig. 4. The dependence of Dy^{3+} emission intensity I of the band $^4F_{9/2} \rightarrow {}^6H_{13/2}$ at 575 nm with annealing temperature for material consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$. The lines are drawn as guide to the eyes.
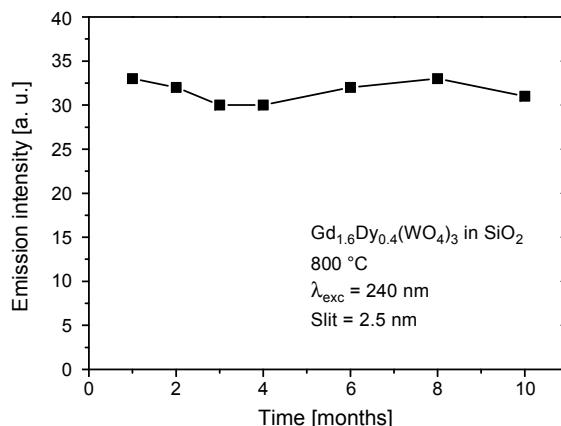

Fig. 5. The dependence of Dy^{3+} emission intensity I of the band $^4F_{9/2} \rightarrow {}^6H_{13/2}$ at 575 nm with time for material consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$. The lines are drawn as guide to the eyes.

since the formation of mixed lanthanide silicate and tungstate salt could occur. Additionally, material consisting of $Gd_{1.6}Dy_{0.4}(WO_4)_3$ incorporated into silica xerogel heated up to the temperature around 1000 °C could transform into glassy material.

The good luminescent material should be resistant to UV–VIS radiation and water absorption from the air atmosphere for long time. Therefore, it has not shown changes in emission intensity during illumination by the sun radiation. As it is shown in Fig. 5, the emission intensity of material consisting of silica xerogel doped with $Gd_{1.6}Dy_{0.4}(WO_4)_3$ is constant within the experimental error for ten months.

4. Conclusions

The new material consisting of $Gd_{1.6}Dy_{0.4}(WO_4)_3$ incorporated into silica xerogel was prepared and the luminescence properties were studied using spectroscopic techniques. Our experiments have confirmed that effective energy transfer from WO_4^{2-} group to Dy(III) ion takes place. The material under study exhibits the photoluminescence excitation spectra with a broadband related to the O–W(VI) charge transfer transition. Moreover, the strong yellow emission of Dy(III) ions is due to the efficient energy transfer from the excited W(VI) in the tungstate group through O(II) to Dy(III) ions. Decay curve for $^4F_{9/2}$ level of Dy^{3+} ion is non-exponential and average luminescence lifetime is close to $\tau_{av} = 4.7$ µs.

The Dy(III) emission intensity in the studied materials increases with the temperature increasing up to 800 °C. It is due to removing of O–H quenchers from the coordination sphere of Dy(III) ions and from silica xerogel. The emission intensity of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ band has been constant for ten months.

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