

The effect of WO_4^{2-} group in xerogels doped with $\text{Ln}_{2-x}\text{Pr}_x(\text{WO}_4)_3$ where $\text{Ln} = \text{La, Gd}$

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We present a synthesis of highly efficient xerogels doped with $\text{Ln}_{2-x}\text{Pr}_x(\text{WO}_4)_3$, where $\text{Ln} = \text{La}$ or Gd as novel phosphors. For comparison, the synthesis of xerogels doped only with Pr(III) and La(III) ions was made. The photoluminescence properties of Pr(III) ions in xerogels were studied by means of luminescence spectroscopy. In particular, an efficient energy transfer from WO_4^{2-} to Pr(III) ions was observed and demonstrated by their enhanced luminescence intensity. Especially interesting seems to be strong red acceptor emission observed upon excitation at 240 nm (donor excitation). Therefore, $4f-4f$ emission makes the system usable for red phosphor applications. Additionally, the emission intensity of the materials was improved by reducing concentration of such quenchers as water molecules and OH groups by the thermal treatment.

Keywords: photoluminescence, praseodymium(III) ions, sol-gel method, energy transfer process.

1. Introduction

Rare earth doped xerogels are being studied for use as lasers, materials for amplifier devices, phosphors for color television, fluorescent tubes and medical imaging [1]. In the luminescent materials field, phosphors based on lanthanide ions play an important role because of the sharp absorption and emissions lines. 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, 3].

On the other hand, it is known that trivalent praseodymium ion exhibits very interesting luminescence as an activator ion. The energy levels of Pr(III) ion contain several metastable multiplets $^3P_{0,1,2}$, 1D_2 and 1G_4 that offer the possibility of efficient emissions, such as red ($^1D_2 \rightarrow ^3H_4$), green ($^3P_0 \rightarrow ^3H_4$), and blue ($^1S_0 \rightarrow ^3H_4$) in the spectral region [4, 5]. Additionally, the emission of Pr(III) ions depends on the kind of host matrix. Oxides with perovskite structure such as $\text{CaTiO}_3:\text{Pr}^{3+}$ or

$\text{SrTiO}_3:\text{Pr}^{3+}$ exhibit usually red emission with maximum placed at about 613 nm [6]. However, to the best of our knowledge, there are no samples doped with Pr(III) ions that have been emitted at 647 nm. Therefore, we focused our attention on the synthesis and luminescence properties of materials consisting of Gd(III) or La(III) tungstate in the presence of Pr^{3+} ions incorporated into silica xerogels. Pr(III) ions for applications in solid-state lasers and electroluminescent devices have to be assembled in transparent composite materials [7]. These xerogels have a wide transmission region, good thermal stability and high nonlinear refractive index. During the last years numerous xerogel matrices were obtained by the sol–gel process [8, 9].

The sol–gel process for production of inorganic or hybrid organic-inorganic amorphous materials occurs at ambient temperature and is an excellent method for obtaining phosphors for luminescent materials [10]. Moreover, this method has the advantage of providing negligible diffusion loss, high quality and purity.

In this study, xerogels doped with $\text{Ln}_{2-x}\text{Pr}_x(\text{WO}_4)_3$ showed three major red emission peaks from 605 to 648 nm. Among them the most intense is the peak placed at about 648 nm. In order to enhance the Pr(III) emission the energy transfer process can be achieved by using xerogels doped with $\text{Ln}_{2-x}\text{Pr}_x(\text{WO}_4)_3$. For comparison purposes the photoluminescence properties of xerogels without WO_4^{2-} groups were studied.

2. Experiment

2.1. Sample preparation

The starting compounds used in these studies were of at least analytical grade. Sodium tungstate was purchased from POCh (Poland); lanthanide(III) nitrates: $\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ from Aldrich Co.; disodium ethylenediamine-tetraacetate, EDTA from POCh (Poland); polyethylene glycol 400, PEG and tetramethoxysilane $\text{Si}(\text{OCH}_3)_4$, TMOS from Aldrich Co.

Sodium tungstate was dissolved in warm water (60 °C). The aqueous solutions of lanthanide(III) nitrates were mixed together. The doping concentration x of the Pr(III) ions was 0.002–2 molar ratio of praseodymium in the $\text{Ln}_2(\text{WO}_4)_3$ (where Ln = Gd, La) host. Then, the solutions of lanthanide(III) nitrates and sodium tungstate in appropriate amounts were mixed. After a while, insoluble white precipitate of $\text{Ln}_{2-x}\text{Pr}_x(\text{WO}_4)_3$ 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. 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 $\text{Ln}_{2-x}\text{Pr}_x(\text{WO}_4)_3$ entrapped in a silica xerogel as a white powder material.

However, xerogels without WO_4^{2-} groups were synthesized in a similar manner, as above. The aqueous solutions of La(III) and Pr(III) nitrates were mixed together. The doping concentration x of Pr(III) ions was similar to the above one. Next, PEG

and TMOS were added to homogeneous solution upon continuous stirring and heating; after several days 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.

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 xerogel samples doped with $Ln_{2-x}Pr_x(WO_4)_3$ 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. However, the emission spectra of xerogels without WO_4^{2-} groups were obtained within absorption bands of Pr(III) ion $\lambda_{exc} = 448$ or 473 nm.

3. Results and discussion

Previously, all the xerogels doped with $Ln_{2-x}Ln'_x(WO_4)_3$ where $Ln = Gd, La$ and $Ln' = Eu, Sm, Tb$ were analyzed by the thermal analysis and FT-IR spectroscopy and they were described in detail in references [2, 3, 11]. Similar effect we obtained for xerogels doped with $Ln_{2-x}Pr_x(WO_4)_3$, therefore we do not present that result in this paper. The analysis of FT-IR spectroscopic results and estimated relations of the mass losses suggest that after heating at 600 °C xerogels doped with $Ln_{2-x}Pr_x(WO_4)_3$ were obtained, which can play the role of phosphors in the luminescent materials [12].

The photoluminescence properties of the xerogels doped with $Ln_{2-x}Pr_x(WO_4)_3$ were examined, keeping in mind their applications as red phosphors for color television. For each material studied, enhancement of the emission intensity of Pr(III) ions was observed because of the energy transfer. It is evidenced by the results of excitation and emission spectra. The high emission intensity of the xerogel samples doped with $Ln_{2-x}Pr_x(WO_4)_3$ 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. For comparison purposes, the photoluminescence properties of xerogels without WO_4^{2-} groups were studied.

The photoluminescence excitation spectra of xerogels doped with $La_{1.9}Pr_{0.1}(WO_4)_3$ or $Gd_{1.9}Pr_{0.1}(WO_4)_3$ and annealed at 900 °C are shown in Fig. 1. The spectra were measured upon the emission wavelength $\lambda = 648$ nm which corresponds to the Pr(III) ${}^3P_0 \rightarrow {}^3F_4$ 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. However, the shoulder at about 250 nm can correspond to the CT transition between $O^{2-} \rightarrow Pr^{3+}$. Along this band, it is also possible to observe several narrow bands located between 420 and 500 nm, which are ascribed to the $f-f$ transitions of Pr(III) ion. They are placed at about 448, 473 and 486 nm. The 448 nm photon absorption causes excitation from 3H_4 to 3P_0 level of Pr^{3+} ion.

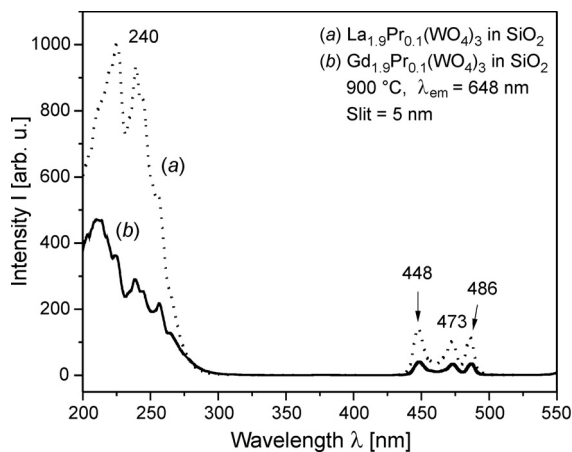


Fig. 1. Excitation spectra of xerogels doped with: $\text{La}_{1.99}\text{Pr}_{0.01}(\text{WO}_4)_3$ (spectrum *a*) and $\text{Gd}_{1.99}\text{Pr}_{0.01}(\text{WO}_4)_3$ (spectrum *b*).

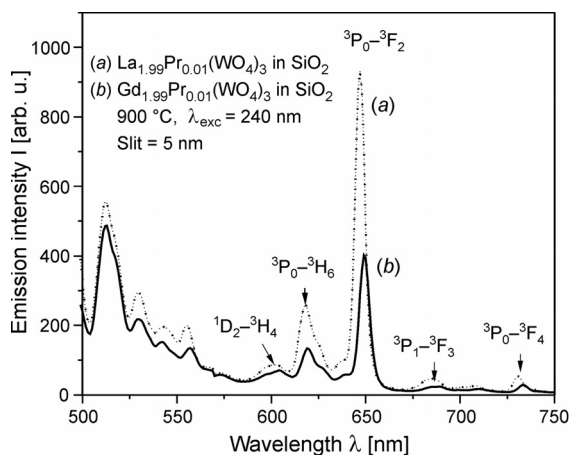


Fig. 2. Emission spectra of xerogels doped with: $\text{La}_{1.99}\text{Pr}_{0.01}(\text{WO}_4)_3$ (spectrum *a*) and $\text{Gd}_{1.99}\text{Pr}_{0.01}(\text{WO}_4)_3$ (spectrum *b*).

Figure 2 shows the photoluminescence emission spectra of xerogels doped with $\text{La}_{1.99}\text{Pr}_{0.01}(\text{WO}_4)_3$ or $\text{Gd}_{1.99}\text{Pr}_{0.01}(\text{WO}_4)_3$ and annealed at 900 °C. Luminescence signals due to Pr(III) were observed in the red region of the spectrum. These signals are due mainly to Pr(III) $^1D_2 \rightarrow ^3H_4$ (605 nm), $^3P_0 \rightarrow ^3H_6$ (618 nm), $^3P_0 \rightarrow ^3F_2$ (648 nm), $^3P_1 \rightarrow ^3F_3$ (680 nm) and $^3P_1 \rightarrow ^3F_4$ (730 nm) transitions, respectively. It is known that the emission of Pr^{3+} depended strongly on the host lattice. In our case, the most intense band is placed at about 648 nm and also is regarded as hypersensitive one. The ratio between 3P_0 and 1D_2 emission intensities shows the dominant character of the 3P_0 transition and is less commonly observed in oxide materials. This suggests that coordination sphere of Pr(III) ion is of low symmetry.

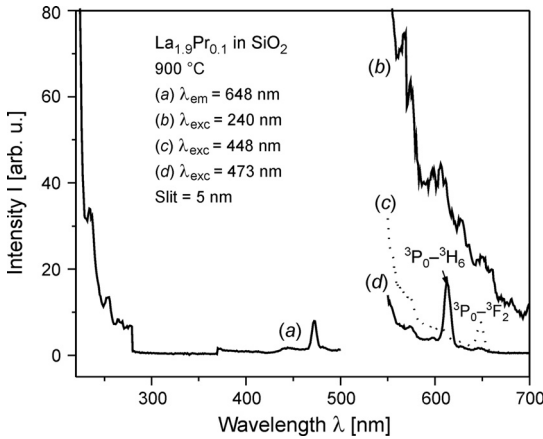


Fig. 3. Excitation and emission spectra of xerogels doped with $La_{1.9}Pr_{0.1}$.

The influence of tungstate groups on Pr(III) luminescence in silica xerogels was studied. Figure 3, spectrum *a* shows excitation spectrum of xerogel doped with Pr(III) and La(III) ions. The spectrum was measured upon the emission wavelength $\lambda = 648$ nm. The small band observed at 473 nm corresponds to $f-f$ transition of Pr(III) ion. However, the band placed at around 250 nm is attributed to the charge transfer between $O^{2-} \rightarrow Pr^{3+}$. The emission spectra of low intensity (Fig. 3, spectra *c* and *d*) correspond to a situation where the material is excited by radiation of $\lambda_{exc} = 448$ or 473 nm. In the case where $\lambda_{exc} = 240$ nm no red emissions at 605, 618 and 648 nm were observed in Fig. 3, spectrum *b*.

In order to avoid emission quenching of O–H oscillators the emission intensity of Pr(III) ion has been studied as a function of annealing temperature in xerogels doped with mixed tungstate. Figure 4 shows that the emission intensity of Pr(III) ion in

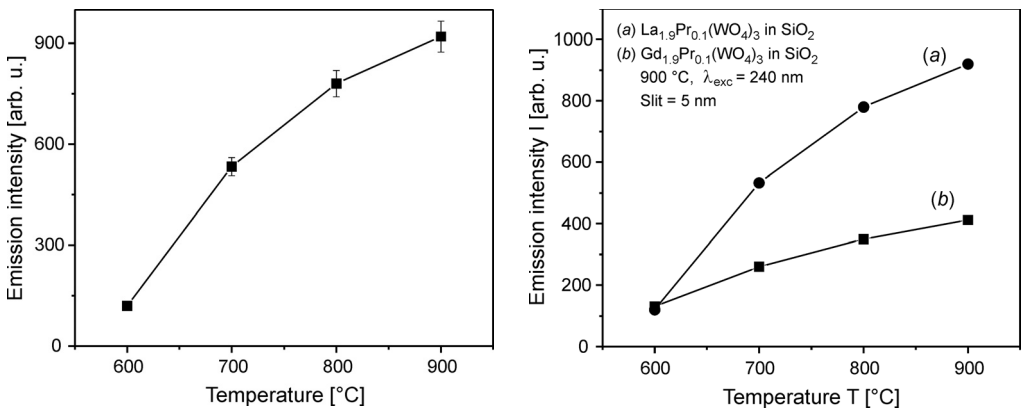


Fig. 4. The dependence of Pr^{3+} emission intensity I of the ${}^3P_0 \rightarrow {}^3F_2$ band at 648 nm with annealing temperature T for xerogels doped with: $La_{1.9}Pr_{0.1}(WO_4)_3$ (curve *a*) and $Gd_{1.9}Pr_{0.1}(WO_4)_3$ (curve *b*). The lines are drawn as guide to the eyes.

the materials studied increases with an increase of temperature up to 900 °C. Water molecules come from both silica matrix and coordination sphere of Pr(III) ion. Thus, removal of O–H groups leads to an increase of the emission intensity. In our previous paper [3], we reported that heating at least up to 1000 °C causes the emission intensity to decrease. This is possible since the formation of mixed lanthanide silicate and tungstate salt could occur. Additionally, xerogels doped with $\text{Ln}_{2-x}\text{Pr}_x(\text{WO}_4)_3$ heated up to the temperature around 1000 °C could transform into glassy material.

The second parameter which affects the enhancement of the emission intensity is the concentration of Pr(III) ion. As we can see from Fig. 5, the highest emission occurs

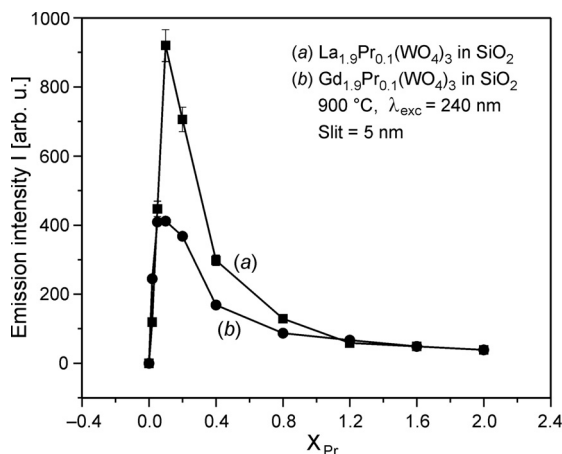


Fig. 5. The dependence of Pr^{3+} emission intensity I of the ${}^3P_0 \rightarrow {}^3F_2$ band at 648 nm with Pr(III) content x for xerogels doped with: $\text{La}_{1.9}\text{Pr}_{0.1}(\text{WO}_4)_3$ (curve a) and $\text{Gd}_{1.9}\text{Pr}_{0.1}(\text{WO}_4)_3$ (curve b). The lines are drawn as guide to the eyes.

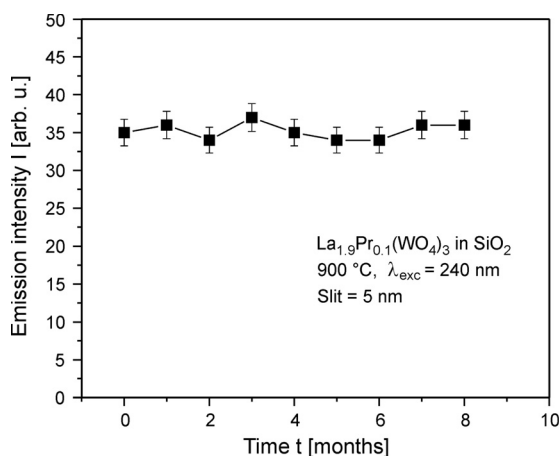


Fig. 6. The dependence of Pr^{3+} emission intensity I of the ${}^3P_0 \rightarrow {}^3F_2$ band at 648 nm with time t for xerogels doped with $\text{La}_{1.9}\text{Pr}_{0.1}(\text{WO}_4)_3$. The lines are drawn as guide to the eyes.

for $x = 0.1$ for xerogels doped with $Ln_{2-x}Pr_x(WO_4)_3$ or $Gd_{2-x}Pr_x(WO_4)_3$. The decrease above the maximum (x) is due to the concentration quenching.

A good luminescent material should be resistant to UV-Vis radiation and water absorption from the air atmosphere for a long time. Therefore, it has not shown changes of emission intensity during illumination by the sun radiation. As can be seen in Fig. 6, the emission intensity of silica xerogel doped with $La_{1.9}Pr_{0.1}(WO_4)_3$ is constant within the experimental error for eight months.

4. Conclusions

The materials under study show UV-Vis reflectance spectra with a band placed at about 240 nm, related to $O \rightarrow W$ charge transfer transition. The Pr(III) ion presents its enhanced emissions (${}^3P_0 \rightarrow {}^3F_2$) in the materials studied owing to the efficient energy transfer from the excited W(VI) states in tungstate group via O to Pr(III) ions. The energy transfer from WO_4^{2-} groups to Pr(III) ions is particularly effective for xerogels doped with mixed systems of the compositions: $La_{1.9}Pr_{0.1}(WO_4)_3$ and $Gd_{1.9}Pr_{0.1}(WO_4)_3$. The Pr(III) emission intensity in the materials studied increases with temperature increasing up to 900 °C. This is due to the removal of O–H quenchers from the coordination sphere of Pr(III) ions. The Pr(III) emission intensity has been constant for eight months.

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