Luminescence based on energy transfer in xerogels doped with $Tb_{2-x}Eu_x(WO_4)_3$

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A series of luminescent materials consisting of $Tb_{2-x}Eu_x(WO_4)_3$ entrapped in silica xerogel were successfully prepared. The parameter x in the formula changed from 0.4 to 2. Spectroscopic properties such as absorption and luminescence of optically active ions were studied at room temperature. Owing to the energy transfer from the WO_4^{2-} groups (ligand–metal charge transfer, (LMCT)) the lanthanide ions show their characteristic emissions in $Tb_{2-x}Eu_x(WO_4)_3$ entrapped in silica xerogel, *i.e.*, $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) transition for Eu^{3+} ion and $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transition for Tb^{3+} ion. The energy transfer is effective for the mixed tungstate salt $Tb_{1.35}Eu_{0.65}(WO_4)_3$ entrapped in silica xerogel. The Eu(III) emission intensity in the materials under study increases with an increase in the annealing temperature from 600 to 900 °C. This is due to the removal of the effective O–H quenchers from the coordination sphere of the Eu(III) ion.

Keywords: photoluminescence, lanthanide(III) ions, sol–gel method, energy transfer.

1. Introduction

Luminescent materials are known to exhibit luminescence which is taken advantage of in solid state materials, cathode ray tubes, phosphors for color television, fluorescent tubes, and medical imaging (X-ray and tomography) [1, 2]. Most of the lanthanides with well-defined stoichiometry can be employed as the source of excitation, but often they play the role of dopants in different matrices. In general, solid-state luminescent compounds consist of a host and an activator. The host is usually an optically inert, crystalline oxide or salt, such as Y_2O_3, $Ln_2(WO_4)_3$, $La(BO_3)_3$. However, Eu(II), Tb(III) and Eu(III) ions can play the role of the activator to obtain the three basic emission colors: blue, green and red, respectively [3]. Among lanthanide(III) ions, europium(III) ion is the most extensively studied of the various luminescent materials [4–6]. First of all, the very well-known Eu(III) ion emission in the red spectra region ascribed to the $^5D_0 \rightarrow {}^7F_2$ transition allows Eu^{3+} ion to be frequently applied as a spectroscopic probe in vitreous or crystalline systems and ceramics because of its great sensitivity to the surrounding chemical environment [7]. Additionally, the $^5D_0 \rightarrow {}^7F_0$ transition

is referred to as a hypersensitive transition and gives information about impurity or whether this ion occupies more than one site symmetry [8]. On the other hand, Eu(III) ion exhibits a much lower luminescence intensity and shorter lifetime as aquated ion. The weak luminescence of the aquated Eu(III) ion indicates that the high energy vibrations of O–H groups present in the crystal lattice provide an efficient mechanism for the non-radiative de-excitation of the Eu(III) excited state. In order to enhance emission intensity of Eu(III) ion it is needed that the quenching O–H oscillators be removed from the material [9]. Therefore, in the present work, the author makes use of the $Tb_2(WO_4)_3$ lattice as a host for Eu^{3+} ions to minimize the influence of water. Additionally, the sample was entrapped in silica xerogel by the sol–gel process.

The sol–gel process is an excellent method for the preparation of phosphors due to the good mixing of the starting compounds and low temperature of reaction [10]. Moreover, this method has the advantage of providing negligible diffusion loss, high quality and purity.

To purpose of this work is to report on the preparation and luminescence properties of the materials consisting of Tb(III) tungstate doped with Eu(III) ions entrapped in silica xerogel and to expect that there is energy transfer from the WO_4^{2-} groups via Tb^{3+} ions to Eu^{3+} ions in the material consisting of double $Tb_{2-x}Eu_x(WO_4)_3$ salts entrapped in silica xerogel.

Additionally, the influence of concentration and temperature on the emission intensity of Eu(III) activated $Tb_2(WO_4)_3$ was discussed in detail.

2. Experimental

2.1. Sample preparation

The starting materials used in the study were of at least analytical grade. Sodium tungstate (POCh, Poland); lanthanide(III) nitrates: $Eu(NO_3)_3 \cdot 5H_2O$ and $Tb(NO_3)_3 \cdot 5H_2O$ (Aldrich Co.); disodium ethylenediaminetetraacetate, EDTA (POCh, Poland); polyethylene glycol 400, PEG and tetramethoxysilane $Si(OCH_3)_4$, TMOS (Aldrich Co.).

Sodium tungstate was dissolved in warm water (60 °C). The aqueous solutions of Ln(III) nitrates were mixed together. The doping concentration x of the Eu(III) ions was 0.4–2 molar ratio of terbium in the $Tb_2(WO_4)_3$ host. Then, the solutions of Ln(III) nitrates and sodium tungstate taken in appropriate amounts were mixed. After a while, insoluble white precipitate of $Tb_{2-x}Eu_x(WO_4)_3$ was obtained. In the next step, EDTA was added to this mixture to form a stable complex with Ln(III) ions, while WO_4^{2-} groups remained solvated in the solution. Polyethylene glycol and TMOS were added to the homogeneous solution with continuous stirring and heating; after several hours a transparent gel was formed by means of the sol–gel process. In the last step, the product was calcined in the temperature range 600–900 °C for 3 h. Finally, we obtained terbium tungstate doped with Eu(III) ions entrapped in silica xerogel as a white powder. The final concentration of the system $Tb_{2-x}Eu_x(WO_4)_3$ in the xerogel was $5 \cdot 10^{-5}$ mole·g^{-1} of SiO_2.

2.2. Apparatus

Thermal analysis was carried out using an OD-103 derivatograph (Monicon) in the air atmosphere with α-Al$_2$O$_3$ as a reference. Other operating conditions were as follows: the heating rate was 5 K·min^{-1}; sensitivities of differential thermogravimetry (DTG) and differential thermal analysis (DTA) galvanometers were 1/5 and 1/2, respectively; TG sensitivity equalled 100 mg.

FT-IR spectra were recorded on a Bruker IR IFS 66 Fourier transform infrared spectrometer (MIR, spectral range 4000–400 cm^{-1}). Samples were prepared by the standard KBr pellet method.

The photoluminescence excitation and emission spectra were recorded on a Perkin–Elmer LS 50B spectrofluorimeter with a reflection spectra attachment. The emission spectra of the xerogel samples doped with Tb$_{2-x}$Eu$_x$(WO$_4$)$_3$ were obtained using excitation wavelengths within absorption band range of the WO$_4^{2-}$ at 240 nm.

3. Results and discussion

3.1. Thermal analysis

The DTG, DTA and TG curves for Tb$_{1.35}$Eu$_{0.65}$(WO$_4$)$_3$ entrapped in silica xerogel in the air atmosphere show that the decomposition occurs in two stages (Fig. 1). Step 1 was observed up to *ca.* 300 °C and it was accompanied by water evaporation, which was physically occluded inside the pores of silica matrix. Additionally, the following
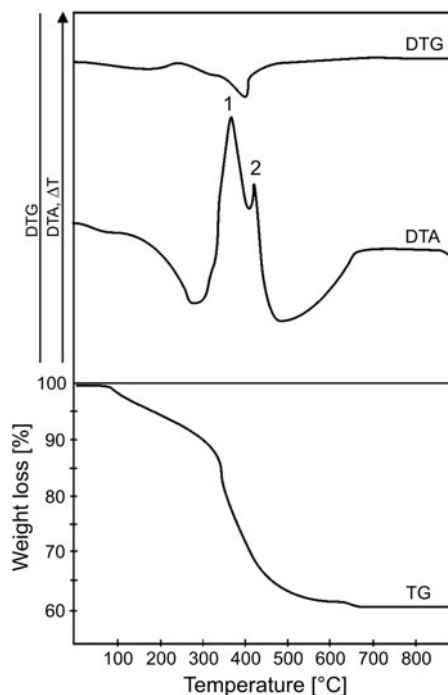

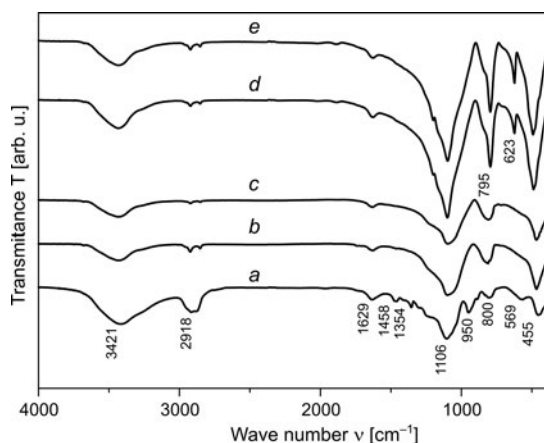Fig. 1. DTG, DTA, TG curves of Tb$_{1.35}$Eu$_{0.65}$(WO$_4$)$_3$ entrapped in silica xerogel.

Fig. 2. FTIR spectra of $Tb_{1.35}Eu_{0.65}(WO_4)_3$ entrapped in silica xerogel and annealed at temperatures: RT (*a*), 600 °C (*b*), 700 °C (*c*), 800 °C (*d*), 900 °C (*e*).

loss of nitrate groups was observed: $NO_3^- \rightarrow NO_2 + O^-$. The released nascent oxygen should simultaneously cause oxidation of an organic component of the decomposed material and the exothermic effect observed in this step provides evidence for this process. In the second stage, two thermal effects are present up to 630 °C. The strong exothermic peak 1 centred at 380 °C could correspond to the combustion of volatile organic solvents. The next exothermic peak 2 around 450 °C in DTA curve was present. It can be attributed to the burn-out of organic groups from EDTA and TMOS. At a temperature above 630 °C, in practice no weight loss was noticed. This suggests that in this temperature range the material was calcined to form the mixed tungstate salt with Tb(III) and Eu(III) ions in silica xerogel. Additionally, the decomposition of organic groups in this material occurs at a lower temperature than was previously observed [11, 12].

3.2. FT-IR spectra

Infrared spectroscopy is a convenient technique, which gives information about the structure of both the siloxane network and organic groups present in the material. FT-IR spectra of $Tb_{1.35}Eu_{0.65}(WO_4)_3$ entrapped in silica xerogel are shown in Fig. 2. For the sample dried at room temperature, the spectrum (*a*) shows the bands which arise from the starting compounds such as: PEG, sodium tungstate, lanthanide(III) nitrates, EDTA and TMOS. There are two peaks related to the O–H vibrations such as a broad band peaked at 3421 cm^{-1} and a narrow one at 1629 cm^{-1}. The first band is attributed to the O–H stretching vibrations. The latter band is probably caused by the O–H deformation vibrations in water [13]. The next band placed at 2918 cm^{-1} is related to the ν(CH) modes of the methylene groups which come from PEG and EDTA. The FT-IR spectrum (*a*) also consists of several bands which are assigned to the WO_4^{2-} group (950, 800, 569 cm^{-1}). Moreover, the bands at 1106 and 453 cm^{-1} are related to the Si–O–Si vibrations. Specifically, the high-wavenumber band placed at 1106 cm^{-1}

is attributed to the Si–O–Si symmetric stretching mode in cyclic structures and the band with maximum at 455 cm^{-1} belongs to the briding oxygen atom perpendicular to the Si–O–Si plane [13]. Additionally, the band placed at 1354 cm^{-1} is due to NO_3^- group. The intensity of these bands decreased with an increase of the sintering temperature. This is due to pyrolysis of the organic species and nitrate groups. Thus, for the sample annealed at 600 °C and higher temperatures (spectra *b−e*) the bands of organic groups, water and NO_3^- groups gradually disappeared. Additionally, after the thermal treatment from 700 to 900 °C, the band at 795 cm^{-1} turns stronger (spectra *d* and *e*) and the new band at 623 cm^{-1} appears. This suggests that the alpha-crystobalite phase is formed during the thermal treatment. Besides these features FT-IR spectra should also contain the band at 800 cm^{-1} of the W=O oscillations, but they are overlapped by the strong band of silica. However, for the sample heated at 900 °C (spectrum *e*) there are still two weak bands at 3421 and 1629 cm^{-1}, which are related to the remains of water in the sample.

3.3. Photoluminescence properties

The photoluminescence excitation spectrum of $Tb_{1.35}Eu_{0.65}(WO_4)_3$ entrapped in silica xerogel and annealed at 900 °C, as presented in Fig. 3, was obtained in the spectral range from 200 to 450 nm under the emission connected with the Eu(III) $^5D_0 \rightarrow {}^7F_2$ transition at 612 nm. It can be seen that the spectrum consists of an intense broad band in the range 200–300 nm corresponding to the LMCT states from the O → W and O → Eu^{3+} transitions at around 240 and 250 nm, respectively [5]. The other bands in the range 320–450 nm are ascribed to *f–f* transitions in Eu(III) and Tb(III) ions. Among them the most intense bands are at 394 nm, which corresponds to the $^7F_0 \rightarrow {}^5L_6$ transition and at 380 nm consistent with the $^7F_0 \rightarrow {}^5L_7$ transition of Eu(III) ion [14]. Additionally, the excitation spectrum presents weak band at about 355 nm connected with the $^7F_6 \rightarrow {}^5L_9$ transition in Tb(III) ion [15].
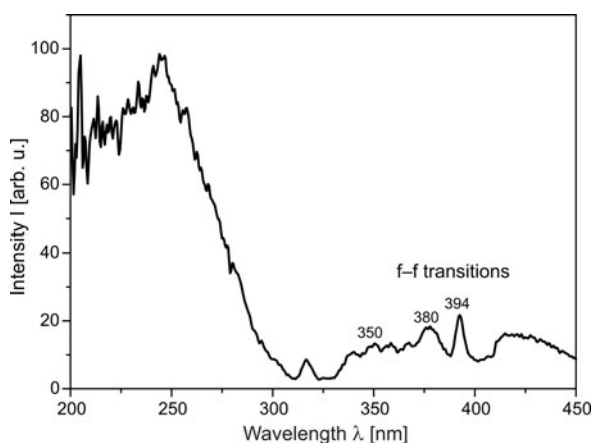

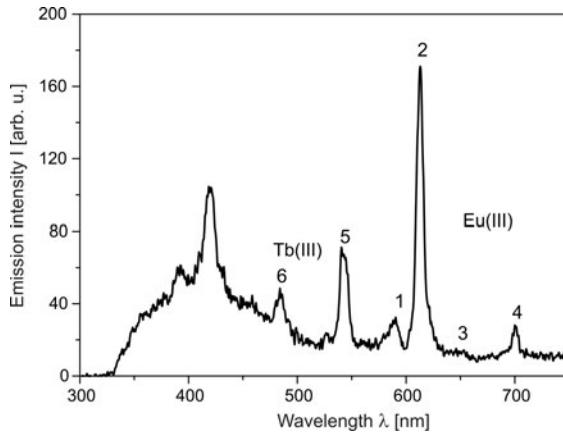Fig. 3. Photoluminescence excitation spectrum of $Tb_{1.35}Eu_{0.65}(WO_4)_3$ entrapped in silica xerogel and annealed at 900 °C (λ_{em} = 612 nm).

Fig. 4. Photoluminescence emission spectrum of $Tb_{1.35}Eu_{0.65}(WO_4)_3$ entrapped in silica xerogel and annealed at 900 °C ($\lambda_{exc} = 240$ nm).

Figure 4 shows the photoluminescence emission spectrum of $Tb_{1.35}Eu_{0.65}(WO_4)_3$ entrapped in silica xerogel. It presents the strong emission bands which are attributed to the transition from $^5D_0$ emission level to one of the ^7F_J levels in Eu(III) ion, when $\lambda_{exc} = 240$ nm is related to the absorption band of the WO_4^{2-} group. In turn, the bands at 590, 612, 650 and 700 nm are attributed to the $^5D_0 \rightarrow {}^7F_J$ spin forbidden transitions, where $J = 1, 2, 3, 4$, respectively. The $^5D_0 \rightarrow {}^7F_1$ is the parity-allowed magnetic dipole transition ($\Delta J = 1$) and its intensity does not vary with the host. On the other hand, the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition ($\Delta J = 2$) is very sensitive to the local environment around Eu^{3+} ion, and its intensity depends on the symmetry of the crystal field around Eu^{3+} ion. It is generally admitted that the ratio of the emission intensities
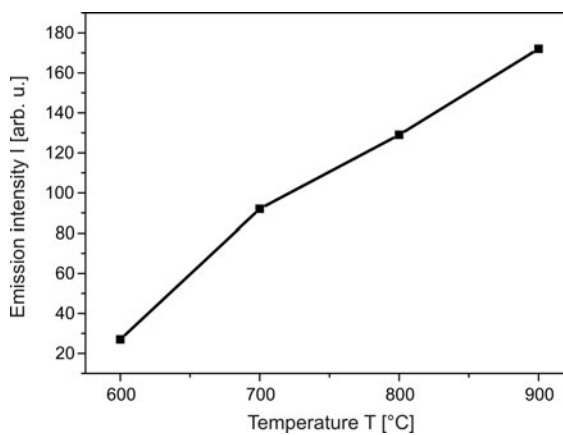

Fig. 5. Emission intensity I of the $^5D_0 \rightarrow {}^7F_2$ band at 612 nm *vs*. annealing temperature T for $Tb_{1.6}Eu_{0.4}(WO_4)_3$ entrapped in silica xerogel ($\lambda_{exc} = 240$ nm).
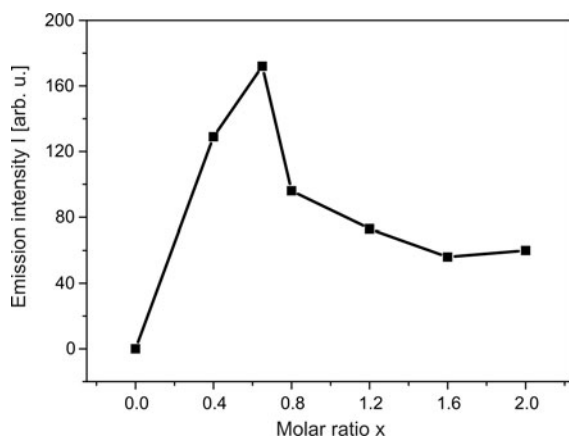
Fig. 6. Emission intensity I of the $^5D_0 \to {}^7F_2$ band at 612 nm *vs*. Eu(III) content x for $Tb_{2-x}Eu_x(WO_4)_3$ entrapped in silica xerogel annealed at 900 °C ($\lambda_{exc} = 240$ nm).

$R = I(^5D_0 \to {}^7F_1)/I(^5D_0 \to {}^7F_2)$ is a symmetry parameter for the Eu^{3+} sites and a measure of the extent of its interaction with surrounding ligands [4]. In this case, the intensity ratio equal to 0.19 suggests that the coordination sphere of europium(III) is of low symmetry. Additionally, the spectrum consists of two emission bands at 491 at 542 nm, which are attributed to the $^5D_4 \to {}^7F_J$ transitions, where $J = 6, 5$, respectively in Tb(III) ion. Besides, there is observed a low intensity band with maximum placed at about 420 nm, which is ascribed to emission of the WO_4^{2-} [5]. This band can also be assigned to the emission from a localized electron–hole pair, *i.e.*, a self-trapped exciton [16].

3.4. Thermal treatment and concentration effect

The photoluminescence emission intensity of Eu(III) ion has been studied as a function of the annealing temperature in materials consisting of $Tb_{2-x}Eu_x(WO_4)_3$ entrapped in silica xerogel. Figure 5 shows that the emission intensity of Eu(III) ion in the materials under study increases with temperature. It is clear that O–H oscillators as water molecules are very effective quenchers of the Eu(III) ion luminescence and the removal of water by the thermal treatment causes that the emission intensity enhancement is observed with an increase in temperature up to 900 °C.

For materials consisting of $Tb_{2-x}Eu_x(WO_4)_3$ entrapped in silica xerogel (where $x = 0.4$–2) the emission intensity of Eu(III) ion is observed to depend on its doping concentration x (Fig. 6). The highest emission occurs for $x = 0.65$, and above this value the effect of concentration quenching is observed.

4. Conclusions

A series of luminescent materials with a general formula $Tb_{2-x}Eu_x(WO_4)_3$ entrapped in silica xerogel were successfully prepared by the sol–gel method.

The materials under study show the photoluminescence excitation spectra with an intense broad band related to the O $\rightarrow$ W(VI) charge transfer transition.

The Eu(III) ion presents its characteristic red emission ($^5D_0 \rightarrow {}^7F_2$) in $\text{Tb}_{2-x}\text{Eu}_x(\text{WO}_4)_3$ phosphors probably owing to the energy transfer from the excited W(VI) states in tungstate group via O to the Eu(III) ions.

The Eu(III) emission intensity in the materials being studied is improved by removing the effective O–H quenchers from the luminescent materials.

The likely energy transfer from tungstate group to the Eu(III) ion is effective for material of the composition $\text{Tb}_{1.35}\text{Eu}_{0.65}(\text{WO}_4)_3$ entrapped in silica xerogel.

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