Absorption and emission spectra of erbium-doped titania xerogels confined in porous anodic alumina

S.A. Klimin a, E.P. Chukalina a, M.N. Popova a,*, E. Antic-Fidancev b, P. Aschehoug b, N.V. Gaponenko c, I.S. Molchan c, D.A. Tsyrkunov c

a Institute of Spectroscopy, Russian Academy of Sciences, 142190 Troitsk, Moscow region, Russia
b Laboratoire de Chimie Appliquée de l’État Solide, CNRS-UMR7574, ENSCP, 11, Rue Pierre et Marie Curie, F-75231 Paris Cedex 05, France
c Belarusian State University of Informatics and Radioelectronics, 6, P. Brovka st., 220013 Minsk, Belarus

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Abstract

We communicate for the first time on the absorption and strong visible luminescence spectra of the film structures “Er-doped titania xerogel/porous anodic alumina”.

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1. Introduction

Thin films doped with luminescent lanthanide ions have attracted considerable attention because of many potential applications in optical technologies and optoelectronics. The low-cost sol-gel techniques allow synthesis of diverse highly doped xerogel films on different substrates and also in the pores of mesoporous materials. The film structures “mesoporous material/lanthanide-doped xerogel” have attractive physical properties and a strong lanthanide-related luminescence. Among different mesoporous materials, the porous anodic alumina [1] exhibiting a regular pore morphology with cylindrical pores running perpendicular to the surface is, probably, the most promising one. The controlled sizes of the pores can be between 10 and 200 nm and the thickness of the porous film up to 200 µm can be achieved (see, e.g., Ref. [2]). Strongly enhanced Er, Tb, and Eu luminescence from xerogels confined in porous anodic alumina has been reported recently (see, e.g., Ref. [2] and references therein). Er emission in these structures has been studied near 1.53 µm. This wavelength falls into a maximum transparency window of optical fibers.

Among the investigated xerogels, titania was found to be an appropriate host material revealing strong...
Table 1
Samples used for spectroscopic studies

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>Anodizing duration (hours)</th>
<th>Average pore diameter (nm)</th>
<th>Xerogel composition Er₂O₃/TiO₂ (wt.%)</th>
<th>Number of spin-on depositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>B4N1</td>
<td>Oxalic acid</td>
<td>12</td>
<td>40</td>
<td>20/80</td>
<td>9</td>
</tr>
<tr>
<td>B4N2</td>
<td>Phosphoric acid</td>
<td>18</td>
<td>80</td>
<td>20/80</td>
<td>9</td>
</tr>
<tr>
<td>B4N3</td>
<td>Phosphoric acid</td>
<td>12</td>
<td>80</td>
<td>50/50</td>
<td>7</td>
</tr>
<tr>
<td>B4N4</td>
<td>Phosphoric acid</td>
<td>18</td>
<td>80</td>
<td>50/50</td>
<td>5</td>
</tr>
</tbody>
</table>

Luminescence of the embedded Er [3], Tb [4], and Eu [5] trivalent ions. The 1.53 μm emission from Er-doped titania obtained via sol-gel route [3] and laser ablation [6,7] was reported, whereas less attention has been payed to the green emission from Er³⁺.

In this Letter we report on our spectroscopic studies in a wide spectral range of both luminescence and absorption of titania xerogels, highly doped with erbium, confined in porous anodic alumina membrane. Visible luminescence of Er³⁺ is discussed.

2. Experimental

The mechanically and electrochemically polished aluminum foils (99.999% purity) were used to prepare porous anodic alumina (PAA) freestanding films. Anodizing was performed in 0.24 M phosphoric acid solution at a constant current 6 mA/cm², and in 0.3 M oxalic acid solution at a constant voltage 40 V. The saturated HgCl₂ solution was further used to separate the PAA film from the aluminum foil. Typically the film thickness of anodic alumina membrane was found to be 125 and 90 μm after anodizing within 12 hours in oxalic acid solution and 11 hours in phosphoric acid solution, respectively.

Coatable colloidal solution of tetraethylorthotitanate Ti(OC₂H₅)₄ in a homogeneous phase with the mixture of water and 96% ethanol (1 : 6 by volume) was used as a precursor for fabrication of Er-doped TiO₂ films. The concentration of TiO₂ in the prepared sols was 27 mg/ml. Further, the certain amounts of erbium nitrate were added to sols (see [3] for the details) for fabrication of TiO₂ xerogel films containing 20 and 50 wt.% Er₂O₃. Deposition of sol into pores of anodic alumina membrane was performed by spin-on route at 2700 rpm for 30 s followed by drying at 200 °C in air for 10 min. To achieve more complete filling of the pore volume with xerogel [8,9], the spinning and drying steps were repeated from 5 to 9 times. Finally, the annealing at 900°C for 30 min in ambient atmosphere was applied to activate the Er ions. The description of samples used in experiments is presented in Table 1.

The visible luminescence of the samples at room temperature was excited either by the third harmonic of the YAG-Nd laser (λexc = 355 nm) or by the output radiation of an optical parametric oscillator (OPO) (λexc = 488 nm) pumped by the third harmonic of a Q-switched Nd:YAG laser. An intensified optical multichannel analyzer (OMA) was used for the detection of the luminescence. Luminescence spectra were not corrected for the sensitivity of the detector.

To detect the absorption spectra, we combined together up to six samples of freestanding films which enhanced an effective thickness of an erbium-containing material. Such a stack was put into a helium-vapor cryostat with variable temperature (4.2–300 K). The spectra were obtained in the spectral region 6000–13000 cm⁻¹ with resolution up to 0.5 cm⁻¹, using a Fourier-transform spectrometer BOMEM DA3.002. Liquid nitrogen cooled InSb and Si detectors for different spectral regions were used.

3. Experimental results and discussion

Fig. 1 shows the spectra of a visible room-temperature Er luminescence from three different samples under the 488 nm excitation into the level ⁴F₇/₂. Three different bands centered at 521, 544, and 658 nm are observed. They correspond to the radiative transitions from the levels ⁵H₁₁/₂, ⁴S₃/₂, and ⁴F₇/₂ to the ground level ⁴I₁₅/₂. The emission band ⁵H₁₁/₂ → ⁴I₁₅/₂ freezes out at decreasing the temperature, due to a rapid phonon relaxation from the ⁵H₁₁/₂ level to the level ⁴S₃/₂ that lies 800 cm⁻¹ lower. At ambient temperature, the level ⁵H₁₁/₂ is thermally populated from the level ⁴S₃/₂. The intensity of the
Fig. 1. Room-temperature visible luminescence spectra of three different freestanding films of erbium-doped titania xerogel confined in porous anodic alumina under the 488 nm excitation.

Fig. 2. Room-temperature visible luminescence spectra of a freestanding film of erbium-doped titania xerogel (the sample B4N4) confined in porous anodic alumina and of a sol-gel erbium-doped glass under the 355 nm excitation.

The strongest green band at about 545 nm is approximately proportional to the product $C(\text{Er})N$, where $C(\text{Er})$ is the concentration of $\text{Er}_2\text{O}_3$ in a xerogel and $N$ is the number of spin-on depositions (see Fig. 1 and Table 1). It is worth noting that no concentration quenching occurs up to the $\text{Er}_2\text{O}_3$ concentration as high as 50 wt.% in xerogel.

The spectrum of the Er luminescence under a short-wavelength excitation 355 nm is more reach (see Fig. 2). Additional emission from high-lying levels $^{4}\text{F}_{5/2}$, $^{2}\text{H}_{9/2}$, $^{2}\text{G}_{7/2}$, and $^{2}\text{G}_{9/2}$ is observed which testifies a low relaxation rate. Possibly, a low relaxation rate is due to a suppression of the low-frequency part of the phonon density of states due to confinement effects [10]. For a comparison, Fig. 2 shows also the luminescence of an erbium-doped sol-gel quartz glass under the excitation 355 nm. The emission is weak and consists of several very broad superimposed bands, the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ band being the strongest one.

The absorption spectra consist of both broad bands typical for disordered glass-like media and relatively narrow lines typical for a crystalline matrix. In the region of the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$ transition of $\text{Er}^{3+}$ there are, for example, two broad bands centered at 6535 and 6800 cm$^{-1}$ (see Fig. 3). The spectrum of the erbium-doped sol-gel glass (also shown in Fig. 3) exhibits similar bands. The narrow lines that are superimposed onto a broad-band spectrum further narrow on decreasing the temperature and some of the lines freeze out (Fig. 4). The latter spectral lines originate, evidently, from excited Stark sublevels of the ground level $^4\text{I}_{15/2}$ split by the crystal field. The number of lines at low temperature exceeds the maximum allowed number for the transition to the $^4\text{I}_{13/2}$ crystal-field manifold, $n = J + 1/2 = 7$ (here $J = 13/2$ is the total momentum), which indicates either two different positions for $\text{Er}^{3+}$ in a crystalline matrix or the presence of two different crystalline...
Fig. 4. Transmission spectra of the sample B4N4 at different temperatures in the region of the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition in Er$^{3+}$.

Fig. 5. Low-temperature transmission spectra of three different freestanding films of erbium-doped titania xerogel confined in porous anodic alumina in the region of the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition in Er$^{3+}$.

Fig. 6. Low-temperature transmission spectra of two different freestanding films of erbium-doped titania xerogel confined in porous anodic alumina in the region of the $^4I_{15/2} \rightarrow ^4I_{11/2}$ transition in Er$^{3+}$.

Fig. 7. Low-temperature transmission spectra of two different freestanding films of erbium-doped titania xerogel confined in porous anodic alumina in the region of the $^4I_{15/2} \rightarrow ^4I_{9/2}$ transition in Er$^{3+}$.

Figures 4, 6, and 7 show transmission spectra of samples B4N4 and B4N2 at different temperatures and wave numbers. The transmission spectra are depicted in the figures.

In summary, we have performed a spectroscopic study of freestanding films of highly erbium-doped titania xerogels confined in porous anodic alumina. Both absorption and luminescence spectra were registered. A strong erbium-related visible luminescence was observed in all the samples. Absorption studies were performed for the first time and revealed two phases. Fig. 5 compares the low-temperature spectra of three different samples. Two narrow lines at about 6590 and 6620 cm$^{-1}$ are present in all the three spectra while the rest of the narrow-line spectra differ considerably. Thus, different crystalline phases are present. Er$_2$O$_3$ is not among them, as follows from our earlier spectroscopic study of erbium oxide. The relative intensities of a broad-band and a narrow-line absorption spectra depend on a particular sample (see Figs. 5–7, and Fig. 3). These two contributions come, probably, from the erbium ions embedded into a glass-like xerogel or into some microcrystallites inside a glass-like matrix.

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spectral contributions associated with glass-like and crystalline matrices for the Er$^{3+}$ ions.

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