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Enhanced luminescence of europium in sol-gel derived $BaTiO_3/SiO_2$ multilayer cavity structure

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ABSTRACT

We report on the sol-gel synthesis and optical properties of an Eu-doped multilayer structure consisting of a Bragg reflector/$BaTiO_3$:Eu/Bragg reflector, with the Bragg reflector comprising of $BaTiO_3/SiO_2$ structures. Depending on the fabrication procedure two set of specimens were generated with Eu out of the cavity or Eu in the cavity. Enhanced Eu luminescence in the direction normal to the surface is observed for the most intense band $^5D_0 \rightarrow {}^7F_2$ at 615 nm of trivalent europium in the cavity and correlates with anisotropy of the luminescence indicatrix, transmittance and reflection bands around 615 nm for the fabricated structure.

1. Introduction

Spontaneous emission (luminescence) of trivalent lanthanides is investigated in optically anisotropic matrices. Enhanced luminescence of light-emitting species at certain directions and narrowing of the luminescence bandwidth are of interest for light-emitting and display technologies, spectral convertors for solar cells, photodetectors, optical sensors, and other applications [1–3]. Enhanced luminescence of lanthanides was observed in several optically anisotropic planar structures. Erbium-implanted SiO_2 active layer of microcavity was fabricated and surrounded by distributed Bragg reflectors Si/SiO_2, generated by electron beam deposition [4]. The peak intensity related to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ band at 1.53 μm of erbium was enhanced by nearly 60 times for erbium in cavity compared to erbium out of cavity. Enhanced by two orders of magnitude erbium luminescence was observed for hydrogenated amorphous silicon [5] as well as for porous silicon microcavities [6,7]. The luminescence is highly directional with a 20° emission cone around the normal axis [6]. The erbium emission from porous silicon microcavity is narrowed to a full width at half maximum (FWHM) of 6 nm [7], while it is above 10 nm for erbium-doped silicon dioxide, porous silicon or other film structures without an engineered microcavity [8–10]. Luminescence of Eu from a sol-gel derived SiO_2 microcavity was enhanced by about 20 times compared with SiO_2:Eu film out of cavity [11]. The luminescence band was narrowed within a FWHM of approximately 0.5 nm. The reason for enhanced luminescence and its confinement within a narrow solid angle as observed for anisotropic structures is redistribution of the local density of photonic states (optical modes) [1].

Application of a sol-gel method for multilayer coating technology leads to reduced cost due to avoiding vacuum deposition and/or epitaxial growth, accelerators for doping ions or high temperature annealing. Most of the investigations were focused on development of sol-gel derived TiO_2/SiO_2 photonic band gap structures [11–13]. Options of using other matrices are also important with respect to influence of the photonic stop band on spontaneous emission of the impurities embedded therein. Barium titanate is investigated as a material possessing spontaneous polarization. At the same time, it is a proper host for light-emitting trivalent lanthanides. Eu red emission was observed at room temperature from Eu-doped $BaTiO_3$ sol-gel derived films [14,15]. Recently we reported that a sol-gel derived amorphous $BaTiO_3/SiO_2$ multilayer structure represents a one-dimensional transparent photonic crystal [16]. The refractive index of a thin amorphous sol-gel derived (xerogel) $BaTiO_3$ film is above 1.8 and increases with sol concentration [16], making good optical contrast with silica xerogel films with refractive index below 1.45 [17]. This difference in refractive indices allows the synthesis of $BaTiO_3/SiO_2$ multilayer structures with anisotropy of photonic density of states.

In this work, we report on the sol-gel synthesis and optical properties of an Eu-doped multilayer structure consisting of a Bragg reflector/$BaTiO_3$:Eu/Bragg reflector with Bragg reflectors comprised of $BaTiO_3/SiO_2$ structures. Depending on the fabrication procedure, two set of specimens were generated, with Eu out of the cavity and Eu in the cavity. Enhanced Eu photoluminescence (PL) normal to the surface is observed for the band $^5D_0 \rightarrow {}^7F_2$ at 615 nm of trivalent europium in cavity and correlates with anisotropy of the luminescence indicatrix, transmittance and reflection bands around 615 nm for the fabricated transparent structure.

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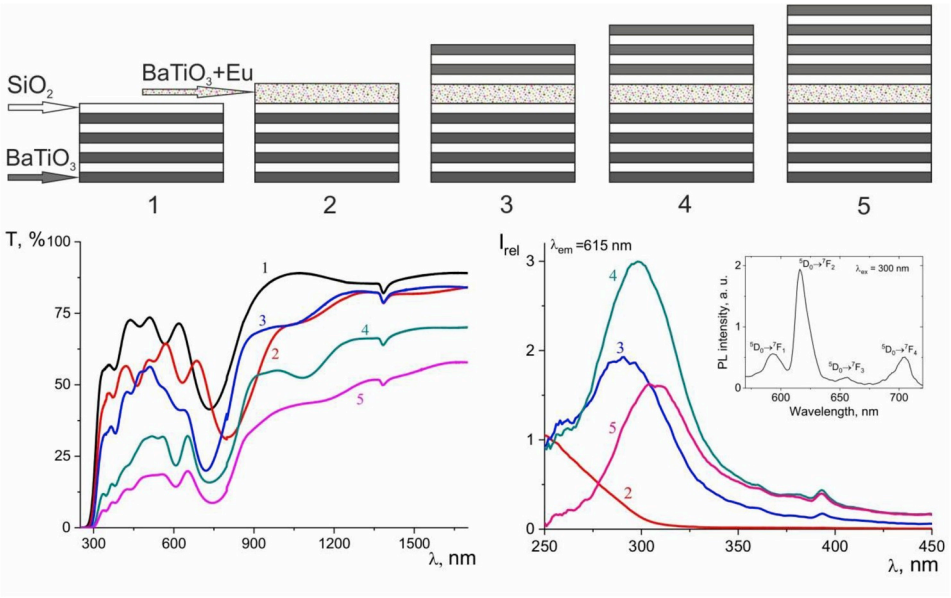
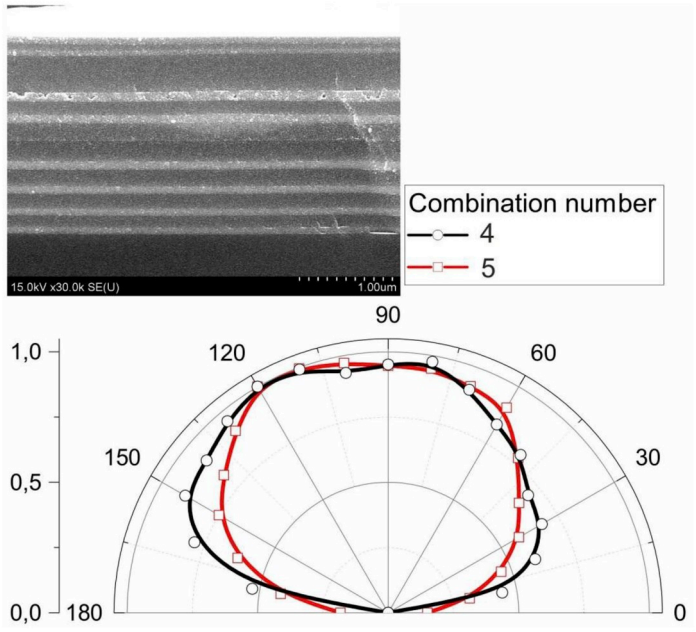


(a)



(b)

Fig. 1. Optical spectra of the specimens N1 – N5 (designated as 1-5) with a diagram of the deposited layers. (a) – Transmission (left) and PLE (right) spectra recorded for the emission wavelength 615 nm. Inset: – PL spectrum of the specimen N4 for the excitation wavelength 300 nm. (b) – Luminescence indicatrices for the specimens N4 and N5, emission wavelength 615 nm, excitation wavelength 337 nm. Inset: scanning electron micrograph of the specimen N5.

Luminescence indicatrices measured in the middle of the structure and at the periphery are compared and illustrate quality of multilayer coating confirming the data of scanning electron microscopy (SEM) examination. We also observed the red shift of the photoluminescence excitation (PLE) spectra of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ band in a $BaTiO_3$ layer with an increasing number of outer $SiO_2/BaTiO_3$ pairs.

2. Experimental

Three types of sols were prepared for fabrication of $BaTiO_3$, SiO_2 and Eu-doped $BaTiO_3$ ($BaTiO_3$:Eu) xerogel layers. For the fabrication of sol corresponding to $BaTiO_3$ xerogel [16], first a solution containing acetylacetone ($C_5H_8O_2$), titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) and acetic acid (CH_3COOH) was prepared, which was thoroughly mixed until all components were dissolved. Barium acetate ($Ba(C_2H_3O_2)_2$) was then added to the solution. The concentration of sol was 60 mg/ml corresponding to a refractive index of 1.8 for the amorphous xerogel film annealed at 450 °C. For synthesis of $BaTiO_3$ xerogel doped with europium ($BaTiO_3$:Eu), 0.05 M europium acetate hydrate ($Eu(CH_3COO)_3*xH_2O$) was dissolved in barium titanate sol. The fabricated sols were stable, with no change of colour, gelation or formation of a deposit after several months.

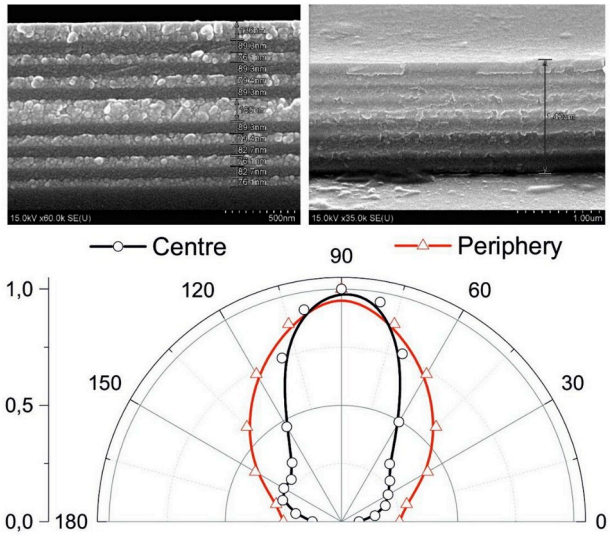


Fig. 2. Luminescence indicatrices of the specimen N6 recorded in the middle of the specimen (centre) and near to its edge (periphery) and scanning electron micrographs taken close to the analysed areas accordingly.

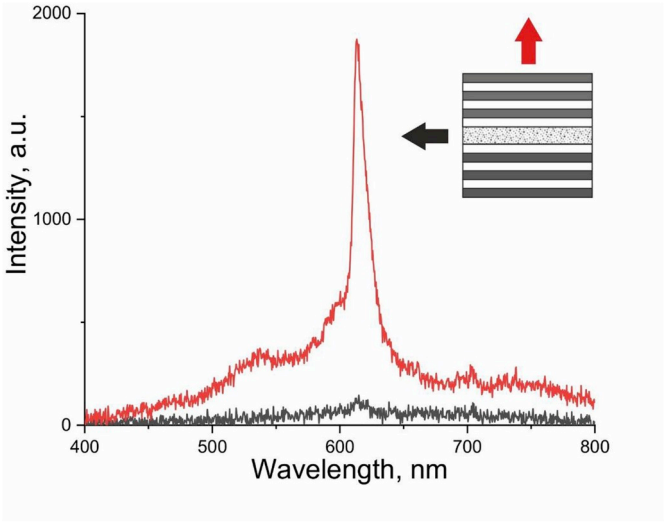
The silica sol was prepared from ethanol (C_2H_5OH), tetraethylorthosilicate ($Si(OC_2H_5)_4$), distilled water (H_2O), and nitric acid (HNO_3). To prepare the sol, ethanol and distilled water were mixed, and the resulting solution was brought to pH = 1 by adding concentrated nitric acid. Subsequently, tetraethylorthosilicate was added to the solution.

The sols were deposited by spinning on 15 × 15 mm fused silica substrates of 3 mm thickness. After spinning, each layer was dried and annealed at 450 °C for 30 min. This temperature allows for development of a multilayer optical filter on a glass substrate with a photonic stop band whilst avoiding any melting and bending of the substrate. According to X-ray diffraction and SEM examination, after annealing at 450 °C the $BaTiO_3/SiO_2$ multilayer xerogel structure is amorphous and the interfaces between the $BaTiO_3/SiO_2$ layers are not mixed [16,18]. On the contrary, heat treatment of either of the alternating layers $BaTiO_3/SiO_2$ at 200 °C leads to mixture of the layers during layer by layer deposition. The interface between the layers vanishes and the photonic band gap for $BaTiO_3/SiO_2$ multilayers does not form.

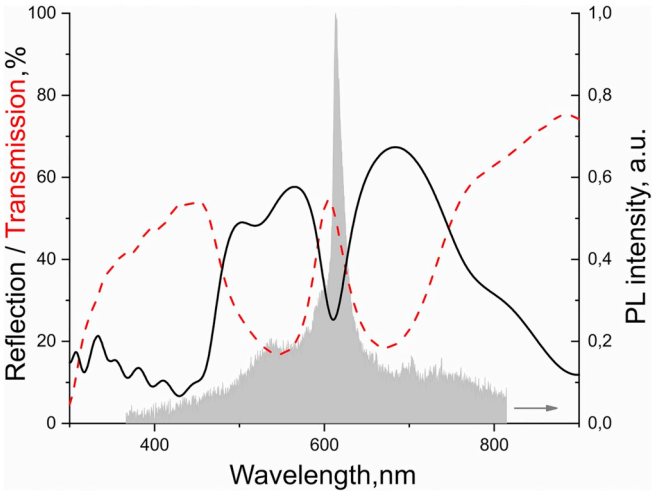
Two types of multilayer structures were fabricated with heat treatment at 450 °C; the specimens are designated as N1 – N5, with Eu out of cavity, and N6, with Eu in cavity. Each layer was generated by spinning followed by drying and annealing at 450 °C. Eight alternating $BaTiO_3/SiO_2$ layers making a bottom Bragg reflector were generated for N1. For N2 – N5, a thicker $BaTiO_3$:Eu layer was deposited on top of the 8 alternating $BaTiO_3/SiO_2$ layers. The thicker layer was fabricated using 3 depositions of $BaTiO_3$:Eu sol. For N3-N5, 2, 3 and 4 alternating $SiO_2/BaTiO_3$ layers were fabricated on top of the $BaTiO_3$:Eu layer for N3, N4 and N5 respectively, completing the top Bragg reflector. Schematic images of N1–N5 specimens showing the layer combinations are displayed in Fig. 1 (a).

N6 specimen was fabricated from the same sols but with a different deposition rate and layer thickness than N1-N5. Three pairs of $BaTiO_3/SiO_2$ were fabricated, followed by deposition of a thicker $BaTiO_3$:Eu layer, topped with 3 pairs of $SiO_2/BaTiO_3$ layers to complete the top Bragg reflector.

Transmission spectra were measured on a Cary-500 Scan UV-VIS-NIR spectrophotometer (Varian, United States & Australia). Reflection spectra were measured with spectrophotometer MS122 (PROSCAN Special Instruments, Belarus). Decay kinetics of luminescence were measured using a Fluorolog-3 spectrofluorometer (Horiba Scientific) supplied with a xenon lamp with 1–3 μs pulse width. The photoluminescence (PL) emission and excitation spectra were recorded using a SOLAR CM2203



(a)



(b)

Fig. 3. Optical spectra of the specimen N6: (a) – luminescence spectra at direction normal to the surface (red) and along the surface plane of the substrate (black), the excitation wavelength 337 nm; (b) – transmission (dashed line) and reflection (solid line) spectra and PL emission spectrum at direction along the normal to the surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

spectrofluorometer, supplied with a high pressure 150 W xenon lamp, under the same fixed incidence and registration angle 30°.

To examine the Eu photoluminescence indicatrix, the LGI-21 pulsed nitrogen laser with a generation wavelength of 337 nm and pulse repetition rate of 100 Hz was employed. Experimental setup was assembled on the basis of the GLOBOFLUX gonio photospectrometer (Stepanov Institute of Physics of NAS of Belarus), with the ability of registration of angular distribution of PL intensity. The luminescence was collected using an optical waveguide and detected with a spectrometer consisting of a Solar TII S-3801 spectrograph with a grating of 150 lines/mm and a liquid nitrogen cooled CCD-camera (LN/CCD-1152-E, Princeton Instruments). A free end of the waveguide was mounted on a motorized rotation stage (8MR174-11, Standa). All measurements were obtained at room temperature.

Morphology of the films was examined using a Hitachi S-4800 scanning electron microscope. Prior to examination, platinum was sputtered onto the cleaved edge of the specimens.

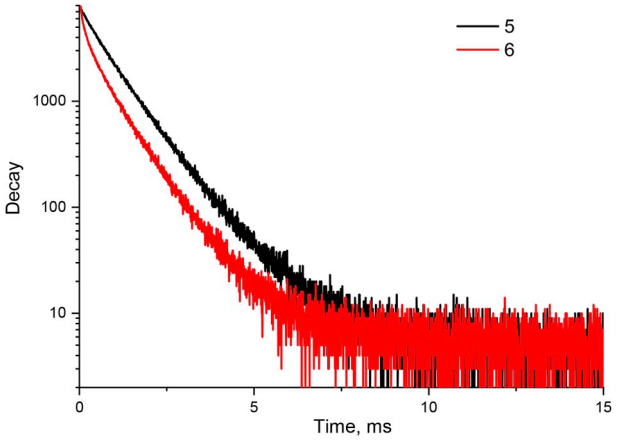


Fig. 4. PL decay curves for the Eu-doped specimens N5 (out of the cavity, upper curve) and N6 (in the cavity, lower curve), emission wavelength 615 nm, excitation wavelength 300 nm.

3. Results and discussion

Sequential deposition of alternating $BaTiO_3/SiO_2$ layers possessing optical contrast of refractive indexes results in the formation of a photonic stop band, observed as the dip in transmission spectra, confirming the recently reported data [16], as shown in Fig. 1.

Photoluminescence excitation spectra for the emission wavelength 615 nm, corresponding to sequentially deposited $SiO_2/BaTiO_3$ pairs (specimens N2 – N5) are shown in Fig. 1a (right). The typical PL emission spectrum of an Eu-doped $BaTiO_3/SiO_2$ multilayer structure is given in the inset in Fig. 1 (a) for the excitation wavelength 300 nm. The observed bands correspond to $^5D_0 \rightarrow ^7F_J$ (J = 1, 2, 3, 4) transitions of trivalent europium in $BaTiO_3$ with the main band at 615 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition. Further, we discuss Eu PL in multilayer structures $BaTiO_3/SiO_2$ at the most intensive band of 615 nm. Interestingly, the presence of 2–4 pairs of alternating $SiO_2/BaTiO_3$ layers results in the appearance of a stronger broad band in the PLE spectra with an approximate 2-3-fold increase in the PL intensity. This is noted despite weak attenuation of transmittance at the emission wavelength 615 nm and at the excitation wavelength 300 nm. The broad excitation band of PL excitation spectra for Eu^{3+} in the UV range is associated with the charge transfer mechanism [15]. The maximum of PL excitation band is red shifted as the number of the outer $SiO_2/BaTiO_3$ pairs increases. This effect could be interpreted as a result of the redistribution of the density of modes for the chosen angle of excitation. However, to our knowledge modification of PL excitation spectra of lanthanides with the number of photonic crystal constituents has not been reported. The PL indicatrices of the specimens N4 and N5 resemble a Lambertian distribution of intensity, confirming that a microcavity for Eu was not formed (Fig. 1 (b)). The scanning electron micrograph given in the inset illustrates the morphology of specimen N5, showing evident deviation in the thickness of the layers comprising the top Bragg mirror. The thickness of the $BaTiO_3$:Eu layer is about 258 nm and exceeds the half-wavelength.

The specimen N6 possesses a more idealized structure. The luminescence indicatrix of this specimen shown in Fig. 2 is anisotropic with concentration of light in a narrow solid angle as compared with the specimens N4 and N5 doped with Eu out of cavity. Moreover, the shape of indicatrix illustrates quality of the multilayer spin-on coating. When comparing the shape of two indicatrices measured from the middle and the periphery of N6, we may conclude that quality of microcavity is more perfect at the central part of the substrate rather than close to the edge of the substrate. Comparison of PL intensity for Eu in the central part of the specimen is illustrated in Fig. 3 (a). The intensity of light emission is proportional to the photonic density of states, and emission was found to be highest at the direction normal to the surface plane.

Fig. 3 (b) illustrates transmission and reflection spectra for the specimen N6. The minimum in the reflectivity stop band at 611 nm results from the $BaTiO_3$:Eu cavity in the structure. According to SEM data (Fig. 2, left inset) the thickness of the $BaTiO_3$:Eu layer is approximately 165 nm, which corresponds to a half-width cavity layer for the wavelength 611 nm and refractive index of 1.85. Further work is needed to make the structure more perfect and tune the stop band position to fit the maximum of the PL peak.

Decay curve for Eu in a cavity exhibits faster decay with more pronounced non-exponentiality, though a thorough analysis will be the subject of further studies (Fig. 4). The luminescence is characterized by the double exponential fitting with the lifetimes $\tau_1 = 6.46 \cdot 10^{-4}$ s (43%), $\tau_2 = 1.15 \cdot 10^{-3}$ s (57%) for Eu out of the cavity (specimen N5) and $\tau_1 = 4.67 \cdot 10^{-4}$ s (24%), $\tau_2 = 9.51 \cdot 10^{-4}$ s (73%) for Eu in the cavity (specimen N6). The obtained data correlate with the existing theory [19] and the observed angular dependence of PL intensity as a result of the anisotropic distribution of the photonic density of states.

4. Conclusion

In conclusion, the low-cost sol-gel method was used to generate an Eu-doped $BaTiO_3$ cavity surrounded with $SiO_2/BaTiO_3$ Bragg reflectors by spinning. Strong enhancement of Eu^{3+} PL was observed at room temperature for the band $^5D_o \rightarrow {}^7F_2$ at 615 nm in the direction normal to the plane of the multilayer. The structure, with a total thickness of approximately 1 μm, was subjected to heat treatment at relatively low temperature 450°C, which makes the method available for deposition on glass substrates. The structures may be attractive for sensing applications when targeted chemicals affect the photonic stop-band position of a microporous xerogel structure and/or influence on Eu luminescence quenching. Luminescence response and photonic stop-band shift depending on external conditions such as electric field, temperature and pressure, from viewpoint of ferroelectric/paraelectric properties of the described structure may also receive attention for further investigations.

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