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Eu luminescence from $BaTiO_3/SiO_2$ multilayer xerogel structures

N. Gaponenko*[,†,§], D. Parafinyuk*, P. Kholov*, T. Raichenok[‡] and S. Prislopski[‡]
*Belarusian State University of Informatics and Radioelectronics
P. Browki Street 6, 220013 Minsk, Belarus
[†]National Research Nuclear University
MEPhI (Moscow Engineering Physics Institute)
31 Kashirskoe Shosse, 115409 Moscow, Russia
[‡]B. I. Stepanov Institute of Physics
National Academy of Sciences of Belarus
220072, Nezavisimosti Avenue 68, Minsk, Belarus
[§]nik@nano.bsuir.edu.by

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Sol–gel technology was applied to fabricate Eu-doped $BaTiO_3/SiO_2$ multilayer structures by spinning on silicon and fused silica substrates. Eu photoluminescence (PL) was investigated depending on the annealing temperature of these structures. The samples demonstrate the room temperature luminescence corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$) transitions of trivalent europium with the most intensive band at 615 nm. For the structure on fused silica with Eu in the $BaTiO_3$ cavity, increase of the annealing temperature from 450°C to 700°C results in modification of the luminescence indicatrix and lowering of the luminescence intensity in the direction along the surface normal. For $BaTiO_3/SiO_2$ multilayer structure generated on silicon, scanning electron microscopy (SEM) analyses reveal disordering after annealing at 1000°C. This heat treatment provides also an increase of the Eu luminescence intensity.

Keywords: Photonic crystal; Bragg reflector; sol–gel; europium; luminescence.

1. Introduction

Barium titanate is extensively investigated as ferroelectric material possessing spontaneous polarization.[1] $BaTiO_3$ films have been fabricated using pulsed laser ablation,[2] metal organic chemical vapor deposition,[3] ion beam sputtering,[4] the sol–gel method[5] and other techniques. At the same time, this material is a proper host for rare earth elements including trivalent europium. An efficient Eu^{3+} red emission was observed at room temperature from Eu-doped $BaTiO_3$ sol–gel derived films and xerogels.[6,7] Recently, we reported that $BaTiO_3/SiO_2$ multilayer sol–gel derived amorphous structure is one-dimensional transparent photonic crystal.[8] Enhanced Eu^{3+} luminescence at direction normal to the surface was observed for the band $^5D_0 \rightarrow {}^7F_2$ at 615 nm in the $BaTiO_3$ cavity surrounded with the $BaTiO_3/SiO_2$ Bragg mirrors.[9] This enhanced luminescence correlated with anisotropy of luminescence indicatrix, transmittance and reflectance bands around 615 nm was reported recently in Ref. 9 for these films annealed at the temperature of 450°C.

Considering that increase of the heat treatment temperature makes influence on the photonic stop band position of the sol–gel derived multilayer structure,[8] in this work we investigate influence of the annealing temperature upon Eu photoluminescence (PL) in the $BaTiO_3/SiO_2$ multilayer structure with the Eu-doped $BaTiO_3$ layers. We consider two types of samples: the $SiO_2/BaTiO_3$ Bragg mirror with each $BaTiO_3$ layer doped with Eu (designated as sample #1) and $BaTiO_3$ cavity doped with Eu (sample #2). Both types of samples were subjected to heat treatment at different temperatures.

2. Experimental

The sol corresponding to the composition of $BaTiO_3$ xerogel was prepared from acetylacetone, titanium isopropoxide, acetic acid and barium acetate. Europium acetate was dissolved in the barium titanate sol to fabricate the samples of Eu-doped $BaTiO_3$ xerogels ($BaTiO_3$:Eu). The silica sol was prepared from ethanol (C_2H_5OH), tetraethyl orthosilicate ($Si(OC_2H_5)_4$), distilled water (H_2O) and nitric acid (HNO_3).

The first sample was grown on silicon and comprised three pairs of alternating $BaTiO_3$:Eu/SiO_2 layers, with each $BaTiO_3$ layer doped with Eu. This sample was cut in several parts, which then were annealed within the temperature range from 450°C to 1000°C.

The fabrication procedure of the second sample (with Eu in $BaTiO_3$ cavity) on fused silica substrate was described in

Ref. 9. Each layer was generated through spinning, drying and annealing at 450°C, then next layers were deposited followed by the same heat treatment procedure. Starting from the deposition of the first $BaTiO_3$ layer, eight alternating $BaTiO_3/SiO_2$ layers were generated making the bottom Bragg reflector. After deposition of all eight layers the thicker $BaTiO_3$:Eu layers were fabricated using several deposition cycles of $BaTiO_3$:Eu sol. Finally, four pairs of $SiO_2/BaTiO_3$ layers were fabricated completing the bottom Bragg reflector. PL from this sample was recorded after its sequential annealing at 450°C and 700°C.

Morphology of the films was analyzed using a Hitachi S-4800 scanning electron microscope (SEM).

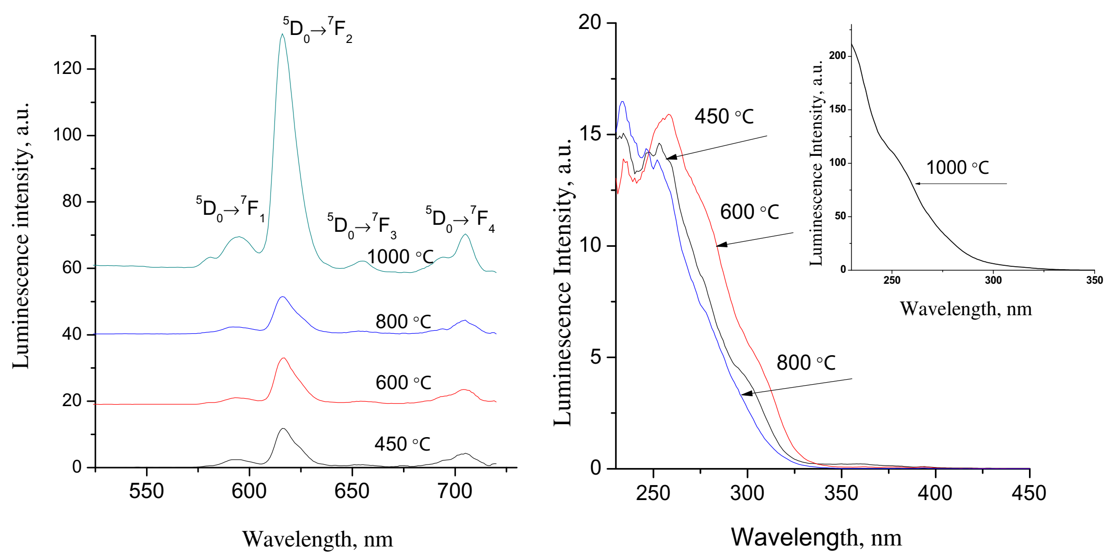
Transmission spectra were measured on a Cary-500 Scan UV-VIS-NIR spectrophotometer (Varian, United States and Australia). PL and photoluminescence excitation (PLE) spectra were recorded using a SOLAR CM2203 spectrofluorimeter supplied with a high pressure xenon lamp of 150 W, under the same fixed incidence and registration angles 30°. To examine the Eu PL indicatrix, a LGI-21 pulsed nitrogen laser with the wavelength of 337 nm and pulse repetition rate of 100 Hz was used. Experimental setup was assembled on the basis of a GLOBOFLUX gonio photospectrometer (Institute of Physics of NAS of Belarus) with the ability to monitor 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). The sample was placed in a vertical plane. The plane of movement of the waveguide connected to the detector was vertical and perpendicular to the plane of the sample. The plane defined by the sample normal and by the incident beam was horizontal. The laser beam was fixed at an angle of 40° to the normal of the sample plane. The center of rotation of the waveguide and the point of incidence of the laser beam coincide. All measurements were done at room temperature.

3. Results and Discussion

Both types of the samples demonstrate room temperature luminescence corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$) transitions of Eu^{3+} with the most intensive band $^5D_0 \rightarrow {}^7F_2$ at 615 nm (Fig. 1). The PL intensity of the most intensive band $^5D_0 \rightarrow {}^7F_2$ remains the same after annealing of the sample #1 within the temperature range of 450–800°C, but it increases drastically for the annealing temperature of 1000°C.

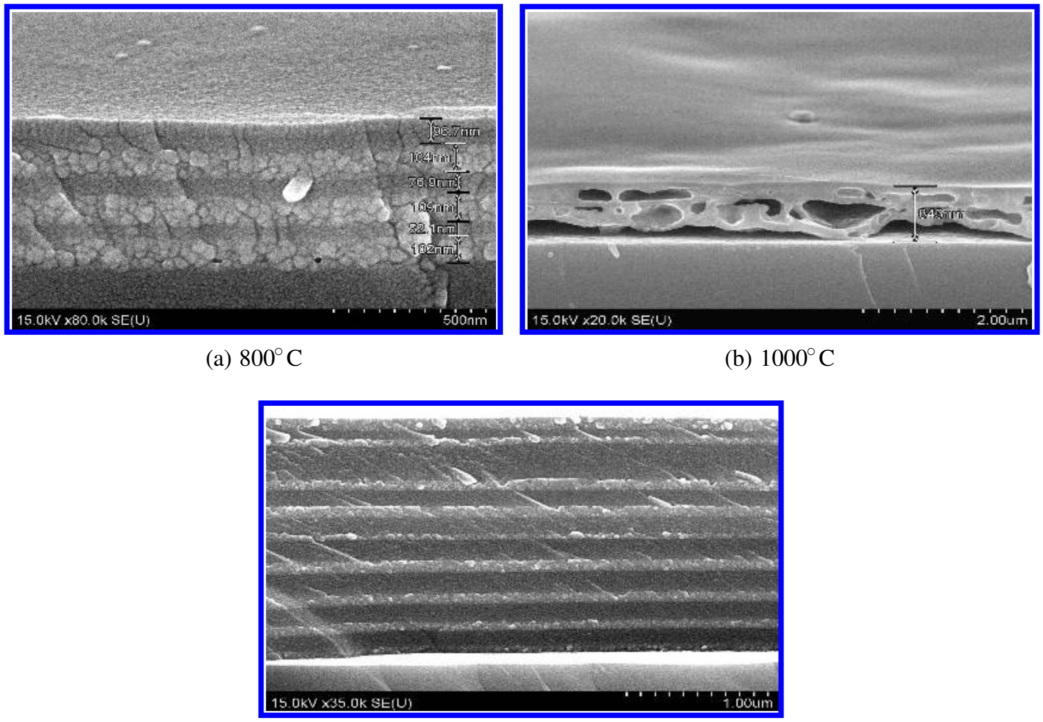
The SEM images of the analyzed parts of the sample #1 annealed at 800°C and 1000°C are given in Figs. 2(a) and 2(b), respectively. Explicit degradation of the structure occurs at 1000°C with formation of the macropores.

For the sample #2 (with Eu in cavity, Fig. 2(c)) there is the clear transmission window with the highest transmittance of 54% at 606 nm within the photonic stop band displayed in Fig. 3. Also, the enhanced Eu PL at the direction normal to the surface is observed in the cavity for the $^5D_0 \rightarrow {}^7F_2$ band at the wavelength of 615 nm. Annealing of this sample results in the blueshift of the transmission window maximum from



(a) (b)

Fig. 1. PL (a) and PLE (b) spectra of $BaTiO_3$:Eu/SiO_2 samples (#1) annealed at different temperatures. PL excitation wavelength is 260 nm (a) and emission wavelength is 615 nm (b). PL spectra (a) are shifted vertically for clarity.



(a) 800°C (b) 1000°C

(c) 450°C

Fig. 2. Typical SEM images of the multilayer $BaTiO_3/SiO_2$ structures: $BaTiO_3/SiO_2$ Bragg mirror where each $BaTiO_3$ layer was doped with Eu (sample #1) after annealing at 800°C (a) and 1000°C (b); Eu in $BaTiO_3$ cavity surrounded with $SiO_2/BaTiO_3$ Bragg mirrors (sample #2) after annealing at 450°C (c).

606 to 597 nm along with reduction of transmittance in maximum down to 39%. The blueshift results in significant modification of the luminescence indicatrix. There are the decrease of PL intensity in the direction normal to the surface (90°) and appearance of the additional emission at the angle of 135° (Fig. 4). We attribute the observed influence of the annealing temperature on the PL indicatrices to redistribution of the density of photonic states in the $BaTiO_3$: Eu cavity confined with the $SiO_2/BaTiO_3$ Bragg mirrors."

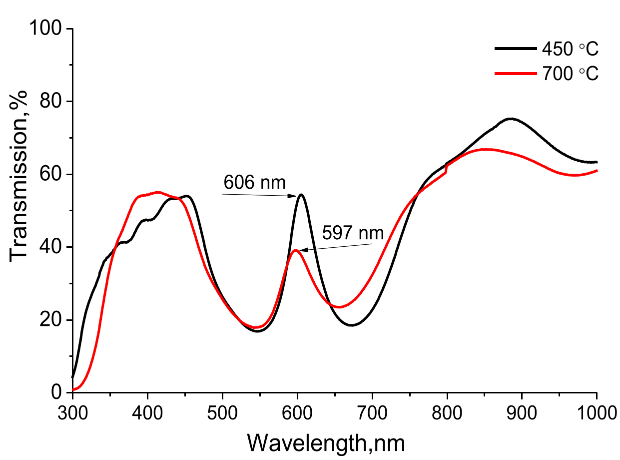


Fig. 3. Transmission spectra at direction along the normal to the surface of the sample #2 (Eu in $BaTiO_3$ cavity) after annealing at 450°C and 700°C.

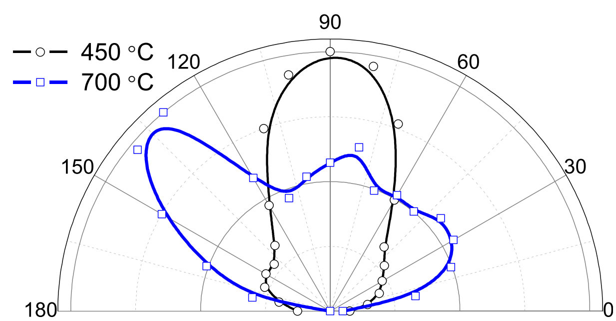


Fig. 4. Luminescence indicatrices of the sample #2 (Eu in $BaTiO_3$ cavity) after annealing at 450°C and 700°C. The registration angle 90° corresponds to horizontal direction along the sample normal, passing through the point of incidence of the laser beam.

4. Conclusion

In conclusion, we demonstrated the influence of the annealing temperature on optical properties of two types of $BaTiO_3/SiO_2$ multilayer structure with Eu-doped $BaTiO_3$ layer. The $BaTiO_3$: Eu cavity structure surrounded with $BaTiO_3/SiO_2$ Bragg mirrors fabricated at 450°C reveals the enhanced PL at the direction normal to the surface, but after annealing at 700°C the angular redistribution of the PL intensity occurs because of 9 nm blueshift of the transmission window. Further work is needed to find softer heat treatment conditions for tuning the photonic band gap position and luminescence spectra of lanthanides from $BaTiO_3/SiO_2$ multilayer structures. An improvement of technology towards ferroelectric $BaTiO_3$ phase in photonic crystals doped with lanthanides may find wide application as light-emitting structures sensitive to external conditions near the Curie point.[10] For the disordered $BaTiO_3/SiO_2$ multilayer structure on silicon formed after annealing at 1000°C, the strong PL of Eu^{3+} is observed. The possible reason of luminescence enhancement from this mesoporous structure can be multiple scattering effects and efficient trapping of exciting light in the disordered dielectric materials with fluctuation of refractive index on the light wavelength scale.[11,12]

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