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SOL-GEL FABRICATION AND LUMINESCENCE PROPERTIES OF MULTILAYER Eu-DOPED $BaTiO_3/SiO_2$ XEROGEL NANOSTRUCTURES

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With the use of sol-gel method $BaTiO_3/SiO_2$ multilayer structures were fabricated on glass or fused silica substrates employing dipping or spinning procedure. The photonic stop band was observed in the reflection and transmission spectra of the multilayer structure annealed at 450 °C. It is red shifted with an increase of the thicknesses of $BaTiO_3$ and SiO_2 layers. For structures comprising Eu-doped $BaTiO_3$ layers of different thicknesses photoluminescence with the main band at 614 nm was detected. It is characterized with the double-exponential decay with the lifetimes of about 0.5 and 1.1 ms which do not depend significantly on the photonic stop band position.

Keywords: sol-gel, photonic stop band, barium titanate, europium.

1. Introduction

$BaTiO_3$ known as a ferroelectric has also received significant attention as host material for lanthanides. Luminescence of Eu,[1] Ho[2] and other lanthanides in $BaTiO_3$ was reported. Another attractive property of this material is relatively high refractive index. Recently, formation of 1D photonic crystal with the photonic stop band at 636 nm was reported for the sol-gel derived $BaTiO_3/SiO_2$ multilayer structures.[3] It was manifested in transmission and reflection spectra.

In the present paper we present further optical and structural properties of $BaTiO_3/SiO_2$ multilayer xerogel structures fabricated by dipping or spinning. The red shift of the photonic stop band with an increase of the thicknesses of $BaTiO_3$ and SiO_2 films is shown. The Eu luminescence in $BaTiO_3$ embedded within $BaTiO_3/SiO_2$ layers is discussed.

2. Experimental

Barium acetate and titanium isopropoxide were used as precursors for sol-gel synthesis of $BaTiO_3$. They were dissolved in a mixture of acetic acid and acetylacetone (4:1 by volume). The obtained solution was vigorously stirred at room temperature for 2 h.

For preparation the sols doped with europium, europium nitrate was dissolved in a small amount of water and added to the $BaTiO_3$ sol at different molar concentrations. SiO_2 films were deposited from the sol prepared from $Si(OC_2H_5)_4$.[4] The films were fabricated on glass by dipping (samples 1 – 6) and fused silica (sample 7) substrates by spinning. In the case of the structures deposited by dipping the seventh layer was doped with Eu, and the samples were different from each other by withdrawal rate and film thickness, accordingly.

3. Results and Discussion

SEM images of typical $BaTiO_3/SiO_2$ multilayer structures deposited by dipping and annealed at 450 °C is given in Fig. 1. The total thickness of the structures is within the range of 1000 – 1600 nm. It was determined by the deposition rate.

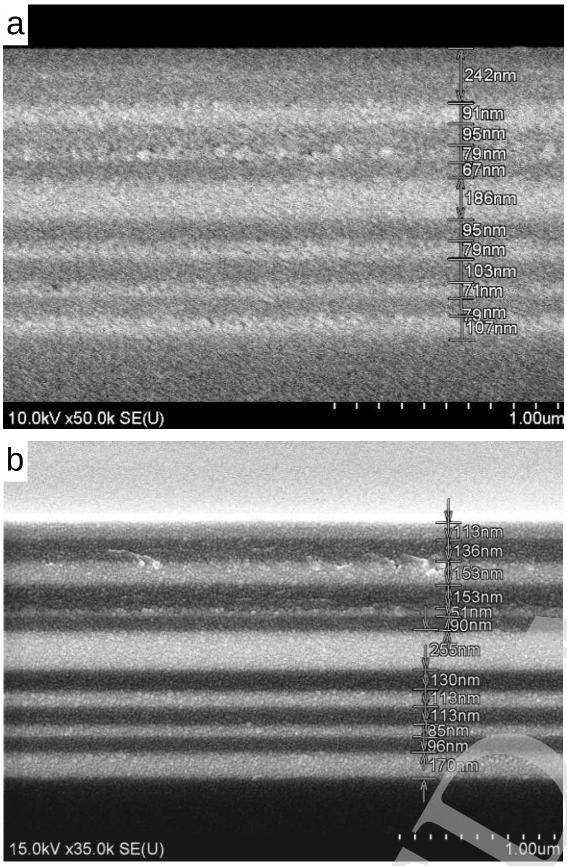

Fig. 1. SEM images (samples 2 (a) and 4 (b)) of $BaTiO_3/SiO_2$ multilayer structures. The seventh layer (from the bottom) was doped with Eu.

The SEM images show that the structures have an eroded interface between the $BaTiO_3$ and SiO_2 layers. They are amorphous according to XRD data. However, they exhibited the photonic stop band effect that is confirmed with transmission and reflection spectra shown in Fig. 2. The minimum transmission for the fabricated series of the 6 samples is located within 600 – 690 nm. According to the simulation by the matrix method,[3] the increase of the film thickness of $BaTiO_3$ and SiO_2 with refractive indexes 1.9 and 1.45, respectively, results in the red shift of the photonic stop band.[4] This is confirmed by the study of the thicker $BaTiO_3/SiO_2$ multilayer structure deposited from the same sols by spinning (Fig. 3).

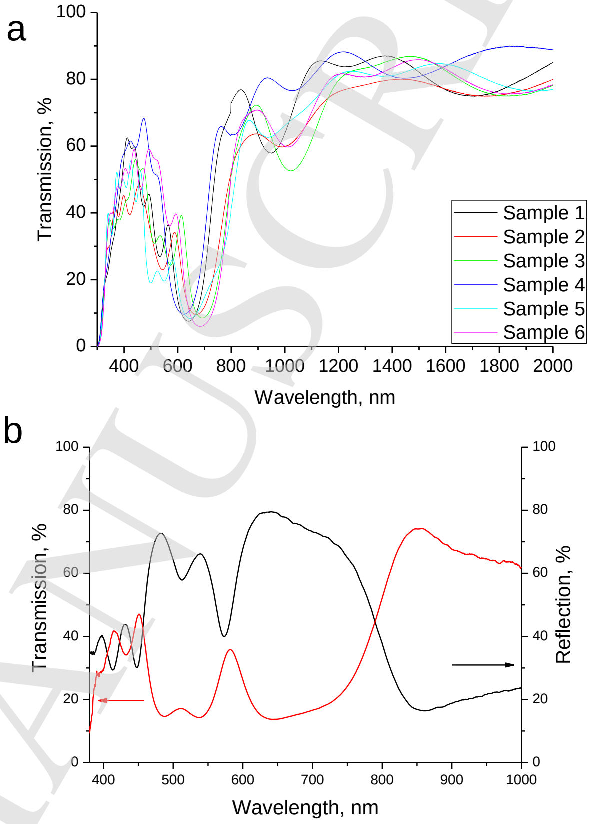

Fig. 2. Transmission (a,b) and reflection (b) spectra of $BaTiO_3/SiO_2$ multilayer structures with $BaTiO_3$:Eu layer on glass substrates annealed at 450 °C, sample 5.

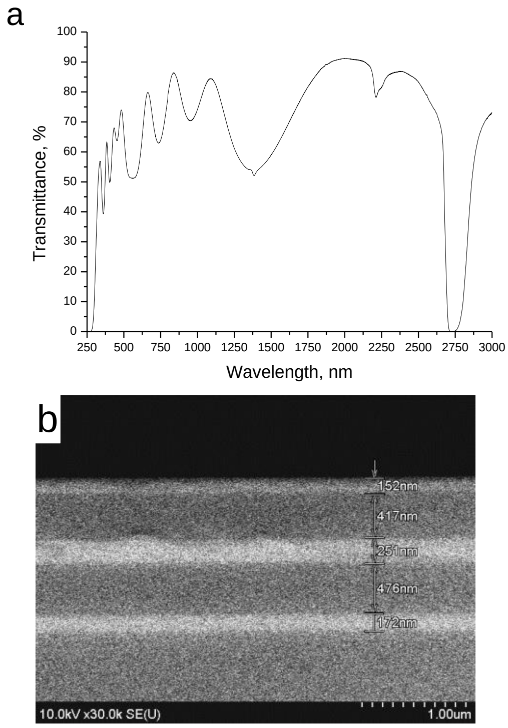

Fig. 3. Transmission spectrum (a) for the $BaTiO_3/SiO_2$ multilayer structure deposited by spinning (sample 7) and its SEM image (b).

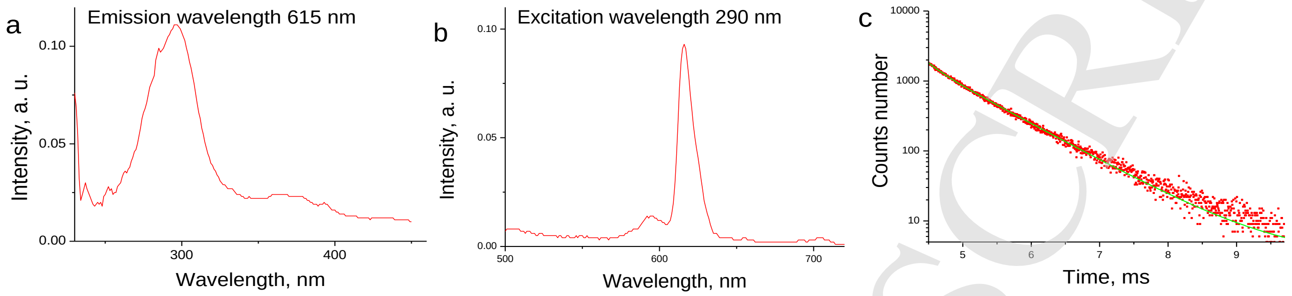

Fig. 4. Excitation (a) and PL spectra (b) and time-decay (c) for the sample 4 (time calibration is 0.005333344 ms/channel, the emission wavelength is 615 nm).

Fig. 4 presents PL and PL excitation spectra, and time decay for the sample 4 fabricated by dipping. The PL spectrum demonstrates typical Eu-related emission with the maximum at 614 nm associated with $^5D_0 - {}^7F_2$ transition in the Eu^{3+} ion. The luminescence is characterized by the double exponential decay with the lifetimes of 0.5 and 1 ms. According to the obtained data of PL decay, there are no significant changes in the lifetime for all fabricated samples 1 – 7.

4. Conclusion

Sol-gel derived $BaTiO_3/SiO_2$ multilayer amorphous structures fabricated by dipping or spinning possess the photonic stop band. Its position depends on the thicknesses of the layers. Further study is needed to understand whether their optical properties can be influenced by the spontaneous emission of lanthanides. This work could be developed towards increasing the quality factor of Eu-doped microcavity by adjustment the layers thickness of the Bragg mirrors and microcavity. The in-depth distribution of Eu and confinement within the half-wave layer should also be taken into account.

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