

Synthesis of luminescent Gd_2SiO_5:Ce^{3+} films by sol-gel method

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The transparent luminescent films of cerium activated gadolinium oxyorthosilicate Gd_2SiO_5:Ce^{3+} have been produced by the sol-gel method. The optimal synthesis conditions and molar ratio of the precursors have been specified. The obtained films are polycrystalline with the grain size of about 100 nm. Luminescent properties of the films have been compared to the GSO:Ce bulk crystal.

Золь-гель методом получены прозрачные люминесцентные пленки оксиортосиликата гадолиния, активированного церием Gd_2SiO_5:Ce^{3+}. Подобраны оптимальные условия синтеза и соотношения исходных компонентов пленкообразующего раствора. По результатам рентгенофазового анализа пленка является поликристаллической со средним размером зерна 100 нм. Проведено сравнение люминесцентных характеристик пленки и монокристалла GSO:Ce.

1. Introduction

The thin-film coating based on fine-dispersed scintillators and luminophors are traditionally used in the systems for detection of X-rays, low-energy gamma-radiation and charged particles in medical devices and luminescent screens. The main disadvantages of such coating are opacity and necessity to use a dispersion binding medium which reduces the coating film density.

The modern methods permit synthesis of scintillation films directly on a substrate. One of the methods is a formation of nanostructured films from the film-forming solutions by the sol-gel technology [1, 2]. Such films have a number of advantages, as compared to the commonly used powder-like ones, such as transparency, high homogeneity and density of the material, and fine-controlled film thickness. Recently, using the sol-gel method, a number of luminescent films of simple oxides and aluminates, silicates, borates, tungstates has been synthesized [3–8].

The crystal of gadolinium oxyorthosilicate activated by cerium ions Gd_2SiO_5:Ce^{3+} (GSO:Ce) is a one of effective scintillators. Due to high light yield, high density and short afterglow they are widely used in medical apparatus and high-energy physics [9–12]. In current work, we present the results on GSO:Ce thin-films synthesis and investigation of their luminescent properties.

2. Experimental

The sol-gel films were prepared by following procedure. First, the initial reaction mixture containing the stoichiometric ratio of tetramethoxyorthosilane (TMOS) and aqueous solutions of $Gd(NO_3)_3$ and $Ce(NO_3)_3$ nitrates were prepared. Aqueous solutions of $Gd(NO_3)_3$ and $Ce(NO_3)_3$ nitrates were obtained by a dilution of appropriate oxides in HNO_3 at 60–80°C. In a case of CeO_2, peroxide H_2O_2 was additionally used for cerium reduction according to the reaction $Ce^{4+} + \bar{e} \to Ce^{3+}$. Distilled water was used to obtain the needed volume of the salts solution.

Table. Properties of film-forming solution at different molar ratio of precursors

Sample	Molar ratio of precursors (TMOS:H_2O:DMF)	Notes
1	1:45:0	Viscid, cracking at drying
2	1:90:0	Cracking
3	1:45:0.2	Viscid
4	1:60:0.1	Not viscid
5	1:90:0.2	Not viscid
6	1:60:0.2	Optimal

Thereafter the mixture was stirred by magnetic stirrer for 24 h at 50°C. To decrease the solution surface tension and prevent film cracking under drying, dimethylformamide (DMF, evaporation temperature 153°C) was also added to the initial solution. It has been experimentally found that the optimal film-forming properties can be reached at TMOS:H_2O:DMF precursors molar ratio = 1:60:0.2 (Table). Obtained sol was transparent and stable during several weeks.

The films were formed by spin-coating on fused silica substrate, dried at 130°C during 2–3 h and annealed at 350°C. To get a specified film thickness, the layer-by-layer deposition technique was used. Each layer was dried and annealed. Finally, the films were annealed at 1100°C in argon atmosphere.

The obtained films are characterized by high transparency and adhesion to a substrate, as well as homogeneous interference color that indicates the film uniformity. Thickness of the films was determined by weighing. The thickness of four layers was in the range of 230–250 nm. The X-ray phase analysis was used for samples characterization. It was shown that the films contain Gd_2SiO_5 crystalline phase with an average grain size of 100 nm.

Luminescence spectra were recorded using an automatic spectrofluorimeter on the base of a grating monochromator MDR-23. Luminescence was excited by a He–Cd laser (λ = 325 nm). The transmission spectra were registered by Specord-200 spectrophotometer. The absorption of a silica substrate was subtracted.

3. Results

Fig. 1 shows the luminescence spectra of GSO:Ce (1 at.%) sol-gel film and single crystal. The spectra represent the typical

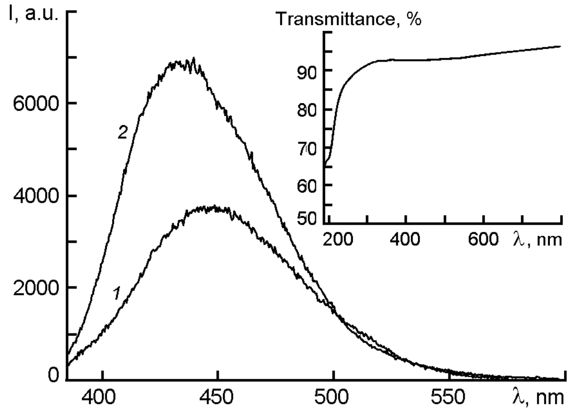

Fig. 1. Luminescence spectra of GSO:Ce film (*1*) and bulk crystal (*2*) at photoexcitation (325 nm). The inset demonstrates the transmission spectrum of the film.

broad band $5d \to 4f$ of the Ce^{3+} luminescence. It is obvious that the film luminescence band is broadened and maximum shifted towards long-wavelength spectral region as compared to the crystal one, (445 and 435 nm, respectively). It is known, that there are two types of optical centers in the GSO:Ce crystal, which are formed as a result of the substitution of two nonequivalent gadolinium cationic sites with cerium ions [13, 14]. Two types of optical centers give two spectral bands with maxima at 430 nm and 485 nm, respectively. The first center is surrounded by nine oxygen ions, whereas the second one — by seven oxygen ions. In GSO single crystal Ce^{3+} ions occupy mainly the first center, therefore the luminescence of the second center is low-intensive and weakly observed in the luminescence spectrum. In the nanostructured film, redistribution of cerium ions between the centers can take place that will result in the red shift of the spectrum. For instance, such redistribution between two optical centers was observed in the thin-films of lutetium oxyorthosilicate LSO:Ce [15].

The inset in Fig. 1 demonstrates the transmission spectrum of the film in the spectral range of 200–800 nm. At the 0.25 μm film thickness, the transmission level at 430 nm is no less than 90 %. In the range of 200 nm, the transmission decreases due to interband absorption of the Gd_2SiO_5 host. The typical absorption bands of Ce^{3+} ions is not observed in the spectrum due to a low thickness of the film.

Fig. 2 shows amplitude spectra of GSO:Ce film and single crystal (10×10×1 mm^3) at alpha-excitation from

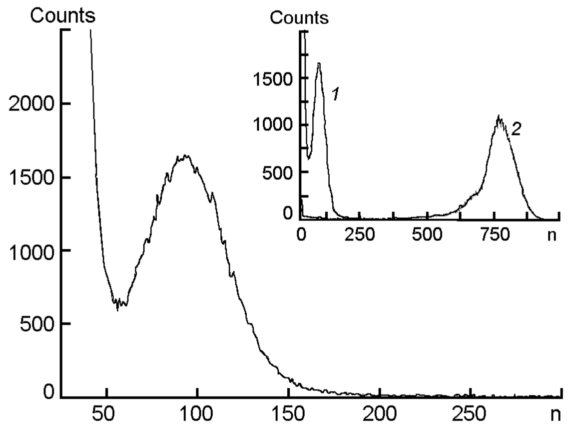

Fig. 2. Pulse height spectra of GSO:Ce film at alpha-excitation from ^{239}Pu source. The position of the film photopeak relative to the GSO:Ce bulk crystal one is represented in the inset. *1* – film, *2* – crystal.

^{239}Pu source. Spectra were obtained using the standard procedure [16]. Energy resolution *R* of the film is about 50 %, for single crystal this value is 12.4 %. The relative light yield of the film is ~15 % as compared to the bulk crystal (inset in Fig. 2). This small value is caused by low registration efficiency of alpha-radiation in thin film, since the range of alpha-particles in gadolinium oxyorthosilicate is about 25 μm [17]. The light yield of the film of ten microns thickness is comparable with that obtained for the bulk crystal [15, 18].

4. Conclusions

Thus, the optimal conditions for the synthesis of polycrystalline $Gd_2SiO_5:Ce^{3+}$ scintillation films have been specified. Obtained films have high transparency and intensive photoluminescence in the visible spectral region. To obtain films with higher scintillation characteristics, it is necessary to improve the synthesis procedure production the optical quality films with thickness of 1–10 μm.

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Отримання люмінесцентних плівок $Gd_2SiO_5:Ce^{3+}$ золь-гель методом

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Золь-гель методом отримано прозорі люмінесцентні плівки оксиортосилікату гадолінію, активованого церієм $Gd_2SiO_5:Ce^{3+}$. Підібрано оптимальні умови синтезу і співвідношення вихідних компонентів плівкоутворювального розчину. За результатами рентгенофазового аналізу плівка є полікристалічною з середнім розміром зерна 100 нм. Проведено порівняння люмінесцентних характеристик плівки та монокристала GSO:Ce.