

Ce doped MGa_2S_4 (M-Ca, Sr) thin films prepared by the Flash evaporation method

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INTRODUCTION

Blue photoluminescence (PL) and electroluminescence (EL) of rare-earth-activated MGa_2S_4 (M-Ca, Sr) thin films are attracting much attention due to their high luminance and luminescent efficiency [1]. Ce doped ternary tiogallates MGa_2S_4 present excellent color coordinates, high lumen equivalents [2] and fast luminescence decay [3].

These phosphors can be successfully used for creation of full color thin film electroluminescent (TFEL) displays [4].

There are several techniques for the deposition of MGa_2S_4 thin films, such as, molecular beam epitaxy (MBE) and multisource deposition (MSD) [7,8], pulsed laser deposition (PLD) [9], Metal-Organic Chemical Vapor Deposition (MOCVD) [10], two-target pulsed–Electron-Beam Evaporation (EBE) [11]. The use of separately elemental sources in MBE and MSD methods can overcome the difficulty of maintaining the stoichiometry. Deposition from Binary Vapours (DBV) [9] method, these practical problems can be avoided by using simultaneous evaporation of the SrS, Ga_2S_3 compounds. However, the specified methods are high-end and expensive, that contradicts requirements of the modern industry.

In the present work are submitted, first, a new relatively simple and inexpensive method of obtaining thin films MGa_2S_4 and also, methods of improvement crystal and luminescence properties thin films by the post deposition annealing.

EXPERIMENTAL TECHNIQUES:

$\text{MGa}_2\text{S}_4:\text{Ce}^{3+}$ (2%) thin films were grown by Flash evaporation method from powder $\text{MGa}_2\text{S}_4:\text{Ce}^{3+}$, which were synthesized by using SrS or CaS, Ga_2S_3 and Ce_2S_3 sources at 900°C for 24 h under $\text{H}_2\text{S}(10\%)+\text{Ar}$. An outline picture for flash evaporation equipment is shown in Fig.1.

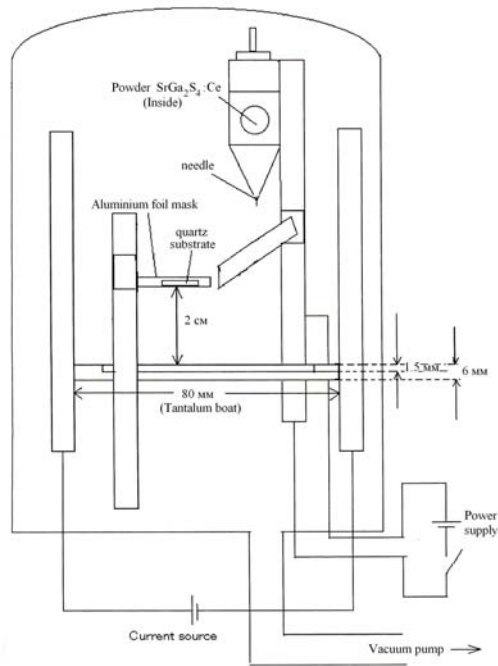


Fig.1. Flash evaporation set-up

The obtained powders were ground and discretely evaporated onto a quartz substrate from a tantalum boat by means of a special feeding appliance. The evaporation process was done at the vacuum level 1×10^{-5} torr. The temperature of the boat was kept approximately 1500°C . The substrate was heated by radiation from the boat. The temperature of the substrate depended on the distance from the boat and could be changed in the range of $200\text{--}600^\circ\text{C}$. The feeder was connected with a regulated DC power supply (9V, 12A) to move a needle (up-and-down-motion) that controlled the amount of powder dropped into the drain. The thickness of the obtained film depended on the number of discrete evaporation and varied within 100-2000 nm.

TFEL device preparation

We made TFEL devices with $\text{SnO}_2\text{-MgGa}_2\text{S}_4\text{:Ce-Al}$ (MSM) threelayer structure (Fig.2). The thickness of phosphor thin film in this structure is $1\ \mu\text{m}$.

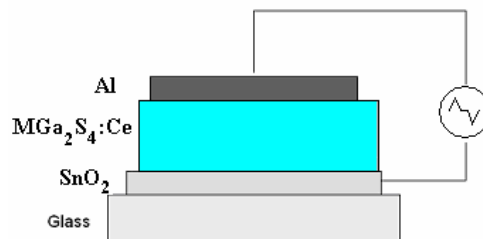


Fig.2. TFEL device structure

RESULTS AND DISCUSSION

X-Ray analysis of thin films

X –ray diffraction spectra of the obtained $\text{MGa}_2\text{S}_4\text{:Ce}$ thin films was measured.

The X-ray diffraction curve for Ce doped SrGa_2S_4 thin film before annealing process is shown at Fig. 3. As seen from the Fig. 3, the film doesn't show any reflection lines and exhibits amorphous behaviour. The temperature and duration of deposition process in flash evaporation method seem to be not enough for the crystallization of deposited film. Therefore the annealing of obtained films is necessary.

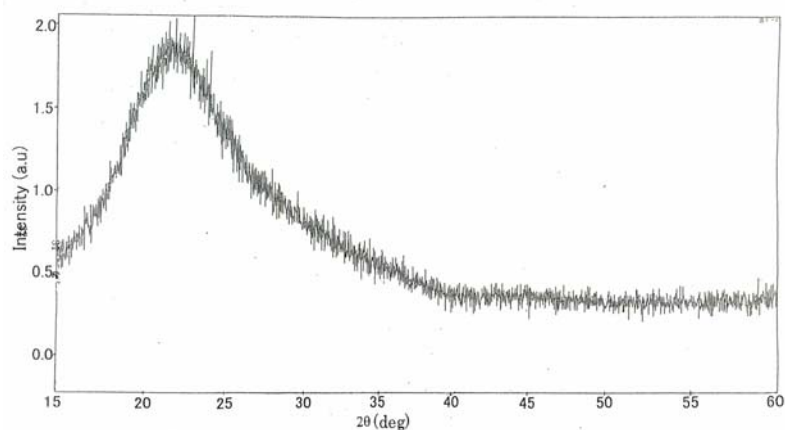


Fig.3. X-ray diffraction for $\text{SrGa}_2\text{S}_4\text{:Ce}$ 4% thin film before annealing process

The annealing in (10% H_2S +Ar) gas stream 750°C leads the appearance of reflection lines of the film (Fig. 4); (4 0 0), (6 2 2) and (2 4 4) which are characteristic for SrGa_2S_4 compound. However, the diffraction curve shows also 2 weak diffraction peaks for Ga_2S_3 compound, (4 0 2) and (4 0 0). The X-ray diffraction results show that the annealing process leads to significant crystallization of obtained amorphous thin films.

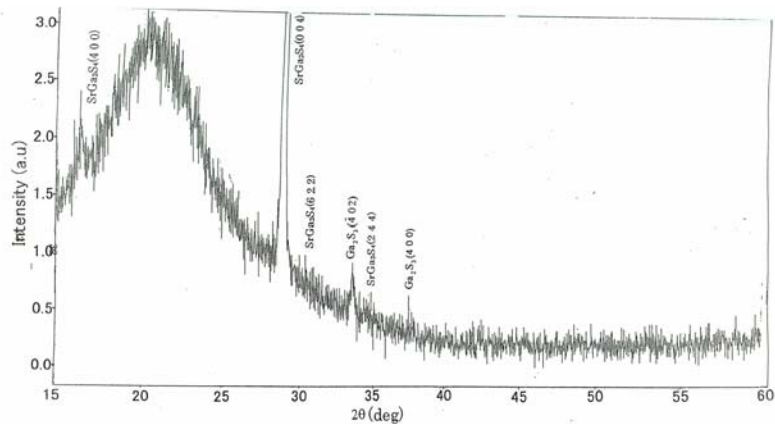


Fig.4. X-ray diffraction for $\text{SrGa}_2\text{S}_4\text{:Ce}$ 4% thin film after annealing process

PL characterisation

The PL emission spectrum for $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ thin film is shown in Fig.5. For the comparison, the PL spectrum of film before annealing process is given in the same scale. After annealing process, the intensity of the emission of the thin film becomes much higher compared with the film before annealing. The photoluminescence spectra of the Ce doped films after annealing process as well as the powder and films before annealing process shows the typical double band emission at 445 and 495 nm. The intensity ratio between 2 bands at short wavelength and long wavelength is about 1.0:0.6. Comparing to the intensity ratio before and after annealing, the result does not show a big difference.

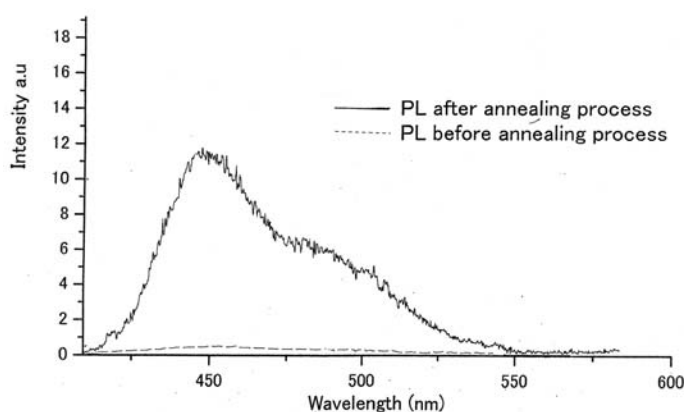


Fig.5. PL spectra for $\text{SrGa}_2\text{S}_4:\text{Ce}^{2+}$ thin films

Absorption

An absorption spectrum provides information on the wavelength of electromagnetic radiation that can be absorbed by the samples under study. This is determined by varying the wavelength and recording the intensity of the transmitted beam. The transmission and absorption spectra of $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ thin film are shown in Fig.6.

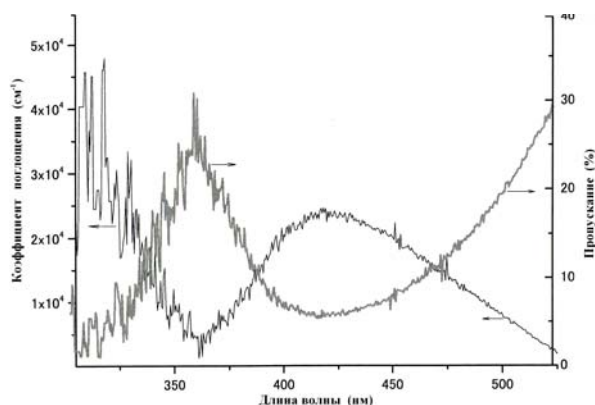


Fig.6. Transmission an absorption for $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ thin film before annealing process

The transmission spectrum was measured over the wavelength range from 300 nm to 550 nm at room temperature. As it is seen from Fig.6, the film shows the transmission edge around 310 nm (4.0 eV). The values of refractive indexes were calculated by formula

$$R = \left(\frac{1 - n_1}{1 + n_1} \right)^2$$

$$R = \left(\frac{n_1 - n_2}{n_1 + n_2} \right)^2 \quad (1)$$

$$R = \left(\frac{n_2 - 1}{n_2 + 1} \right)^2 ,$$

and by using equation

$$\alpha = -\frac{1}{x} \ln \frac{(1 - R_0)(1 - R_1)(1 - R_2)}{(1 - R_1 R_2) / T} \quad (2)$$

the absorption spectrum for thin film before annealing process was calculated (fig.6 (curve 2)) Experiments show, that the annealing process leads to a shift of transmission and absorption edge to higher energies (fig.7). The energy difference between the edges before and after annealing process is about 0.3 eV at the absorption coefficient value $5 \times 10^4 \text{ cm}^{-1}$, which corresponds to edge of crystalline **SrGa₂S₄ (4.4 eV)** .

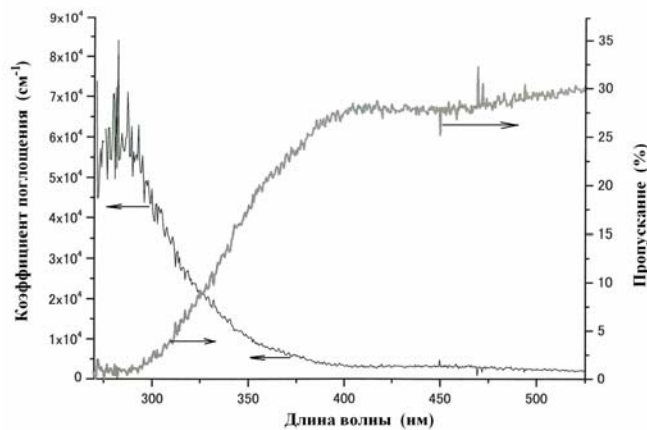


Fig.7. Transmission an absorption for SrGa₂S₄:Ce³⁺ thin film after annealing process

Electroluminescence (EL) characterization

All phosphors consist of a host material and a luminescent center. The requirements for the phosphor host materials are as follows: They have a large enough band gap (>3.5eV) to emit

visible light from the doped luminescent centers without significant absorption. They must hold a high electric field of the order 10^6 V/cm without electric breakdown and they must have insulating characteristics below the threshold voltage.

EL emission spectra of the $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ and $\text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$ thin films for different electric field are shown in fig. 8(a) and 8(b). In both spectra, broad emission blue double bands having peaks at 445 nm and 490 nm for the $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ and 453 nm and 510 nm for the $\text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$, corresponding to the transition from 5 d state to the spin-orbit split states $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ of the Ce^{3+} ions. Energy position of these bands is not change in dependence of excited electric field. EL intensity increased with increasing electric field that is seems from Fig. 9.

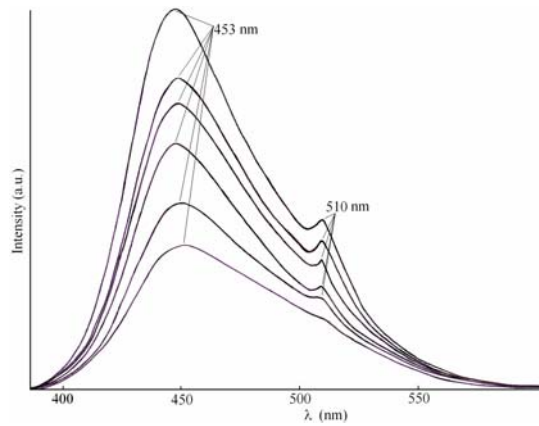


Fig.8 (a). EL emission spectra of $\text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$ at 300 K for different electric field (MV/cm): 1-0.6; 2-0.8; 3-1.0; 4-1.2; 5-1.4; 6-1.6. (Threshold electric field is 0.4 MV/cm).

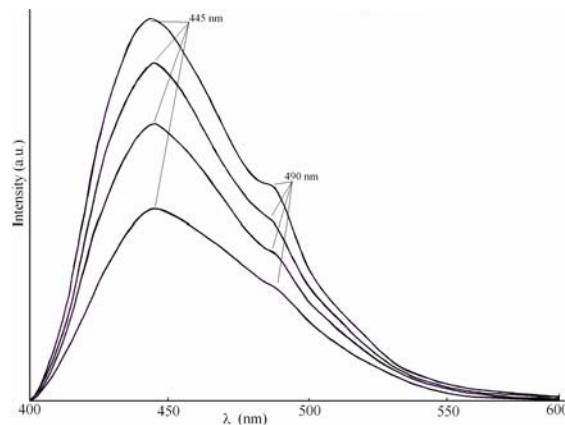


Fig.8(b). EL emission spectra of $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ at 300 K for different electric field (MV/cm): 1-0.8; 2-1.0; 3- 1.2; 4- 1.4; 5-1.6; 6-1.7. (Threshold electric field is 0.6 MV/cm).

Dependence EL intensity from applied voltage increases with increasing frequency in both structure (fig.9 and 10). But this fact is true till frequency 16 kHz for EL structure with phosphor $\text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$ (fig.11). (I can't explain, why?)

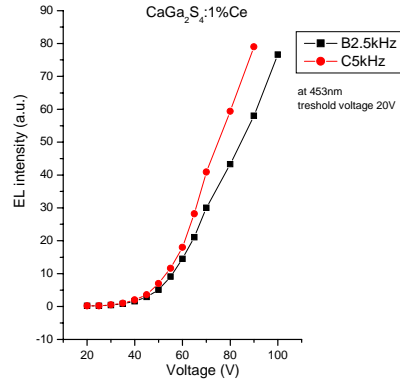


Fig.9. EL intensity versus applied voltage curve of the $\text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$ EL device

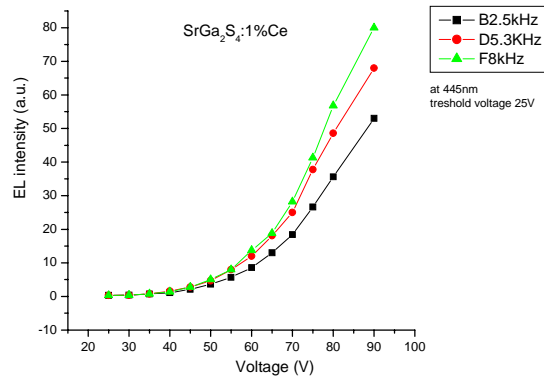


Fig.10. EL intensity versus applied voltage curve of the $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ EL device

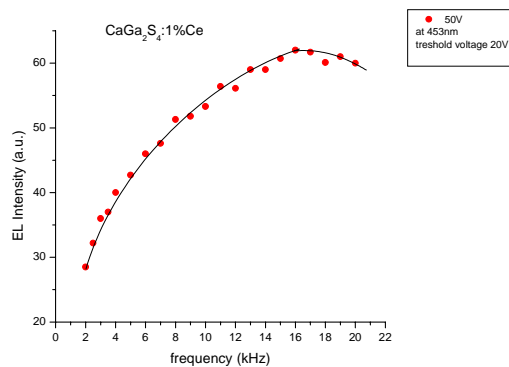


Fig.11. EL intensity versus excited frequency curve of the $\text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$ EL device at applied voltage 50 V

From the point of view of a basic understanding of the thiogallate compounds, the result provides additional evidence that the spectral distribution of Ce^{3+} luminescence in SrGa_2S_4 is independent of the method of thin film deposition. The peak of the emission band is independent of whether electric field or incident photons are used as the means of excitation.

For the practical use it is evident that in principle TFEL devices employing $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ phosphor layers can be prepared by flash evaporation method at relatively low cost and substrate temperatures.

The $\text{SrGa}_2\text{S}_4:\text{Ce}^{3+}$ phosphor achieves the deepest blue color with the CIE color coordinates of $x=0.14$, $y=0.10$, which is close to that standard CRT display ($x=0.157$, $y=0.069$) compared with $\text{CaGa}_2\text{S}_4:\text{Ce}^{3+}$. Very good EL aging characteristics have been demonstrated for the thiogallates, connected with less hygroscopic than the alkaline-earth sulfides. Therefore the thiogallate blue EL phosphors demonstrate sufficient stability, luminance and blue chromaticity to build a full-color TFEL display.

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