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Synthesis and luminescent properties of $SrTiO_3:Pr^{3+}$ phosphors prepared by sol-gel method

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Abstract. New red $SrTiO_3:Pr^{3+}$ phosphor for the field emission displays application was prepared using the sol-gel method. The reaction between starting materials $SrCl_2$, Ti-(O-i-C_3H_7)$_4$ and $PrCl_3$ resulted in a mix of compounds transformed to single-phase $SrTiO_3$:Pr after its annealing in air. Optimal technological conditions for preparation of efficiently radiating $SrTiO_3:Pr^{3+}$ phosphors were found. Both photoluminescence and cathodoluminescence spectra showed the high intensity red peaks at the wavelength λ_{max} = 617 nm. The high luminance of 300 cd/m^2 was obtained at the anode voltage of 10 kV..

Keywords: phosphor, $SrTiO_3$:Pr, photoluminescence, cathodoluminescence, field emission displays, sol-gel method.

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1. Introduction

Field emission displays (FEDs) operating due to electron beam excitation are very attractive and promising because of their advantages, namely: high luminance and contrast, high speed response, wide view angle, wide operating temperature range and a low power consumption [1, 2]. In recent years, many efforts were devoted to develop the high performance phosphors for FEDs. Especially interesting in all the variety of investigated materials are red emitting phosphors with high luminance and color purity. A new red emitting $SrTiO_3:Pr^{3+}$ phosphor has been investigated and characterized [3-5]. $SrTiO_3:Pr^{3+}$ phosphors have been synthesized by mixing $SrCO_3$, TiO_2 and $PrCl_3$ with the subsequent sintering and crushing of the prepared powder.The obtained phosphor shows high luminescent characteristics and can be considered as one of the promising materials for the high quality FEDs application.

In this study, to synthesize $SrTiO_3:Pr^{3+}$ phosphors we used the sol-gel method with starting materials $SrCl_3$, Ti-(O-i-C_3H_7)$_4$ and $PrCl_3$. Using this method, we assumed to get more complete reaction between the starting materials and more uniform distribution of dopant into the host lattice. In this paper, we analyze the structural and luminescent properties of the synthesized phosphor $SrTiO_3:Pr^{3+}$ depending on technological conditions.

2. Synthesis

Preparation of $SrTiO_3:Pr^{3+}$ phosphor is shown in Fig. 1 [6]. The synthesis was carried out in nitrogen atmosphere. The starting materials were strontium chloride $SrCl_2$, praseodymium chloride $PrCl_3$ and titanium tetra-i-propoxide Ti-(O-i-C_3H_7)$_4$ with a corresponding ratio of the starting materials Sr and Ti Sr/Ti = 1 and the fixed concentration of Pr^{3+} of 1 mol.%. After dissolving the starting materials in alcohol and stirring the solution during 3 hours, the solvent was evaporated (under the further stirring) until gel was obtained. This gel was dried at the temperature 150 °C and sintered in a muffle furnace CNOL 6.7/1300. Sintering was carried out within the temperature range 1000 – 1300 ºC in air during 2 to 9 hours. Finally, the obtained material was crushed into powder.

3. Results and Discussion

3.1. XRD-analysis

A structural analysis of the prepared phosphors was carried out using the X-ray diffractometer DRON-3M with Cu Kα radiation (λ = 1.542 Å). The samples annealed in the temperature range 1000 – 1250 ºC during 3 hours were investigated and analyzed. As shown in Fig. 2, the crystals annealed at the lowest temperature (1000 ºC) consist of basic material $SrTiO_3$ and additional

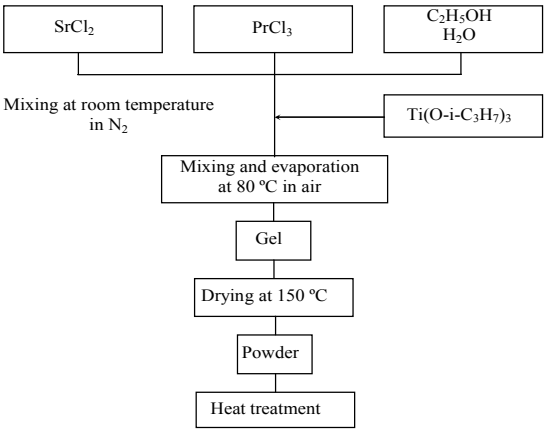

Fig. 1. Preparation of $SrTiO_3:Pr^{3+}$ phosphor.

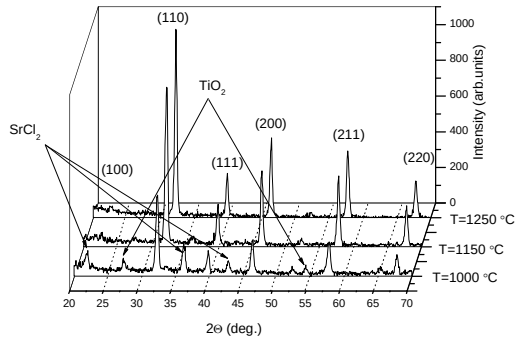

Fig. 2. The XRD spectra of samples annealed at various temperatures (1000 – 1250 °C).

phases TiO_2 and $SrCl_2$. An increase of the sintering temperature results in a gradual decrease of TiO_2 and $SrCl_2$ peaks intensity to zero (at 1250 °C).

3.2. Photoluminescence spectra

The photoluminescence (PL) spectra were measured in the wavelength range 450 – 700 nm under nitrogen laser excitation (excitation wavelength 337 nm, pulse duration 8 ns) at the width of the measuring strobe 75 μs. Investigated $SrTiO_3$:Pr samples were annealed in air within the temperature range of 1000 – 1300 °C during 2 to 9 hours.

The photoluminescence spectra of the samples annealed at various temperatures (annealing time t_{ann} = const = 3 h) are shown in Fig. 3 and have three peaks with a main maximum at the wavelength λ_{max} = 617 nm. The blue emission at λ_{max1} = 488 nm corresponds to the intra-4f transition from the excited state $^3P_0$ to the ground state $^3H_4$ of Pr^{3+}, the green emission at λ_{max2} = 530 nm corresponds to the intra-4f transition from the excited state $^3P_0$ to the ground state $^3H_5$, and the red emission at λ_{max3} = 617 nm corresponds to the intra-4f transition from the excited state $^1D_2$ to the ground state $^3H_4$ [7, 8].

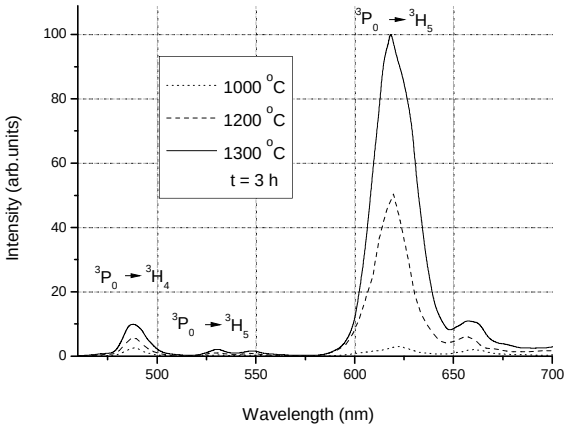

Fig. 3. The photoluminescence spectra of samples annealed at various temperatures (1000 – 1300 °C).

An increase in the annealing temperature from 1000 to 1300 ºC results in redistribution of the intensities of PL peaks. In particular, 35-times increase of the red peak intensity was observed, while an increase of the blue peak intensity was insignificant.

The photoluminescence of $SrTiO_3:Pr3^+$ phosphor originates in absorption of excitation energy of the laser beam by host material $SrTiO_3$, transferring to the Pr^{3+}-luminescence centers and subsequent radiative recombination.

3.3. Cathodoluminescence spectra

The cathodoluminescence (CL) spectra of $SrTiO_3$:Pr samples are shown in Fig. 4. It was observed that increase in the annealing temperature (t_{ann} = const = 3 h) results in a monotonic growth of the cathode-luminescence red band intensity from 2.8 arb. units at T_{ann} = 1100 °C to 100 arb. units at T_{ann} = 1300 °C.

On the other hand, at the annealing temperature T_{ann} = const = 1300 °C monotonic increase of the cathodoluminescence red band intensity with increase of the annealing time from 30 arb. units at t_{ann} = 2 h to 100 arb. units at t_{ann} = 9 h was observed (Fig. 5).

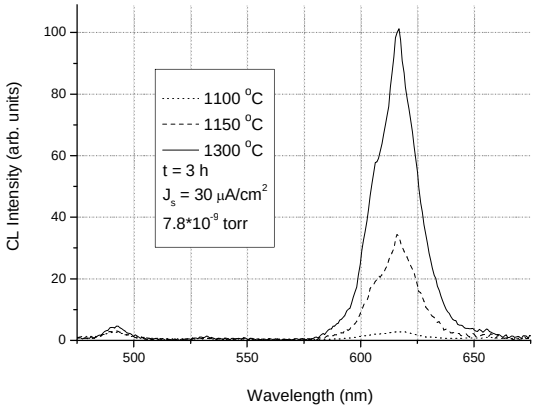

Fig. 4. The cathodoluminescence spectra of samples annealed at various temperatures (1000 – 1300 °C).

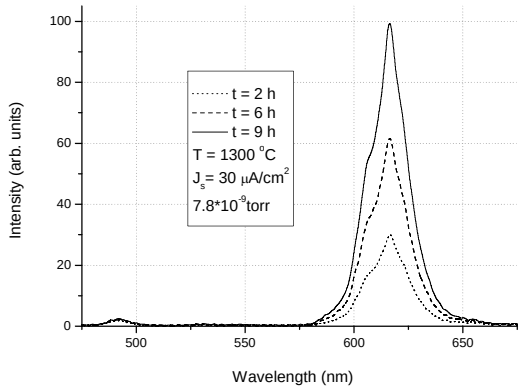

Fig. 5. The cathodoluminescence spectra of samples annealed for various times (2 – 9 hours).

It was shown that the samples annealed at the lowest temperature (T_{ann}) and annealing time (t_{ann}) had a low luminance (5–25 cd/m^2). Increase in the annealing temperature and annealing time up to maximal values results in growth of the luminance up to 300 cd/m^2 (Figs 6, 7).

The photoluminescence and cathodoluminescence mechanisms supposed to be the same ones. The cathodoluminescence of $SrTiO_3$:Pr^{3+} phosphor originates in excitation of host material $SrTiO_3$ by transfer of the electron beam energy to the Pr^{3+}-luminescence centers and subsequent radiative recombination.

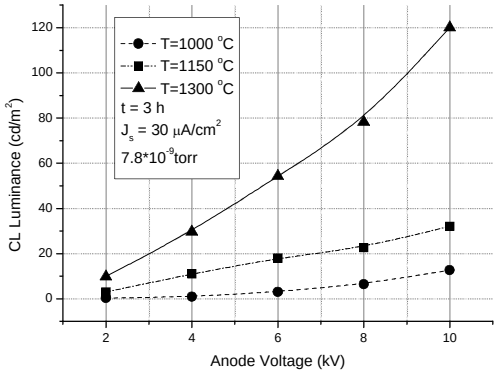

Fig. 6. Dependences of the $SrTiO_3$:Pr^{3+} cathodoluminescence intensity on the anode voltage at various annealing temperatures (1000 – 1300 °C).

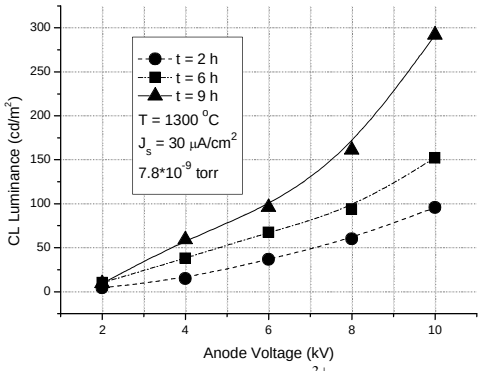

Fig. 7. Dependences of the $SrTiO_3$:Pr^{3+} cathodoluminescence intensity on the anode voltage at various annealing times (2 – 9 hours).

4. Conclusions

It was shown that the mix of compounds $SrCl_2$, Ti-(O-i-C_3H_7)$_4$ and $PrCl_3$ can be transformed to single-phase $SrTiO_3$:Pr phosphor. With increase in a sintering temperature from 1000 to 1250 °C the intensities of $SrTiO_3$ peaks were increased. At the same time, the intensities of TiO_2 and $SrCl_2$ peaks were decreased to zero at 1250 °C. With increase in the annealing temperature from 1000 to 1250 ºC the red peak (λ_{max} = 617 nm) intensity was 35 times increased. With increase in the annealing temperature and annealing time to maximal values the CL brightness increases up to 300 cd/m^2.

The experimental results show that $^1D_2 \rightarrow {}^3H_4$ transitions are more significant than $^3P_0 \rightarrow {}^3H_4$ transitions when the temperature and time of annealing are high and long, respectively. It can be explained by the change of the Pr^{3+}-O^{2-}-distance, when the shortest distance Pr^{3+}-O^{2-} is less than the critical value (0.24 nm) [3].

We have shown that phosphor $SrTiO_3$:Pr prepared by the sol-gel method can be a promising material for further researches and applications as a red-emitting phosphor for the field emission displays.

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