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Investigation of luminescent properties inherent to SrTiO₃:Pr³⁺ luminophor with Al impurity

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Abstract. The red-emitting SrTiO₃:Pr³⁺,Al luminophors that can be used for the white light emitting diodes (LEDs) were prepared using the sol-gel method. The starting materials were SrCl₂, Ti (O-i-C₃H₇)₄, Al(NO₃)₃·9H₂O and PrCl₃. The reaction between them results in a mixture of compounds that transform into single-phase SrTiO₃:Pr³⁺,Al after annealing in air. Displacement of Ti out of the SrTiO₃ lattice caused by substitution with Al and formation of individual crystalline TiO₂ phase (rutile) were observed. PL spectra show the high-intense red peak ($\lambda = 617$ nm), the same high-intense peak with the full width at half maximum (FWHM) 20 nm was found in cathodoluminescence spectra. The increase of the aluminium concentration from 0 up to 15 mol.% leads to approximately two-fold increase in the luminance. The latter increases from 180 up to 350 cd/m² at the anode voltage 10 kV and current density 30 μ A/cm².

Keywords: luminophor, SrTiO₃:Pr³⁺,Al, photoluminescence, cathodoluminescence, LED.

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1. Introduction

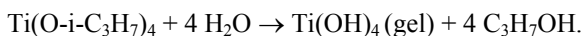
In recent years, white light emitting diodes (LED) have been considered as a next generation of solid-state light sources and used in many applications related with their advantages, namely, their long operation lifetime and low energy consumption [1–2]. A new method to obtain white light is using near UV InGaN-based LEDs covered by RGB-tricolor luminophors (red, green and blue). Commercial red-emitting luminophor for white LEDs is Y₂O₂S:Eu³⁺ that has lower efficiency, shorter operation lifetime under UV irradiation as compared with blue and green luminophors. Moreover, it has instability caused by appearance of sulfide gas [3]. Further, the emission color of Y₂O₂S:Eu³⁺ is inadequate. One of important tasks in LED technologies is search of luminophors with high performances. Therefore, many efforts are devoted to develop new luminophors for white LEDs. Especially, red emitting luminophors with a high luminance and good color purity are required. Based on this background, the red emitting luminophors for LEDs are

currently under investigation. For example, red-emitting SrTiO₃:Pr³⁺ luminophor has been investigated and characterized [4–7]. Essential enhancement of the emission intensity of SrTiO₃:Pr³⁺ can be obtained by Al addition [8]. Impurity of 23 mol.% Al intensifies emission by more than 200 times. As shown earlier, the SrTiO₃:Pr³⁺ luminophor demonstrates high luminescent characteristics and can be rather promising material for LEDs. So far, SrTiO₃:Pr³⁺ luminophors have been synthesized by mixing SrCO₃, TiO₂, PrCl₃ and Al(OH)₃ with the subsequent sintering and crushing the prepared powder.

In this work, to synthesize SrTiO₃:Pr³⁺,Al we used the sol-gel method with SrCl₃, Ti (O-i-C₃H₇)₄, PrCl₃ and Al(NO₃)₃·9H₂O as starting materials. By using this method, we managed to get more complete reactions between the starting materials and to obtain more uniform distribution of the doped materials in the host lattice. In this paper, we report about the influence of Al-addition to luminophor SrTiO₃:Pr³⁺ on its structural and luminescent properties.

2. Synthesis of samples

The studied $\text{SrTiO}_3:\text{Pr}^{3+},\text{Al}$ luminophors were synthesized using the sol-gel method similar to that in [9] (Fig. 1). Starting materials were strontium chloride SrCl_2 , praseodymium chloride PrCl_3 , aluminium nitrate 9-hydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and titanium tetra-*i*-propoxide $\text{Ti}(\text{O}-i-\text{C}_3\text{H}_7)_4$. Synthesis was carried out in nitrogen atmosphere. A ratio of starting materials was $\text{Sr}/\text{Ti} = 1$ and concentration of Pr^{3+} was fixed at 1 mol.%. The aluminium concentration was varied from 0 to 15 mol.%. The starting materials were dissolved in an ethanol 96% (with water content of 4%) and stirred for 3 hours. Dissolution was not observed when SrCl_2 and PrCl_3 were mixed with the dehydrated ethanol as well as with dehydrated methanol. Complete dissolution was observed when SrCl_2 and PrCl_3 were mixed with ethanol containing 4% H_2O . This suggests that water plays the primary role in the process of SrCl_2 and PrCl_3 dissolution despite its small amount. Alcohol is necessary for uniform distribution of small amounts of water throughout the reactionary volume. Besides, water apparently acts as the reagent that interacts with the titanium tetra-*i*-propoxide titanium $\text{Ti}(\text{O}-i-\text{C}_3\text{H}_7)_4$, resulting in formation of titanium hydroxide $\text{Ti}(\text{OH})_4$. This is shown in transformation of transparent colorless solution containing SrCl_2 and PrCl_3 into the white gel-like substance. Apparently, it is caused by the reaction:



Then solvent was evaporated (under the further stirring) until the 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 in air under the optimal temperature regime and time of annealing, 1300 °C and 3 hours, respectively [9]. Finally, the obtained material was crushed into powder.

3. Results and discussion

3.1. Morphology and XRD-analysis

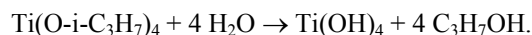
To measure the size of particles, the alcohol suspension of $\text{SrTiO}_3:\text{Pr}^{3+},\text{Al}$ powder was dispersed on a glass substrate. The surface morphology was investigated with raster microscope REM-102E by using the method secondary-emission of electrons. Morphology of $\text{SrTiO}_3:\text{Pr}^{3+},\text{Al}$ particles on glass surface is presented in Fig. 2. In this figure, the arrow shows a single grain of the most probable size. The crystal sizes mainly varied within the range 1 to 5 μm and a small amount of crystals and their conglomerates have sizes up to 10 μm .

The structural analysis of the prepared luminophors was carried out using the X-ray diffractometer DRON-3M with CuK_α radiation ($\lambda = 1.542 \text{ \AA}$). The samples containing various concentrations of aluminium were annealed at 1300 °C for 5 hours and investigated. Fig. 3 shows that Pr- and Al-containing starting materials do not form individual crystalline compounds

in the final product, but incorporate into the crystal lattice of SrTiO_3 and replace Sr and Ti, respectively. This substitution occurs because of the proximity values of ionic radii of Pr and Sr, Al and Ti, respectively, which is consistent with the results reported in [4, 6]. Thus, Al replaces Ti in the lattice SrTiO_3 , which leads to deterioration of the crystallinity. Moreover, Ti is displaced from the lattice SrTiO_3 and forms the individual crystalline phase of TiO_2 -rutile.

We assume that formation of SrTiO_3 can be represented by the following processes:

1. Gel formation:



2. Annealing:

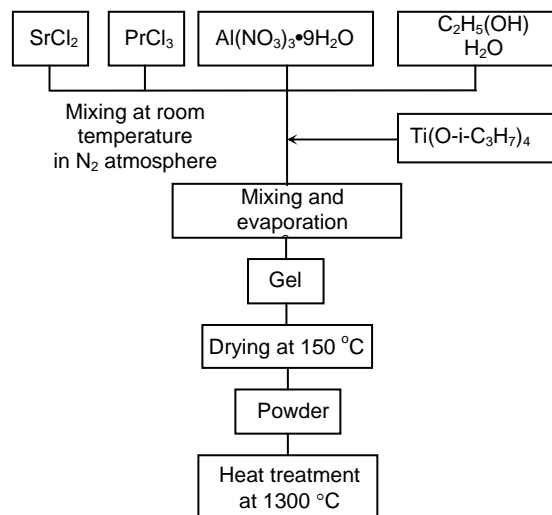
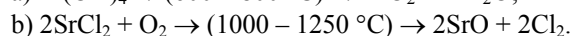


Fig. 1. Preparation of $\text{SrTiO}_3:\text{Pr}^{3+},\text{Al}$ luminophor.

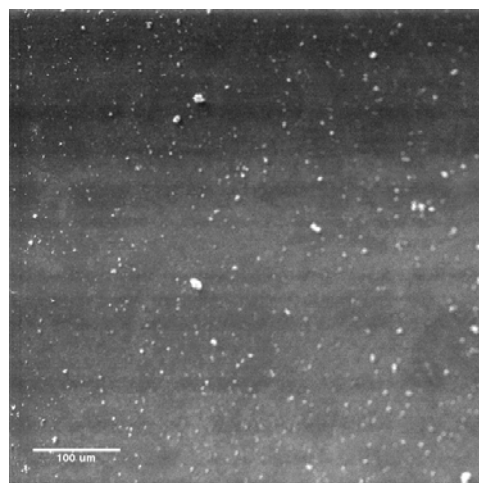


Fig. 2. Microrelief of a glass surface with crystals of $\text{SrTiO}_3:\text{Pr}^{3+},\text{Al}$ luminophor.

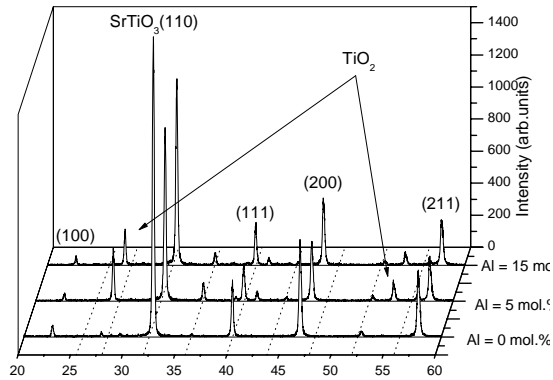
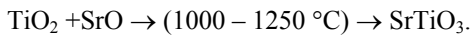


Fig. 3. XRD spectra of the samples with various Al concentrations.

3. Structuring:



Thus, decomposition of titanium hydroxide and formation of strontium oxide occur at different temperatures, so they could not take place simultaneously.

3.2. Photoluminescence spectra

Photoluminescence (PL) spectra were measured within the wavelength range 450 to 750 nm under nitrogen laser (wavelength 337 nm, pulse duration 8 ns) excitation at the width of measuring strobe of 75 μs . Fig. 4 shows the typical PL spectrum of the sample $\text{SrTiO}_3:\text{Pr}^{3+}$ with no additional Al annealed at 1300 $^\circ\text{C}$ for 5 h. The PL spectrum has three peaks, the highest intensity is observed for the peak at $\lambda = 617$ nm. Blue emission with its maximum at $\lambda_{\text{max}1} = 488$ nm corresponds to the intra-4f transition from the excited state $^3\text{P}_0$ to the ground state $^3\text{H}_4$ of Pr^{3+} , green emission with the maximum at $\lambda_{\text{max}2} = 530$ nm corresponds to the intra-4f transition from the excited state $^3\text{P}_1$ to the state $^3\text{H}_5$, and red emission with the maximum at $\lambda_{\text{max}3} = 617$ nm corresponds to the intra-4f transition from the excited state $^1\text{D}_2$ to the ground state $^3\text{H}_4$ [8, 10, 11].

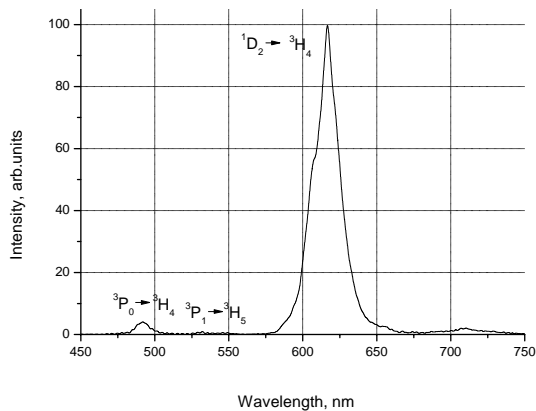


Fig. 4. PL spectrum of the sample $\text{SrTiO}_3:\text{Pr}^{3+}$.

The used increase in aluminium concentration from 0 up to 15 mol.% results in a slight growth of the intensity of the main peak $\lambda_{\text{max}3} = 617$ nm (Fig. 5). Thus, when the aluminum concentration is changed from 0 up to 5 mol.%, an increase in the photoluminescence intensity by 20% is observed. However, the further increase in concentration from 5 to 15 mol.% leads to insignificant decrease in the peak intensity $\lambda_{\text{max}3}$ (Fig. 5, insert).

3.3. Cathodoluminescence spectra

Cathodoluminescence (CL) was also investigated under the electron beam excitation (current density 30 $\mu\text{A}/\text{cm}^2$, anode voltage 2 to 10 kV). The same samples of $\text{SrTiO}_3:\text{Pr}^{3+},\text{Al}$ were investigated. The typical CL spectrum of the sample $\text{SrTiO}_3:\text{Pr}^{3+},\text{Al}$ and its comparison with PL spectra are shown in Fig. 6. It is appeared that the shape of these spectra is completely identical, and no shifts of the main peaks or redistribution of their intensities is not observed. Both, PL and CL spectra have the same intensity of red peak with 20-nm FWHM.

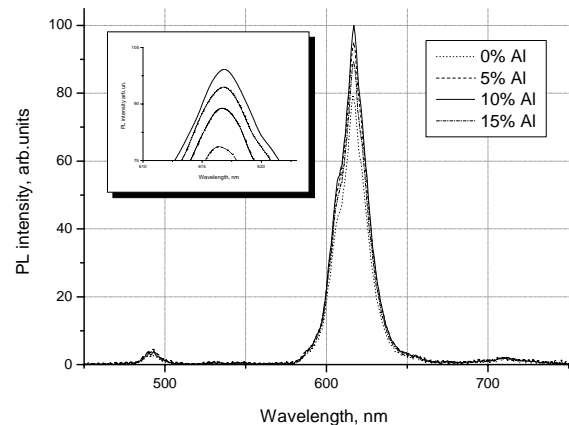


Fig. 5. PL spectra of the samples with various Al concentrations.

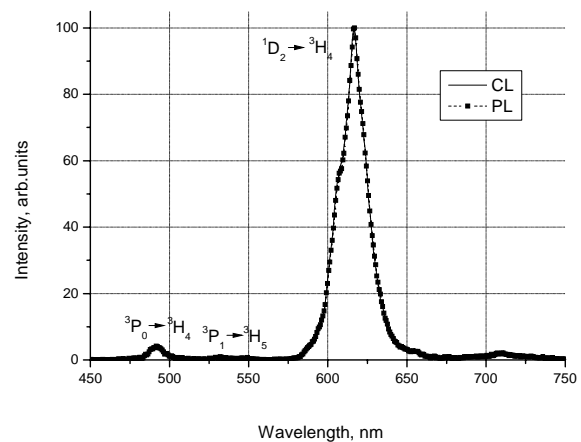


Fig. 6. CL and PL spectra of luminophor $\text{SrTiO}_3:\text{Pr}^{3+},\text{Al}$ (Al = 15 mol.%), the former being measured at $V_a = 2$ kV, $J_s = 30 \mu\text{A}/\text{cm}^2$, $P = 7.8 \times 10^{-9}$ Torr, added together for comparison.

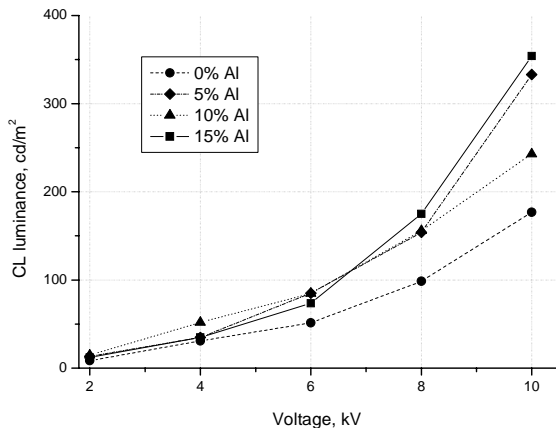


Fig. 7. Dependence of CL luminance on the anode voltage for various Al concentrations. $J_s = 30 \mu\text{A}/\text{cm}^2$; $P = 7.8 \times 10^{-9}$ Torr.

The CL intensity measurements with increasing the anode voltage show that the samples with no aluminium addition have the luminance $177 \text{ cd}/\text{m}^2$. The increase in aluminium concentration from 0 up to 5 mol.% leads to the 2-fold increase in luminance, and the latter reaches $333 \text{ cd}/\text{m}^2$ at the anode voltage close to 10 kV (Fig. 7). A further increase in aluminum concentration from 5 to 15 mol.% does not lead to any significant enhance in luminance as it was reported in [8]. The maximum CL luminance is observed at the concentration of aluminium 15 mol.%, and it reaches $354 \text{ cd}/\text{m}^2$.

Thus, for the samples $\text{SrTiO}_3:\text{Pr}^{3+}$ the high luminance $177 \text{ cd}/\text{m}^2$ was obtained. The Al-addition of 15 mol.% leads to increase in luminance by 2 times, and it reaches $354 \text{ cd}/\text{m}^2$. These results are not consistent with the data reported in the paper [8]. It was reported earlier that initially $\text{SrTiO}_3:\text{Pr}^{3+}$ has an extreme low luminance of the luminescence and only aluminium addition can increase it by more than 200 times. Therefore, such a discrepancy between the results requires further researches.

4. Conclusions

It has been shown that mixture of compounds SrCl_2 , $\text{Ti}(\text{O}-i-\text{C}_3\text{H}_7)_4$, PrCl_3 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ can be transformed to $\text{SrTiO}_3:\text{Pr}^{3+},\text{Al}$ under definite technological conditions. Herewith, displacement of Ti out of SrTiO_3 lattice due to substitution with Al and formation of the individual crystalline TiO_2 -rutile phase take place.

The increase in aluminium concentration from 0 up to 15 mol.% results in a slight growth of the intensity of the main peak $\lambda_{\text{max}} = 617 \text{ nm}$. Simultaneously, the increase in aluminium concentration from 0 up to 15 mol.% leads to the 2-fold increase in luminance, and the latter reaches $354 \text{ cd}/\text{m}^2$ at the anode voltage value 10 kV and current density $30 \mu\text{A}/\text{cm}^2$ (Fig. 7).

A further increase in aluminum concentration from 5 to 15 mol.% does not lead to significant enhance in luminance, as it was reported in [8]. The maximum CL luminance is observed at the concentration of aluminium 15 mol.%, and its value reaches $354 \text{ cd}/\text{m}^2$.

It has been found a significant difference between the PL and CL data reported in this paper as compared with the data reported earlier. This discrepancy between the results requires further researches.

Thus, it has been shown that luminophor $\text{SrTiO}_3:\text{Pr}^{3+},\text{Al}$ prepared using the sol-gel method is promising material for further researches and applications as the red-emitting one for white light emitting diodes.

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