Investigation of luminescent properties inherent to SrTiO$_3$:Pr$^{3+}$ luminophor with Al impurity

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Abstract. The red-emitting SrTiO$_3$:Pr$^{3+}$,Al luminophors that can be used for the white light emitting diodes (LEDs) were prepared using the sol-gel method. The starting materials were SrCl$_2$, Ti (O – i – C$_3$H$_7$)$_4$, Al(NO$_3$)$_3$·9H$_2$O and PrCl$_3$. The reaction between them results in a mixture of compounds that transform into single-phase SrTiO$_3$:Pr$^{3+}$,Al after annealing in air. Displacement of Ti out of the SrTiO$_3$ lattice caused by substitution with Al and formation of individual crystalline TiO$_2$ 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/m$^2$ at the anode voltage 10 kV and current density 30 $\mu$A/cm$^2$.

Keywords: luminophor, SrTiO$_3$:Pr$^{3+}$,Al, photoluminescence, cathodoluminescence, LED.

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 Y$_2$O$_3$:Eu$^{3+}$ 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 Y$_2$O$_3$:Eu$^{3+}$ 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 lumiance and good color purity are required. Based on this background, the red emitting luminophors for LEDs are currently under investigation. For example, red-emitting SrTiO$_3$:Pr$^{3+}$ luminophor has been investigated and characterized [4–7]. Essential enhancement of the emission intensity of SrTiO$_3$:Pr$^{3+}$ can be obtained by Al addition [8]. Impurity of 23 mol.% Al intensifies emission by more than 200 times. As shown earlier, the SrTiO$_3$:Pr$^{3+}$ luminophor demonstrates high luminescent characteristics and can be rather promising material for LEDs. So far, SrTiO$_3$:Pr$^{3+}$ luminophors have been synthesized by mixing SrCO$_3$, TiO$_2$, PrCl$_3$ and Al(OH)$_3$ with the subsequent sintering and crushing the prepared powder.

In this work, to synthesize SrTiO$_3$:Pr$^{3+}$,Al we used the sol-gel method with SrCl$_2$, Ti (O – i – C$_3$H$_7$)$_4$, PrCl$_3$ and Al(NO$_3$)$_3$·9H$_2$O 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 SrTiO$_3$:Pr$^{3+}$ on its structural and luminescent properties.
2. Synthesis of samples

The studied SrTiO$_3$:Pr$^{3+}$,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 Al(NO$_3$)$_3$·9H$_2$O and titanium tetra-i-propoxide Ti(O-i-C$_3$H$_7$)$_4$. Synthesis was carried out in nitrogen atmosphere. A ratio of starting materials was Sr/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$_2$O. 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 Ti(O-i-C$_3$H$_7$)$_4$, resulting in formation of titanium hydroxide Ti(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:

$$\text{Ti(O-i-C}_3\text{H}_7\text{)}_4 + 4 \text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4(\text{gel}) + 4 \text{C}_2\text{H}_5\text{OH}.$$ 

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 SrTiO$_3$:Pr$^{3+}$,Al powder was dispersed on a glass substrate. The surface morphology was investigated with a scanning microscope REM-102E by using the method secondary-emission of electrons. Morphology of SrTiO$_3$:Pr$^{3+}$,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$_{\alpha}$ radiation ($\lambda = 1.542$ Å). 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:
$$\text{Ti(O-i-C}_3\text{H}_7\text{)}_4 + 4 \text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4(\text{gel}) + 4 \text{C}_2\text{H}_5\text{OH}.$$ 
2. Annealing:
   a) Ti(OH)$_4$ → (600 – 800 °C) → TiO$_2$ + 2 H$_2$O;
   b) 2SrCl$_2$ + O$_2$ → (1000 – 1250 °C) → 2SrO + 2Cl$_2$.

![Fig. 1. Preparation of SrTiO$_3$:Pr$^{3+}$,Al luminophor.](image)

![Fig. 2. Microrelief of a glass surface with crystals of SrTiO$_3$:Pr$^{3+}$,Al luminophor.](image)
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 aluminium 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 $\mu$A/cm$^2$, anode voltage 2 to 10 kV). The same samples of SrTiO$_2$:Pr$^{3+}$,Al were investigated. The typical CL spectrum of the sample SrTiO$_2$:Pr$^{3+}$,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.
The CL intensity measurements with increasing the anode voltage show that the samples with no aluminium addition have the luminance 177 cd/m². The increase in aluminium concentration from 0 to 5 mol.% leads to 2-fold increase in luminance, and the latter reaches 333 cd/m² at the anode voltage close to 10 kV (Fig. 7). A further increase in aluminium 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 cd/m². Thus, for the samples SrTiO₃:Pr³⁺, the high luminance 177 cd/m² was obtained. The Al-addition of 15 mol.% leads to increase in luminance by 2 times, and it reaches 354 cd/m². These results are not consistent with the data reported in the paper [8]. It was reported earlier that initially SrTiO₃:Pr³⁺ has an extreme low 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 SrCl₂, Ti(O – i – C₂H₅)₄, PrCl₃ and Al(NO₃)₃·9H₂O can be transformed to SrTiO₃:Pr³⁺,Al under definite technological conditions. Herewith, displacement of Ti out of SrTiO₃ lattice due to substitution with Al and formation of the individual crystalline TiO₂-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 $\lambda_{\text{max}} = 617$ 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 cd/m² at the anode voltage value 10 kV and current density 30 μA/cm² (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 aluminum 15 mol.%, and its value reaches 354 cd/m².

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 SrTiO₃:Pr³⁺,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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**References**