SrAl$_2$O$_4$:Eu^{2+} (1%) luminescence under UV, VUV and electron beam excitation

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ABSTRACT

This paper reports the luminescence properties of nanosized SrAl$_2$O$_4$:Eu^{2+} (1%) phosphors. The samples were prepared by combustion method at 600 °C, followed by annealing of the resultant combustion ash at 1000 °C in a reductive (Ar + H$_2$) atmosphere. X-ray diffraction (XRD), photo luminescence (PL) and cathodoluminescence (CL) analysis and thermal stimulated luminescence (TSL) method were applied to characterize the phosphor. For the first time a peak at 375 nm was observed in CL spectra of SrAl$_2$O$_4$:Eu^{2+} (1%) nanophosphors. Luminescence excitation spectra analysis have shown that this peak is related to crystal defects. Also in TSL curve one strong peak was observed in the region above room temperature (T = 325 K), which is attributed to lattice defects, namely oxygen vacancies. A green LED was fabricated by the combination of the SrAl$_2$O$_4$:Eu^{2+} (1%) nanosized phosphor and a 365 nm UV InGaN chip.

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1. Introduction

Due to high quantum efficiency in the visible spectral region [1], good stability, color purity, excellent physical and chemical properties, SrAl$_2$O$_4$:Eu^{2+} alkaline earth aluminates are very useful in preparation of pc LEDs [2,3]. In addition, due to their excellent luminescence properties, they also have potential applications in fluorescent lamps, plasma display panels and also can be utilized as persistent luminescence materials [4–6].

Usually two emission bands at 445 and 520 nm are observed in SrAl$_2$O$_4$:Eu^{2+}. At room temperature the blue band is quenched and only green band is observed. The origin of these bands has been the subject of discussions for many years. Poort et al. [7] explained these two emission bands with the preferential orientation of d orbitals of Eu^{2+} ion on Sr sites. Clabau et al. [8] explained blue emission band with charge transfer from the ground level of the 4f^7 configuration of Eu^{2+} to the valence band. More recently, Botterman et al. [9] reported a detailed investigation of the origin of both emission bands in SrAl$_2$O$_4$:Eu. In spite of the similarity in oxygen coordination, differences in bond lengths to the oxygen ligands for the two sites and in coordination number were used to explain the difference in emission and excitation spectra. Nowadays it is generally accepted that these two bands are attributed to emission from Eu^{2+} ions placed in the two different lattice sites (Sr1, Sr 2) in crystal structure of SrAl$_2$O$_4$.

In this paper, Eu^{2+} doped SrAl$_2$O$_4$ nanophosphors were synthesized by energy effective, fast and low-cost combustion method. Homogeneous, high crystallinity and good morphology samples were obtained as a result of the synthesis. In this paper, a photoluminescence (PL) analysis was carried out for Eu^{2+} doped SrAl$_2$O$_4$ aluminates under UV-VUV excitation. The results of the photoluminescence (PL) and cathodoluminescence (CL) of SrAl$_2$O$_4$:Eu^{2+} (1%) nanophosphors were compared and discussed. Experimental results prove that the peak at 375 nm in CL spectrum is related to crystal defects. TSL glow curve peaks at 220 and 325 K are explained by existence of the crystal structure defects, namely oxygen vacancies.

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2. Experimental section

For the synthesis, stoichiometric amounts of $Sr(NO_3)_2$ (99,99%), $Al(NO_3)_3 \cdot 9H_2O$ (99,99%), $Eu(NO_3)_3 \cdot 6H_2O$ (99,99%), $CO(NH_2)_2$ (99,3%) and H_3BO_3 (99,9%) were dissolved together in 20 ml of deionized water for obtaining a transparent solution. Small amount of boric acid was used as flux and urea as fuel. The components were mixed together and the solution was stirred using a magnetic bar at 70 °C for 2 h [10,11]. Every 15 min the temperature of the solution was raised by 10 °C up to 130 °C. A white viscous gel was obtained. The gel was placed in a preheated muffle furnace at 600 °C. At this temperature the solution evaporated, generating large amounts of gases, e.g. oxides of carbon and nitrogen. The combustion process lasted for about 5–10 min and white ash was obtained. The size of particles is in the range 50–70 nm [10] (Fig. 1).

At the next step, the obtained white ash was annealed at 1000° C for 1 h under reductive (Ar, 20% H_2) atmosphere for the reduction of Eu^{3+} ions to Eu^{2+}.

X-ray diffraction patterns were recorded using a Bruker 5000 diffractometer in standard (θ-2θ) geometry using Cu Kα radiation.

Elemental analysis was performed on a Peltier cooled dry EDS system (Thermo Scientific Noran System 7, energy resolution of 125 eV).

Photoluminescence (PL) properties were investigated by measuring the excitation and emission spectrum with a FS920 fluorescence spectrometer (Edinburgh Instruments) equipped with a Hamamatsu R928P red-sensitive photomultiplier (wavelength range from 250 to 850 nm) between 100 and 400 K temperature.

The measurements of luminescence and luminescence excitation spectra were also performed using synchrotron radiation in UV - VUV energy regions at the branch-line FINEST (energy region 5–22 eV) at MAX-lab, Lund. The excitation spectra were corrected using sodium salicylate. The luminescence spectra were measured with ARC Spectra Pro 300i monochromator equipped with Hamamatsu H6240-01 photon counting head in the temperature range 5–300 K.

The measurements of cathodoluminescence spectra and TSL curves were performed under irradiation with electrons (5 keV, 0.4 μA, spot ≈ 1 mm^2). TSL was measured with a linear heating rate

0.167 K/s. All measurements were carried out in a liquid helium vacuum cryostat (5–400 K temperature range, 2*10^{-7} Torr vacuum) equipped with Lake Shore 331 Temperature Controller. The luminescence was detected using the UV-VIS-NIR (200–1700 nm) monochromator ARC SpectraPro-2300i equipped with Hamamatsu photon counting head H6240.

Green light was obtained by combination of $SrAl_2O_4:Eu^{2+}$ (1%) phosphor silicone epoxy mixture with an UV LED (365 nm) chip with a power of 3 W. Light parameters were measured by using an Everfine PMS-80 integrating sphere at the driving currents 20 mA and 350 mA for comparison of stability of color coordinates of light in different currents. The spectra of the UV LED with and without phosphor coating were recorded on the Horiba Jobin Yvon 1250M monochromator coupled with Andor Newton CCD detector.

3. Results and discussion

3.1. X-ray diffraction analysis

X-ray diffraction (XRD) analysis was used to identify the crystal structure and phase purity of the undoped and Eu doped $SrAl_2O_4$ phosphors. It is clear from the XRD analysis that the main peaks in the $SrAl_2O_4:Eu^{2+}$ (1%) sample shows good consistence to the data from the standard powder diffraction file (JCPDS-01-024-11-87) of $SrAl_2O_4$. No obvious shift in the diffraction peaks is observed for $SrAl_2O_4:Eu^{2+}$ phosphor, indicating that adding of a small amount of doping Eu^{2+} ions has no strong influence on the structure of the host due to the similar ionic radius of Sr (1,21 Å) and Eu (1,20 Å). However, one of the intensive peaks (32°) does not coincide with the monoclinic $SrAl_2O_4$ ICDD data and corresponds to cubic phase $Sr_3Al_2O_6$ (a = b = c = 15,844 Å). The intensity of this peak (32°) is higher in the undoped $SrAl_2O_4$ crystal structure than in Eu^{2+} doped $SrAl_2O_4$ (Fig. 2).

3.2. Luminescence properties of $SrAl_2O_4:Eu^{2+}$ (1%)

Photoluminescence properties were investigated at 100–400 K temperature range to determine if synthesized phosphors are suitable for use in fabrication of phosphor-converted pc W- LEDs. For instance, measurements of luminescence spectra at high temperatures (up to 400 K) is required to check whether the synthesized nanophosphors are stable at high temperatures for the application in LEDs which are operating at temperatures exceeding the room temperature. As shown in Fig. 3, in the 100–400 K temperature range, there was not observed any considerable shift of

Fig. 1. $SrAl_2O_4:Eu^{2+}$ (1%) ash synthesized by combustion method.

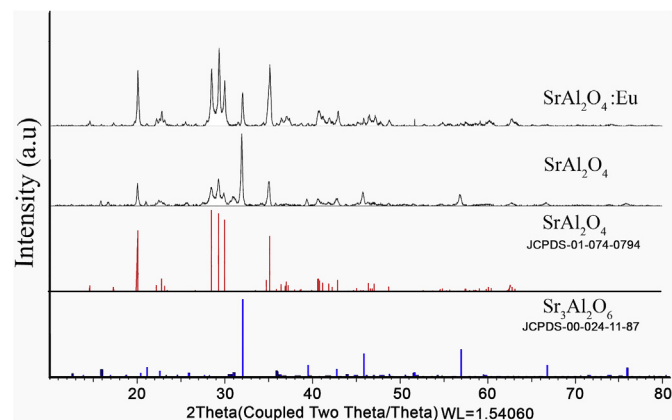**Fig. 2.** XRD patterns of $SrAl_2O_4$ and $SrAl_2O_4:Eu^{2+}$ (1%) phosphors and PDF Cards No. JCPDS-01-074-0794, JCPDS-01-024-11-87.
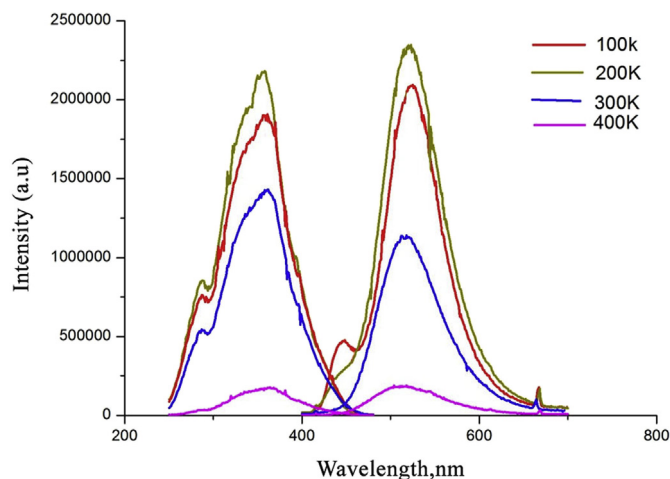
Fig. 3. The excitation (λ_{em} = 517 nm) and emission (λ_{ex} = 360 nm) spectra of SrAl$_2$O$_4$: Eu^{2+} (1%).

Fig. 4. Cathodoluminescence spectra of SrAl$_2$O$_4$: Eu^{2+}(1%) nanophosphors at different temperatures.

peak maximum (517 nm) in the emission spectra of SrAl$_2$O$_4$:Eu^{2+} crystal which confirmed color stability of this phosphor at high temperatures (Fig. 3).

In Fig. 3, the temperature dependence of both blue and green emission bands intensity under UV excitation (360 nm) is shown. By heating up the sample from 100 to 400 K a gradual decrease of the overall emission intensity is observed. This behavior is expected due to the loss of energy by means of nonradiative transitions at higher temperatures. The intensity of the blue emission band decreases quickly upon increasing temperature and vanishes at temperatures around 275 K, leaving only the green emission band at higher temperatures. Strong temperature quenching of luminescence is a serious obstacle for application of strontium aluminate in LEDs. It is worth nothing that for the studied samples the thermal quenching starts at lower temperatures than for SrAl$_2$O$_4$:Eu^{2+} (0.1%) studied in Ref. [12] with T (1/2) = 440 K. It indicates lower activation energy of the quenching process that may be connected with three different factors (or their combination), namely (i) presence of the defect states in the vicinity of the bottom of conduction band (ii) higher concentration of Eu^{2+} in our samples and (iii) small dimensions of our samples. Additional studies are needed to clarify, which factor is the most essential.

CL spectra were measured under irradiation of the sample with high energy electrons that allowed to obtain the most complete data on the emission bands in SrAl$_2$O$_4$: Eu^{2+} (Fig. 4). Beside the well-known peaks at 445 and 520 nm related to Eu^{2+} additional peaks were observed at 375, 610, 650 and 700 nm. The latter three peaks are ascribed to traces of Eu^{3+} in the sample. For the first time an intense peak at 375 nm in the CL spectra was observed in SrAl$_2$O$_4$:Eu^{2+}. The intensity of this peak is comparable with the main peaks at 445 and 520 nm at low temperatures. Its intensity decreases with the rise of temperature similarly to that of the blue emission band at 445 nm. For determination of the origin of this peak, the results of CL were supplemented with the results obtained under excitation with synchrotron radiation in the VUV energy region for undoped and Eu doped SrAl$_2$O$_4$ crystals. In the PL spectra, two peaks (375 and 250 nm) were observed for both samples (Fig. 5). These results indicate that these two peaks cannot be attributed to emission from Eu^{2+} ions. It is worth noting that similar emission peaks at 250 and 360 nm were observed by Kamada in undoped SrAl$_2$O$_4$ and in SrAl$_2$O$_4$ co-doped with Eu and Dy material and attributed the host material [13]. The origin of the peaks at 250 and 375 nm was determined by analysis of excitation spectra of these emission bands at low temperature (T = 13 K)
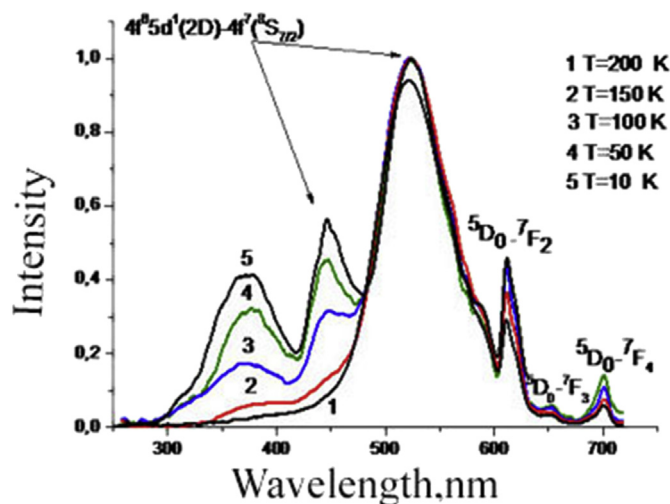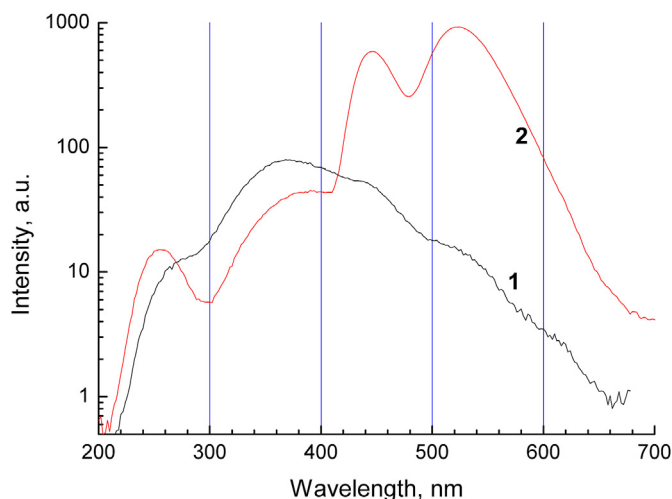

Fig. 5. Photoluminescence spectra of the undoped (1) and Eu doped (2) SrAl$_2$O$_4$, under synchrotron radiation excitation, E$_{ex}$ = 8 eV, T = 15 K.

(Fig. 6). The excitation spectrum of the band at 250 nm demonstrates an onset at 6.7—6.8 eV, which corresponds to the fundamental absorption edge. The emission band at 250 nm cannot be excited in the transparency region of the crystal and therefore can be attributed to the intrinsic emission of self-trapped excitons. On the contrary, the luminescence band at 375 nm can be excited in the transparency region of crystal where the excitation band at 6.0 eV is clearly observed. Therefore, the observed emission band at 375—380 nm can be related to the defects of crystal structure. (Figs. 5 and 6), It is worth noting that according to XRD data there is an additional phase of Sr$_3$Al$_2$O$_6$ in the studied samples. The broad bands at 405, 435, 538 and 625 nm are inherent for the emission of Sr$_3$Al$_2$O$_6$:Eu [12]. Therefore, the emission band at 375 nm cannot be ascribed to Sr$_3$Al$_2$O$_6$.

3.3. Thermally stimulated luminescence

Thermally stimulated luminescence (TSL) is a potentially useful research tool for trap-level analysis. The presence of co-dopants, vacant lattice sites or other structural defects may form
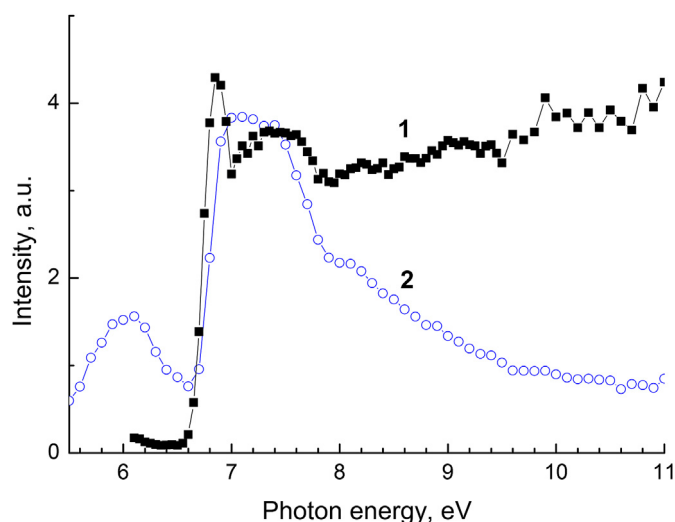
Fig. 6. PL excitation spectra of the SrAl$_2$O$_4$:Eu^{2+} (1%) at λ_{em} = 255 nm (1) and 380 nm (2), T = 13 K.

unoccupied energy levels (traps) in the bandgap that have the capability of detaining the charge carries before their recombination with the luminescent centers, thereby delaying the luminescence. These traps are denoted as hole or electron traps. If host defects can play the role of traps then they could be useful for increasing the duration of SrAl$_2$O$_4$:Eu^{2+} afterglow even without co-dopant.

The SrAl$_2$O$_4$:Eu (1%) nanophosphor was irradiated by 5 keV electrons at 20 K. With the increase of temperature an emission from the luminescent center occurs at temperatures, which correspond to the thermal release of traps. As a result, three intensive glow peaks are observed at 190, 220 and 325 K accompanied by less intensive low-temperature peaks at 59 and 75 K. The presence of five pronounced glow peaks (Fig. 7) indicates the presence of five types of trapping centers with different trap depths in the host lattice [14–16]. In this work co-dopant (R^{3+}) was not used, so it can be assumed that the presence of defects in the host, create a series of discrete levels which play the role of traps that capture the charge carriers before their recombination with the luminescent centers [16–19]. The depth of the traps can be estimated using the
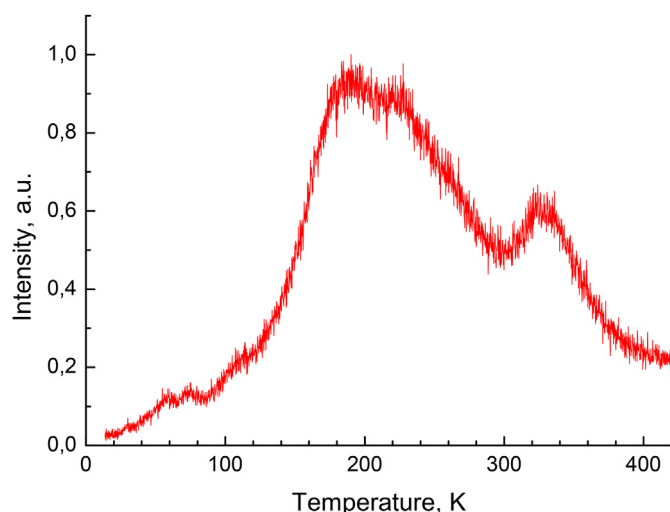
simple formula E$_T$ = T$_m$/500 [20], where E$_T$ is the activation energy of the trap and T$_m$ is the temperature of the maximum of the TSL peak. The values of activation energies of observed TSL peaks were estimated as 0.12, 0.15, 0.38, 0.44 and 0.65 eV.

The well- known defects in SrAl$_2$O$_4$ are V$_O$ or V$_{Sr}$ [21,22]. Based on electronic band structure calculations, V$_{Sr}$ is located at 0.15 eV above the valence band top and the V$_O$ level is at 0.60 eV below the conduction band bottom [8]. According to more recent calculations there are a set of traps connected with V$_O$ at 0.13, 0.46 and 0.64 eV below conduction band and 1.72 eV above the valence band [23]. The hole traps connected with V$_{Sr}$ are shallow traps located at 0.008 and 0.062 eV above the valence band while those of V$_{Al}$ − at 0.29, 0.5 and 0.65 eV above the valence band. Defects connected with V$_{Sr}$ and Vo can be created due to the evaporation of SrO during the combustion reaction. Cation vacancies also exist in the materials as a result of charge compensation when the Eu^{3+} ion replaces the Sr^{2+} host cation. The presence of Eu^{3+} in synthesized powders is confirmed by CL data (Fig. 4) where the sharp peaks at 610, 650 and 700 nm are attributed to $^5D_0$ − $^7F_{2,3,4}$ transitions in Eu^{3+} (Fig. 7).

In the TSL spectrum, only one strong peak in the region above room temperature (325 K) was observed, indicating a long after-glow of this crystal. A trap depth of around 0.6−0.7 eV is often stated as ideal to achieve efficient persistent luminescence at room temperature [24]. The calculated activation energy of the glow peak at 325 K is 0.65 eV. The value corresponds to that of V$_O$ or V$_{Al}$. We can conclude that this peak is caused by electron thermal release from the traps formed by the oxygen vacancies because other energy levels calculated for the V$_O$ defect at 0.13 and 0.46 eV also correspond to the activation energies of the observed TSL peaks at 59 K and 220 K.

3.4. Light parameters of the obtained phosphor converted pc-LED

Nanophosphors play an important role in the manufacture of pc-LEDs. Unlike microphosphors, nanoparticles reduce internal scattering inside the material. This property is very useful for
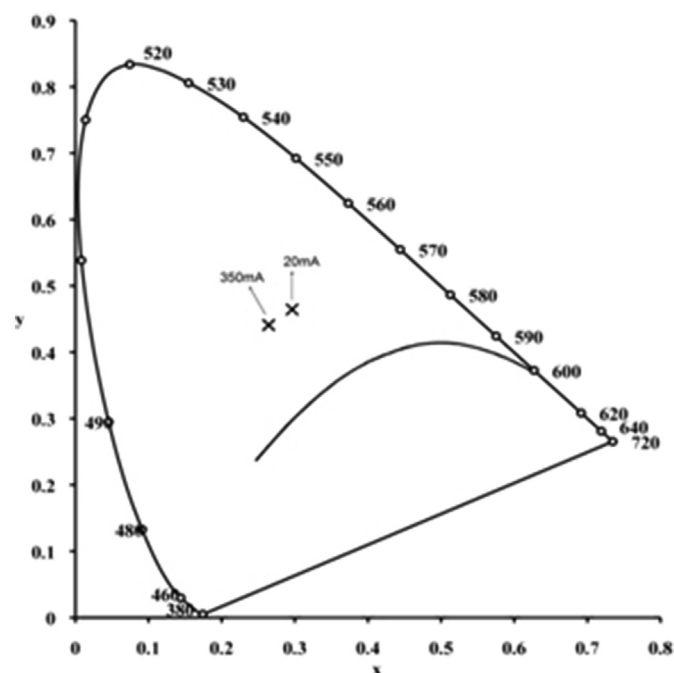

Fig. 7. TSL glow curve of SrAl$_2$O$_4$:Eu^{2+} registered at 520 nm.

Fig. 8. The color coordinates of pc-LEDs based on SrAl$_2$O$_4$:Eu (1%) under I$_f$ = 20, 350 mA in the CIE chromaticity diagram.

eliminating losses due to the scattering of the emitted light back into the primary semiconductor light crystal, which prevents chip heating.

In this paper, the light parameters of the manufactured pc- LED were measured at two different currents (20 mA, 350 mA). For fabrication of green pc- LED, the synthesized $SrAl_2O_4$:Eu^{2+} (1%) nanophosphor and silica gel mixture was coated with a thin layer on the UV LED (365 nm) chip. The nanophosphor is very well excited by 365 nm and corresponds to the green region in CIE chromaticity diagram with the peaks of 550 nm at 20 mA and 535 nm at 350 mA (Fig. 8).

Fig. 8 shows the dependence of the color coordinate of the fabricated green LED on different forward - bias currents (IF = 20, 350 mA) plotted in CIE 1931 chromaticity diagram. This diagram confirm that obtained pc-LED is in the green region and color coordinates are x = 0.288 and y = 0.47 at 20 mA. It is observed that the color coordinates of the fabricated pc-LED shifts slightly at different currents which reaffirm that this is stable ideal green emitting phosphor for using in fabrication of white LEDs.

4. Conclusion

Homogeneous, high crystallinity, nano-sized $SrAl_2O_4$:Eu (1%) samples with good morphology were synthesized by energy effective, low cost combustion method in short time.

The UV excited $SrAl_2O_4$:Eu (1%) crystal shows two emission bands in the green (515 nm) and blue (445 nm) regions at low temperatures. Besides these well-known emission bands for the first time a very intensive peak at 375 nm in the CL spectra of $SrAl_2O_4$:Eu^{2+} (1%) was observed. For determination of the origin of this peak, the results of CL were complemented with the results received by synchrotron radiation in the VUV energy region for undoped and Eu - doped $SrAl_2O_4$ crystals. It was shown that observed emission band at 375 nm is related to the defects of crystal structure. The glow peaks at 59, 220 and 325 K were attributed to the thermal release of electrons from the V_O defect sites. A green pc-LED was fabricated by the combination of the $SrAl_2O_4$:Eu^{2+} (1%) nanosized phosphor with a 365 nm UV InGaN chip. CIE chromaticity diagram confirmed that obtained pc-LED emits bright green light and its color coordinates (x = 0.288 and y = 0.47) shifts slightly at different currents. However, strong temperature quenching of luminescence of $SrAl_2O_4$:Eu^{2+} at high temperatures is a serious drawback for application of strontium aluminate in LEDs.

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