PHOTOLUMINESCENCE CHARACTERIZATION OF Sm^{3+} DOPED SrIn$_2$O$_4$ PREPARED BY A SOLUTION COMBUSTION METHOD**

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Sm^{3+} doped SrIn$_2$O$_4$ phosphors were prepared by a solution combustion method. The synthesized phosphors were characterized using powder XRD. The excitation and emission spectra of Sm^{3+} doped SrIn$_2$O$_4$ materials were analyzed at room temperature. SrIn$_2$O$_4$:Sm^{3+} phosphor emits 568–578, 606–617, 660, and 720 nm light under ultraviolet excitation of 300 nm. The photoluminescence properties of the synthesized phosphors with different Sm^{3+} doping concentrations were investigated. The optimum concentration of Sm^{3+} ion in SrIn$_2$O$_4$ was found to be 0.02 mol.

***Keywords:** photoluminescence, Sm^{3+} ion, combustion synthesis, SrIn$_2$O$_4$.*

ХАРАКТЕРИСТИКА ФОТОЛЮМИНЕСЦЕНЦИИ ЛЕГИРОВАННОГО Sm^{3+} SrIn$_2$O$_4$, ПОЛУЧЕННОГО МЕТОДОМ СЖИГАНИЯ РАСТВОРА

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Люминофоры SrIn$_2$O$_4$, легированные ионом Sm^{3+}, получены методом сжигания раствора. Синтезированные люминофоры охарактеризованы с использованием порошкового рентгенодифракционного анализа. Спектры возбуждения и эмиссии легированных Sm^{3+} SrIn$_2$O$_4$ материалов проанализированы при комнатной температуре. Люминофор SrIn$_2$O$_4$:Sm^{3+} излучает в областях 568—578, 606—617, 660 и 720 нм при УФ возбуждении на λ = 300 нм. Исследованы фотолюминесцентные свойства синтезированных люминофоров с различными концентрациями ионов Sm^{3+}. Установлено, что оптимальная концентрация ионов Sm^{3+} в SrIn$_2$O$_4$ составляет 0.02 моль.

***Ключевые слова:** фотолюминесценция, ион Sm^{3+}, синтез в процессе горения, SrIn$_2$O$_4$.*

Introduction. Samarium ion with $4f^5$ electronic configuration is a common rare earth activation ion, which usually exists in triply ionized form (Sm^{3+}) [1]. The Sm^{3+} ion is widely used as activator of reddish orange emission due to its $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) transitions [2, 3], which from a practical viewpoint is the most suitable source for lighting and display. Therefore, luminescence properties of Sm^{3+} ion in different hosts such as silicates [4], oxides [5], borates [6], vanadates [7], titanates [8], and phosphates [9] have been extensively investigated by the scientists. The compound of SrIn$_2$O$_4$ is an example of alkaline-earth metal indates. It is characterized by having an association of distorted InO$_6$ octahedra sharing edges and corners, and eight-fold coordinated strontium atoms. The crystal structure of SrIn$_2$O$_4$ has been studied in detail by different groups [10, 11]. SrIn$_2$O$_4$ is a useful luminescent host for activator ions such as Eu^{3+}, Dy^{3+}, Pr^{3+}, and Tb^{3+} ions [10–14]. Recently, the luminescent properties of Sm^{3+} doped SrIn$_2$O$_4$ have been reported by Shaohua and co-workers [15]. They synthesized this phosphor at high temperature (1200ºC) by solid state

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reaction. It is known that the emission intensity of the phosphors change based on the sintering temperature. Also, some studies showed a decrease in the emission intensities of luminescent materials prepared at high temperatures due to excessive sintering and aggregation of particles [16–18]. Thus, some weak bands in the emission spectrum may not be observed. For example, the $^4G_{5/2} \rightarrow ^6H_{11/2}$ transition of Sm^{3+} ion is not seen in the paper reported by Shaohua and coworkers. Also, some $4f \rightarrow 4f$ transitions in the excitation spectrum are missing. Therefore, it is necessary to synthesize this phosphor at low temperature using a different synthesis technique.

In the present work, $SrIn_2O_4:Sm^{3+}$ phosphors were prepared by a solution combustion method. The synthesized materials were characterized using powder X-ray diffraction. After synthesis and characterization of all phosphors, the photoluminescence properties of the synthesized phosphors were studied using a spectrofluorometer at room temperature.

Experimental. Sm^{3+} doped $SrIn_2O_4$ materials were prepared by a solution combustion synthesis method followed by heating of the precursor combustion ash at 950ºC in air. $Sr(NO_3)_2$, $In(NO_3)_3$, $Sm(NO_3)_3$, and urea were used as starting materials. The stoichiometric amounts of starting materials were dissolved in a minimum amount of distilled water and placed in porcelain containers. The precursor solutions were introduced into a muffle furnace and maintained at 500ºC for 10 min. The precursor powders were removed from the furnace. The voluminous and foamy combustion ashes were easily milled to obtain a precursor powder of $Sr_{1-x}Sm_xIn_2O_4$ ($x = 0.005$, 0. 01, 0.02, 0.03, and 0.04). The well-mixed precursor powders were then slowly heated at 950ºC for 6 h in air.

The XRD structural analysis of Sm^{3+} doped $SrIn_2O_4$ materials were performed on a Phillips X'Pert Pro system equipped with CuK_α (30 kV, 15 mA, $\lambda = 1.54051$ Å) radiation at room temperature. Scanning was generally performed between $2\theta = 10º$ and $90º$. Measurement was made with 0.0330º step size at 25°C temperature. The photoluminescence spectra were measured at room temperature with a Thermo Scientific Lumina fluorescence spectrometer equipped with a 150 W xenon lamp. Magnesium oxide was used as the scattering material due to its uniform efficiency in scattering various wavelength.

X-Ray powder diffraction analysis. $SrIn_2O_4$ was reported to have the orthorhombic crystal structure with space group of *Pnam*, and the lattice parameters values were found as: $a = 9.809$ Å, $b = 11.449$ Å, $c = 3.265$ Å [19]. Figure 1 shows the XRD pattern of $SrIn_2O_4:Sm^{3+}$ phosphors. The positions and relative intensities of all diffraction peaks are in agreement with JCPDS Card No: 33-1336. The structures of $SrIn_2O_4:Sm^{3+}$ consist of $SrIn_2O_4$, and doping of Sm^{3+} ion does not significantly influence the crystal structures of the synthesized phosphors.
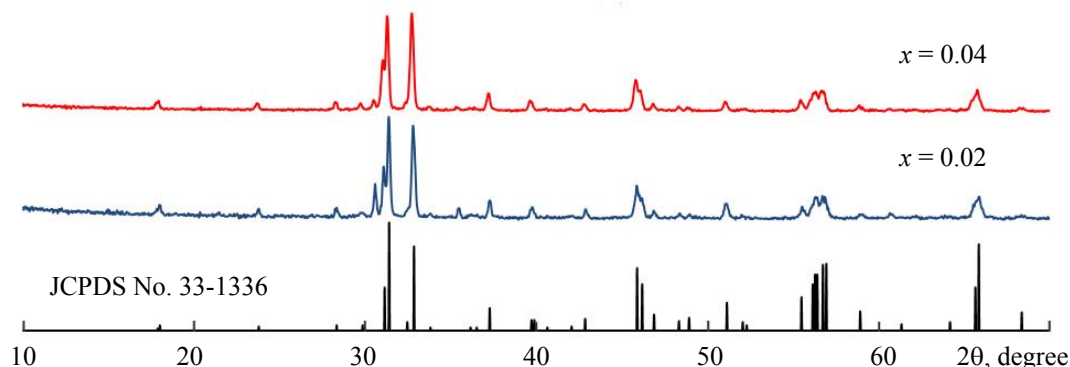

Fig. 1. XRD pattern obtained for $Sr_{1-x}Sm_xIn_2O_4$ ($x = 0.02$ and 0.04).

Photoluminescence properties of $SrIn_2O_4:Sm^{3+}$. Figure 2a shows the excitation spectrum of $Sr_{1-x}Sm_xIn_2O_4$ ($x = 0.04$) phosphor. The excitation spectrum was recorded in the wavelength range of 190–525 nm measured by monitoring at 617 nm emission. As seen in Fig. 2a, the excitation spectrum of Sm^{3+} is composed of the host lattice absorption band around 300 nm and the $4f \rightarrow 4f$ transition between 350–500 nm. It is known that the strong absorption bands around 300 nm are due to the transitions from valence bands (consisting of the $2p$ orbital of O) to conduction bands (composed of the $5s$ and $5p$ orbital of In) [20], which is in agreement with the excitation spectra of the $SrIn_2O_4:Sm^{3+}$. This result indicates that the excitation spectrum

of SrIn$_2$O$_4$:Sm^{3+} has the host lattice absorption around 300 nm. The presence of the SrIn$_2$O$_4$ host band in the excitation spectrum indicates that an energy transfer takes place from the SrIn$_2$O$_4$ host lattice to the doped Sm^{3+} ion, i.e, the emission arises from a host-sensitized effect. Thus, an efficient host-sensitized luminescence of Sm^{3+} occurred in SrIn$_2$O$_4$:Sm^{3+}, like SrIn$_2$O$_4$:Dy^{3+}, and SrIn$_2$O$_4$:Pr^{3+}, SrIn$_2$O$_4$:Tb^{3+} reported previously [12]. The other excitation peaks at 360, 375, 404, 417, 461, and 477 nm have been assigned to the transition from $^6H_{5/2}$ to $^4D_{3/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$, and $^4I_{11/2}$ of Sm^{3+}, respectively [21, 22].

Figure 2b shows the emission spectrum of Sr$_{1-x}$Sm$_x$In$_2$O$_4$ ($x = 0.04$) phosphor. The emission spectrum was recorded in the wavelength range of 450–800 nm measured by monitoring at 300 nm excitation. It is composed of four bands corresponding to the transitions from the $^4G_{5/2}$ to the $^6H_{5/2}$ (568–578 nm), $^6H_{7/2}$ (606–617 nm), $^6H_{9/2}$ (660 nm), and $^6H_{11/2}$ (720 nm). The strongest one is located at 606–617 nm due to the $^4G_{5/2}{\rightarrow}^6H_{7/2}$ transition of Sm^{3+} [21–27].
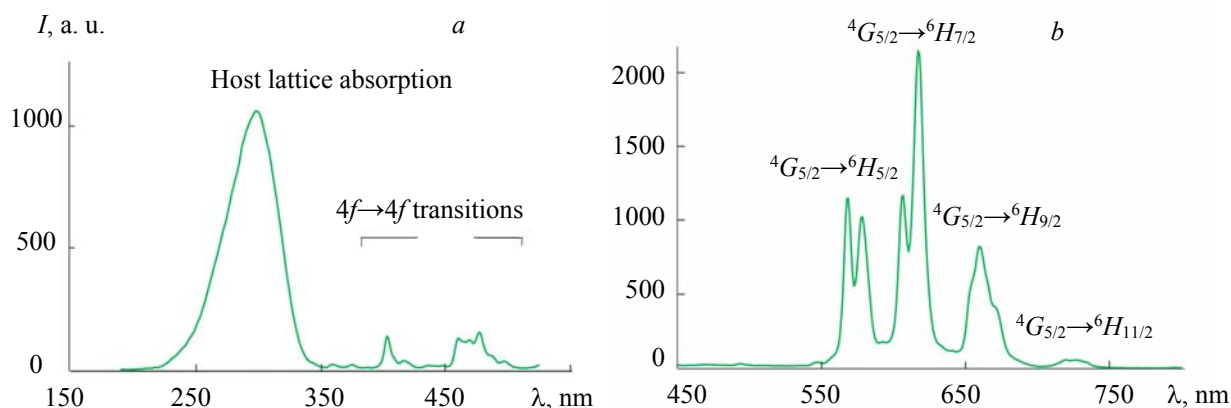

Fig. 2. The excitation (a) and emission (b) spectra of Sr$_{1-x}$Sm$_x$In$_2$O$_4$ ($x = 0.04$) at room temperature ($\lambda_{em} = 617$ nm, $\lambda_{exc} = 300$ nm).

Finally, the effect of the dopant ion concentration on the emission spectrum of SrIn$_2$O$_4$:Sm^{3+} was studied. The emission spectra of Sr$_{1-x}$Sm$_x$In$_2$O$_4$ ($0.005 \leq x \leq 0.04$) phosphors with different Sm^{3+} molar fractions are shown in Fig. 3. With increasing Sm^{3+} concentration in SrIn$_2$O$_4$, the emission intensity of the synthesized phosphors increases and reaches a maximum at 0.02 mol. Then, when the molar concentration of Sm^{3+} ion exceeds this concentration level, the emission intensity decreases due to concentration quenching. Thus, it can be said that the optimum concentration of Sm^{3+} ion in SrIn$_2$O$_4$ was observed at 0.02 mol.
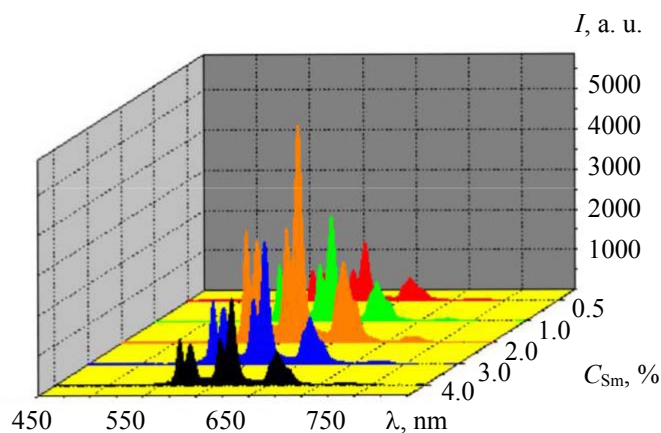

Fig. 3. Emission spectra of SrIn$_2$O$_4$:Sm^{3+} (0.5, 1, 2, 3, and 4 mol.%) phosphors ($\lambda_{exc} = 300$ nm).

Conclusion. Sm^{3+} doped $SrIn_2O_4$ phosphors were prepared by a solution combustion method. The synthesized phosphors were characterized using powder XRD. The excitation and emission spectra of the synthesized phosphors were analyzed in detail at room temperature. The excitation spectrum of Sm^{3+} is composed of the host lattice absorption band around 300 nm and the $4f{\rightarrow}4f$ transition between 350–500 nm. The emission spectrum is composed of four bands corresponding to the transitions from the $^4G_{5/2}$ to the $^6H_{5/2}$ (568–578 nm), $^6H_{7/2}$ (606–617 nm), $^6H_{9/2}$ (660 nm), and $^6H_{11/2}$ (720 nm). Finally, the photoluminescence properties of the synthesized phosphors with different Sm^{3+} doping concentrations were analyzed. The optimum concentration of Sm^{3+} ion in $SrIn_2O_4$ was found to be 0.02 mol. Consequently, $SrIn_2O_4$ could be considered as a useful luminescent host for Sm^{3+} ions.

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