Synthesis and photoluminescence properties of Sm$^{3+}$ doped LaOCl phosphor with reddish orange emission and it’s Judd-Ofelt analysis

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Keywords: rare earth, oxychloride, photoluminescence, Judd-Ofelt

Abstract

Present paper reports the study on luminescence and optical behaviour of samarium doped lanthanum oxychloride (LaOCl:Sm$^{3+}$) nanophosphor for their potentiality in display devices. The conventional solid state route was employed to synthesize the phosphor La$_{1-x}$Sm$_x$OCl ($x = 0$, 0.01, 0.03, 0.05, 0.07 and 0.09). Tetragonal phase of the prepared compound was confirmed by PXRD. An agglomerated and spherical like structure were seen of the samples from FE-SEM analysis. The Wood and Tauc relation was employed to find out band gap energy and is around 4.23 eV. At an excitation wavelength of 408 nm, a high intense peak of emission was observed at 608 nm for transitions ($^4$G$_{5/2} ightarrow ^6$H$_{7/2}$) of Sm$^{3+}$ ions in the PL spectra. Colour co-ordinates ($X,Y$) were used for the analysis of measured photoluminescence spectra. For the optimized concentration of Sm$^{3+}$ (La$_{1-x}$Sm$_x$OCl with $x = 0.05$), the intensity parameters ($\Omega_2$, $\Omega_4$ and $\Omega_6$) were determined. The trend of $\Omega_6 > \Omega_4 > \Omega_2$ was observed. An emission cross section and Branching ratio are found to be 3.98 $\times$ 10$^{-22}$ cm$^2$ and 59% respectively for $^4$G$_{5/2} ightarrow ^6$H$_{7/2}$ transition that makes it suitable for laser designs and application. The obtained results reveal that the LaOCl phosphor doped with samarium can be used on the screens of optical electronic systems and also is suitable for emission of reddish orange colour.

1. Introduction

Host material plays a significant role in the up conversion method, specifically due to its contribution in luminescence efficiency. An ideal host is expected to have good chemical stability to maintain the physical integrity of the nano materials. Host should have less phonon energy so as to reduce non-radiative processes contributing in enhancing the radiative emission component Wang and Liu 2009. In this regard Lanthanum oxychloride (LaOCl) is found to have high chemical stability, non toxicity, high light absorption efficiency and conduction, making it useful for lighting and displays devices. Moreover among the Lanthanide ions, La$^{3+}$ ions have largest ionic radius and can easily substituted by another Ln$^{3+}$ ions in the lattice structure [1]. Thus LaOCl serves to be a promising host matrix for doping with various Ln$^{3+}$ ions. Further lanthanum oxychloride nanophosphor have gained special attention due to desired luminescence properties and applications like catalyst supports, gas sensors [2, 3] and solid state lighting in WLED’s etc [4, 5]. Controlled synthesis of a distinct nanophosphor plays vital role in the bonding, electronic structure, chemical reactivity and surface energy which intern dependent on their size and morphology [6].

Judd-Ofelt theory was utilized to explain the behaviour of the spectral intensities within the host and hence the spectral intensities characterize the rare earth ions in the host. The magnetic dipole (MD) and electric dipoles (ED) contributes for various optical intensities due to f-f transitions. Within the 4f shell the ED transitions were forbidden because of them having the same parity. The forced ED transitions outside the 4f shell by mixing in...
opposite parity states from higher lying configurations shell is promoted due to the perturbation caused by non-centricosymmetric crystal field. In J-O theory the mixed parity states were due to the impact of static odd order terms of the crystal field. The importance of the even order terms in energy level arrangement on the ion be able to explained through a number of JO parameters [7–9]. The performances of the luminescent and laser materials can be evaluated where J-O terms ($\Omega_2$, $\Omega_4$ and $\Omega_6$) plays a crucial role which are sensitive to the local environment. $\Omega_2$ can be enriched by covalent bonding and is usually dependent on Nephelauxetic effect whereas $\Omega_4$ and $\Omega_6$ are dependent on the long range effect [10].

Several methods are adopted meant for the synthesis of LaOCl that includes sol-gel, solid-state, combustion, liquid-phase method, mechanochemical grinding, surfactant-assisted solvothermal reaction and solvothermal method [11–16]. Amongst various methods of synthesizing due to its large scale production, highly pure products, good compositional control and solvent/surfactant free process solid-state reaction method is used the most.

Various studies have been carried out on Eu$^{3+}$ doped phosphors with red emission [17, 18] and also Sm$^{3+}$ doped phosphors with reddish-orange emission [19–22]. In this paper, we reported the study of luminescence and Judd-Ofelt analysis of La$_{1-x}$Sm$_x$OCl ($x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.09$) Nano phosphor synthesized via solid state which was carried out for short duration and at low temperature. The crystallographic parameters, functional groups, morphological and luminescence properties be analyzed via powder x-ray diffraction, FTIR spectroscopy, FE-SEM & TEM and photoluminescence (PL) accordingly. Further from the absorbance data, the Judd-Ofelt parameter, radiative emission rates, radiative lifetime, branching ratio and asymmetry ratios are identified.

2. Experimental section

2.1. Synthesis of La$_{1-x}$Sm$_x$OCl ($x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.09$) Nano phosphor

Sm$^{3+}$ activated LaOCl phosphors were prepared via solid-state method. The starting materials for the synthesis were La$_2$O$_3$, Gd$_2$O$_3$, Eu$_2$O$_3$ (rare-earth oxides) and NH$_4$Cl procured from Sigma Aldrich. Before weighing, for about 6 h all the rare-earth oxides were calcined at 800 °C. Stoichiometric amount of La$_2$O$_3$, Eu$_2$O$_3$ and NH$_4$Cl (20% excess) were finely ground with a pestle in an agate mortar. Calcination at 700 °C was done for the obtained fine powder by taking it in a porcelain crucible for 2 h and cooled down to room temperature. The chemical reaction written as:

$$(1 - x)La_2O_3 + xSm_2O_3 + 2NH_4Cl \rightarrow 2La_{1-x}Sm_xOCl + 2NH_3 + H_2O \quad (1)$$

2.2. Instruments

Investigation of the crystallinity and phase purity of the synthesized sample were carried out by Shimadzu x-ray diffractometer using Cu Kα radiation ($1.5406$ Å) with nickel filter. From an angle of $2\theta = 10^\circ–80^\circ$, diffracted intensities were recorded. The morphology of the nanophosphor were observed with Hitachi 3000 SEM. TEM analysis (Hitachi H-7100 with an accelerating voltage of 120 kV and solvent as methanol) – 4 cm$^{-1}$ resolution in the range 350–4000 cm$^{-1}$. UV-visible spectra were noted by analytic jena spec cord 250 +. Photoluminescence (PL) measurements were carried out using Horiba Fluro Log-3 modular Spectrofluorimeter with nanophosphors excited using linearly polarized, 40 μW, 633 nm or 532 nm lasers using a 100 × NA = 1.4 oil immersed microscope objective.

3. Results and discussion

3.1. Powder x-ray diffraction

Figure 1 represents the PXRD pattern of La$_{1-x}$Sm$_x$OCl ($x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.09$) nanophosphor. The formation of single phase LaOCl compound with samarium as dopant is confirmed by the single and sharp peaks of diffraction which are indexed to tetragonal phase of space group p4/nmm [18]. No other impurity peaks were seen confirms the purity of the product. Bragg’s equation $\lambda = 2d \sin \theta$ was employed to calculate the interplanar distance ‘d’ between the adjacent planes. Making use of the lattice geometry equations the interplanar spacing, lattice constants (a, b, c) and primary cell volume are determined [23] and obtained values were tabulated in table S1 is available online at stacks.iop.org/MRX/7/015003/mmedia.
The calculation of particle size was done using Debye-Scherer equation.

\[ d = \frac{k \lambda}{\beta \cos \theta} \]  

Here ‘d’ is the size of the particle nm, k is constant = 0.94, \( \theta \) is diffraction angle, ‘\( \lambda \) = 1.540 A°’ represents wavelength for Cu K\(_{\alpha}\) radiation, and \( \beta \) is the FWHM (full width at half maximum intensity).

It is found that the particle size were in the order of 45–48 nm determined by Williamson and Hall method. The strain (\( \varepsilon \)) and particle size (d) contributes to the linear combination that gives rise to FWHM s (\( \beta \)) through the W-H relation [18].

\[ \beta \cos \theta = \frac{0.9 \lambda}{d} + 4 \varepsilon \sin \theta \]  

Above equation is of the form \( y = mx + c \) represents straight line. Figure 2 shows the W-H plot which exhibits a straight line obtained by plotting \( \beta \cos \theta \) versus \( 4 \sin \theta \) for Sm\(^{3+}\) doped LaOCl. The strain factor (\( \varepsilon \)) is obtained from the straight line slope whereas \( y \)-axis intercept \( \left( \frac{0.9 \lambda}{d} \right) \) gives the particle size which is found to be 61–68 nm for La\(_{1-x}\)Sm\(_x\)OCl (\( x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.09 \)) nanophosphor. The values of particle size obtained for La\(_{1-x}\)Sm\(_x\)OCl (\( x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.09 \)) using W-H and Scherer’s method are tabulated in table 1.

3.2. Electron microscopy (SEM and TEM)

SEM micrographs and the composition of elements are as shown in figures 3(a) and (b) of La\(_{1-x}\)Sm\(_x\)OCl (\( x = 0.05 \)) phosphor. It is clear from the images that the morphology of the nanophosphor are agglomerated, which may be due to the method of synthesis.

To understand the particle size distribution La\(_{1-x}\)Sm\(_x\)OCl (\( x = 0.05 \)) phosphor is examined through TEM and HRTEM. A close view of TEM images in figures 4(a) and (b) reveals so as the phosphor is in the nano system. The lattice fringes as observed in figure 4(b) and suggest 0.34 nm as its interplanar distance, which corresponds to the plane (101) in LaOCl. Figure 4(c) shows the SAED pattern of La\(_{1-x}\)Sm\(_x\)OCl (\( x = 0.05 \)), which exhibited diffraction circles composed of diffraction dots.
3.3. FTIR- fourier transform infrared spectroscopy

Figure 5 represents the transition spectra of La$_{1-x}$Sm$_x$OCl nanophosphor with $x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.09$ from 400–4000 cm$^{-1}$. At about 511 cm$^{-1}$ appeared the vibration peaks of (La–O) metal oxygen bands in the low frequency domain [24]. The band at 1617 cm$^{-1}$ signifies asymmetric stretching vibrations of C=O carboxyl groups, whereas bands at 3458 and 1391 cm$^{-1}$ are attributes of stretching bands and bending of O–H group respectively [25].

3.4. UV-Visible spectra

Figure 6 represents the energy band gap diagram for La$_{1-x}$Sm$_x$OCl with $x$ as 5 mol%. Using the data of absorption spectra the optical band gap energy was estimated by means of wood and Tauc relation given by.

$$\alpha h \nu = A (h \nu - E_g)^n$$

here, $\alpha$ denotes absorption co-efficient, $A$ is proportionality constant, $h \nu$ is the photon energy, $E_g$ is the optical energy band gap and $n$ is influenced by the properties of the transition in semiconductor. For forbidden direct, forbidden indirect, allowed direct, and allowed indirect transitions. 'n' takes the value of 3/2, 3, 1/2 or 2 respectively. As the absorption spectrum is administered by direct electronic transition value of $n$ is $1/2$ for LaOCl nanophosphor [26]. The value of energy band gap is taken from the intercept of tangent to the x-axis and is found to be 4.23 eV for La$_{1-x}$Sm$_x$OCl where $x = 0.05$.

Figure 7 represents the optical absorption spectrum of LaOCl: 5 mol% Sm$^{3+}$ at room temperature from wavelength range 800–1600 nm. The 5 mol% samarium doped LaOCl revealed several bands allotted to f-f transition from ground state to different excited states of Sm$^{3+}$ ions in the absorption spectra. It consisted of absorption band positioned at 948, 1089, 1239, 1367, 1464 and 1564 nm assigned to the transitions from $^6$H$_{5/2}$ to various excited states $^6$F$_{11/2}$, $^6$F$_{9/2}$, $^6$F$_{7/2}$, $^6$F$_{5/2}$, $^6$F$_{3/2}$ and $^6$F$_{1/2}$ of Sm$^{3+}$ ions respectively. Table 2 includes the data of absorption band wavenumbers for 5 mol % Sm$^{3+}$ ions doped LaOCl nanophosphor and aqua ions [26] along with nephelauxetic ratio $\beta$ and bonding parameter $\delta$. Here $\delta$ is given by $\delta = \left[ \frac{\alpha - \beta}{\beta} \right] \times 100$ where the average $\bar{\beta} = \frac{\sum_{i=1}^{N} \beta_i}{N}$, and $\beta = \frac{\nu_{np}}{\nu_{a}}$ where $\bar{\beta}$ is found using $N$ the number of levels, $\nu_{np}$ and $\nu_{a}$ are the wavenumbers of the corresponding transition in 5 mol % Sm$^{3+}$ ions doped LaOCl nanophosphor and aqua ions respectively.
Table 1. Calculated crystallite size from PXRD peak broadening and CIE colour co-ordinates, CCT and measured asymmetric ratio values for La$_{1-x}$Sm$_x$OCl ($0.01 \leq x \leq 0.09$).

| Concentration of Sm$^{3+}$ X | Crystallite size (nm) | Scherrer’s W-H Strain $\varepsilon \times 10^{-3}$ | $x$ | $y$ | $u'$ | $\nu'$ | CCT (K) | $\int I_{20d}\lambda$ counts.nm $\times 10^{6}$ | $\int I_{20d}\lambda$ counts.nm $\times 10^{6}$ | Asymmetric ratio ($\lambda$) |
|-----------------------------|----------------------|-----------------------------------------------|-----|-----|-----|-----|-------|-----------------------------|-----------------------------|-----------------------------|
| 0.00                        |                      | 45.09                                        | 0.96| 0.5618| 0.4400| 0.5334| 1962  | 2.618                                     | 1.380                                     | 1.897                             |
| 0.01                        |                      | 48.49                                        | 1.03| —    | —    | —    | —     | —                                           | —                                           | —                                           |
| 0.03                        |                      | 45.69                                        | 0.98| 0.5633| 0.4402| 0.5337| 1955  | 2.787                                     | 2.224                                     | 1.253                             |
| 0.05                        |                      | 46.57                                        | 1.27| 0.5639| 0.4400| 0.5337| 1950  | 4.005                                     | 3.386                                     | 1.182                             |
| 0.07                        |                      | 45.56                                        | 1.20| 0.5621| 0.4408| 0.5340| 1964  | 3.710                                     | 3.223                                     | 1.151                             |
| 0.09                        |                      | 47.91                                        | 1.32| 0.5603| 0.4404| 0.5333| 1972  | 1.387                                     | 1.058                                     | 1.311                             |
The value of bonding parameter $\delta$ being negative or positive represents the ionic and covalent bonding respectively for $\text{Sm}^{3+}$-ligands. In the present paper bonding parameter $\delta$ is obtained as $-1.08$ indicating ionic nature of $\text{Sm}^{3+}$ ligand bond in LaOCI nanophosphor.
3.5. Photo-luminescence, CIE chromaticity diagram and correlated color temperature

Figure 8 represents the excitation spectra of Sm$^{3+}$ doped LaOCl nanophosphor indicating that the excitation wavelength is 408 nm. Under this excitation the phosphor exhibited emission of reddish orange luminescence. Figure 9 represents the emission spectrum of La$_{1-x}$Sm$_x$OCl ($x = 0.01, 0.03, 0.05, 0.07, 0.09$) nanophosphor at 408 nm as its excitation wavelength. Inset of figure 9 indicates the difference in emission intensities with samarium ion concentration. Four emission bands were exhibited corresponding to the transition $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{11/2}$ at 564, 608, 650 and 708 nm respectively.

![Figure 5. FTIR spectra of La$_{1-x}$Sm$_x$OCl (0.01 $\lesssim x \lesssim 0.09$) nanophosphors.](image)

![Figure 6. Energy band gap from Tauc-plot of La$_{0.95}$Sm$_{0.05}$OCl nanophosphors.](image)

![Figure 5. FTIR spectra of La$_{1-x}$Sm$_x$OCl (0.01 $\lesssim x \lesssim 0.09$) nanophosphors.](image)

![Figure 6. Energy band gap from Tauc-plot of La$_{0.95}$Sm$_{0.05}$OCl nanophosphors.](image)
Figure 7. Room temperature absorption spectrum of La$_{0.95}$Sm$_{0.05}$OCl nanophosphors.

Table 2. Absorption transition wavenumbers for Sm$^{3+}$ ions doped in La$_{1-x}$Sm$_x$OCl ($x = 0.05$) Nano phosphor $\nu_{np}$ and aqua-ions $\nu_a$ along with nephelauxetic ratio $\beta$ and bonding parameter $\delta$.

| Transition (From) | $\nu_{np}$ (cm$^{-1}$) | $\nu_a$ (cm$^{-1}$) | $\beta = \frac{\nu_{np}}{\nu_a}$ |
|------------------|------------------------|---------------------|-------------------------------|
| $^4H_{11/2}$     | 10 549                 | 10 500              | 1.005                         |
| $^4P_{11/2}$     | 9183                   | 9200                | 0.9982                        |
| $^4P_{9/2}$      | 8071                   | 8000                | 1.009                         |
| $^4P_{7/2}$      | 7315                   | 7100                | 1.030                         |
| $^4P_{5/2}$      | 6831                   | 6630                | 1.030                         |
| $^4P_{1/2}$      | 6394                   | 6400                | 0.999                         |

$\beta = 1.011 \delta = -1.08$ (ionic bonding).

Figure 8. Excitation spectra of La$_{0.95}$Sm$_{0.05}$OCl nanophosphors.
The emission peak corresponding to $^{4}G_{5/2} \rightarrow ^{6}H_{7/2}$ transition at wavelength 608 nm appears to be maximum than others. The intensity of emission increased with raise in the samarium ion concentration and is seen to be maximum for 5 mol \% Sm$^{3+}$ concentration after which for higher concentration of Sm$^{3+}$ the emission intensity decreased which attributed to the effect of quenching.

Quenching effect arises due to the non-radiative energy transfer as an impact of radiation re-absorption, exchange interaction or multipole-multipole interaction.

Firstly, because of the broad overlap of fluorescent spectra of the activator and the sensitizer rate of re-absorption of radiation for transfer of energy occurs [22]. It is clear from the PL spectra of emission and excitation that radiation re-absorption is not responsible for the quenching effect.

Secondly as per Blasse et al [28], $R_c$ the critical transfer distance is as follows

$$R_c = 2 \left( \frac{3 V}{4 \pi N X_c} \right)^{1/3}$$  \hspace{1cm} (5)

$V = a^3 c$ is unit cell volume = 0.117 (nm)$^3$, in a unit cell for LaOCl $N = 4$ the no. of cationic sites vacant, $X_c = 0.05$ is the optimum concentration of Sm$^{3+}$ ion. Hence the value of critical transfer distance for the present nano phosphor $R_c$ is found to be 10.37 Å°. $R_c$ less than 3–4Å° implies through exchange interaction the non-radiative transfer of energy is possible [29]. Since for LaOCl it is not less than 3–4Å°, the energy transfer is not due to exchange interaction.

Thirdly, the multipolar interaction leads to non-radiative energy transfer if the transfer of energy is relative to $(x)^{\theta/3}$ with $x$ being dopant concentration where $x = C/C^*$, $C^*$ is critical transfer concentration of quenching and $C$ is quenching ion concentration and $\theta = 10, 8, 6$ indicates quadruple-quadruple, dipole-quadruple or dipole-dipole interaction respectively [30]. The correlation of emission intensity and activator gives the energy transfer in the host matrix [29] which is written as

$$\frac{I}{x} = k[1 + \beta x^{\theta/3}]^{-1}$$  \hspace{1cm} (6)

$\beta$ and $k$ are constants, $\frac{I}{x}$ the emission intensity/activator ion. Further equation (6) can also be represented as

$$\log \left( \frac{I}{x} \right) = k - \frac{\theta}{3} \log (x)$$  \hspace{1cm} (7)
Critical concentration for LaOCl:Sm$^{3+}$ is found to be 0.05. Identifying the integrated intensity for $x = 0.05, 0.07, 0.09, \log \left( \frac{I}{x} \right)$ versus log (x) graph is plotted which is a linear fit as shown in the figure 10. Slope $\left( -\frac{\partial \theta}{\partial x} \right)$ value is found to be $-1.7988$ and hence the value of $\theta$ is equal to 5.39. As $\theta$ value is nearer to 6 confirms that the d-d interaction is liable for quenching of samarium ions in LaOCl host.

For transitions $^4G_{5/2} \rightarrow ^6H_{5/2}, ^4G_{5/2} \rightarrow ^6H_{7/2}, ^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{11/2}$ the variation of PL intensity as a function of samarium ion concentration is represented in inset of figure 9. Highest peak intensity was exhibited by $^4G_{5/2} \rightarrow ^6H_{7/2}$ whereas lowest peak intensity is being exhibited by $^4G_{5/2} \rightarrow ^6H_{11/2}$ transition and the other two $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ revealed modest intensities. The magnetic dipole transitions were observed for $^4G_{5/2} \rightarrow ^6H_{5/2,7/2}$ that obeyed selection rules $\Delta J = 0 \pm 1$. Solely electric dipole transition was seen for $^4G_{5/2} \rightarrow ^6H_{9/2,11/2}$ [31, 32]. Due to high asymmetry the electric dipole transition exhibits higher peak intensity. The orange to red peak intensity ratio (O/R) for $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition were found to be 1.897, 1.253, 1.182, 1.151 and 1.311 for 1, 3, 5, 7 and 9 mol % respectively.

The radiative and non-radiative transitions for samarium are as shown in the energy level diagram figure 11. Critical concentration of LaOCl:Sm$^{3+}$ phosphor serves to be one component for white emission by connecting it to phosphor exhibiting blue-green. Thus, LaOCl:Sm$^{3+}$ finds application in NUV-based WLED’s. CCT lower than 5000 K, declares that the current phosphor perhaps will be helpful for solid state lighting and warm white LED application.

### 3.6. Absorption spectrum and J-O analysis

Figure 7 represents the optical absorption spectra in wavelength series of 900 to 1600 nm consisting of six absorption band with wavelengths 948, 1089, 1239, 1367, 1464 and 1564 nm corresponding to transitions $^6H_{5/2} \rightarrow ^6F_{11/2}, ^6H_{5/2} \rightarrow ^6F_{9/2}, ^6H_{5/2} \rightarrow ^6F_{7/2}, ^6H_{5/2} \rightarrow ^6H_{5/2}, ^6H_{5/2} \rightarrow ^6F_{3/2}$ and $^6H_{5/2} \rightarrow ^6F_{1/2}$ respectively for La$_{1-x}$Sm$_x$OCl with $x = 5$ mol %. All the transitions are originating from $^6H_{5/2}$ to different higher energy states and are accredited to intra configuration (f–f) transitions.
As said by Judd Ofelt theory, the line strength of an electric dipole transition between initial \((S, L) J \rangle\) and final manifold \((S', L') J' \rangle\) is as follows,

\[
S_{\text{calc}}(J \rightarrow J') = \sum_{t=2,4,6} \Omega_t |\langle (S, L) J | U^{(t)} | (S', L') J' \rangle|^2
\]

Using intermediate-coupling approximation the fundamentals \(|U^{(t)}|\) doubly reduced unit tensor operator are found. For the chosen \(\text{Sm}^{3+}\) bands Carnall et al [27] is taken as reference for the values of unit tensor operators.

The measured values of line strength is measured using the equation,

\[
S_{\text{meas}} (J \rightarrow J') = \frac{3\text{hc}(2J+1)}{8\pi^2e^2\lambda} \left(\frac{3}{\lambda^2 + 2}\right)^2 \int \sigma(\lambda) d\lambda
\]

In equation (9), \(\lambda\) is average wavelength that corresponds to the particular absorption band of a transition, \(J\) is the total angular momentum of initial state, \(n\) is the host refractive index \(\int \sigma(\lambda) d\lambda\) is integrated absorption cross section. The absorption cross section is determined using \(\alpha(\lambda) = \frac{2.303 \times A}{t \times N}\) with ‘t’ as its thickness of sample = 0.1 cm, \(A = \) absorbance, and \(N = 6.023 \times 10^{20}\) is concentration of \(\text{Sm}^{3+}\) ion per cm\(^3\) for 5 mol % doped LaOCl [34, 35].

By means of least square fitting technique among the measured and computed line strength of \(\text{Sm}^{3+}\) in LaOCl nanophosphor, the J-O parameters were evaluated and are obtained as,

\[
\Omega_2 = 0.4081 \times 10^{-20}\text{cm}^2, \quad \Omega_4 = 0.4842 \times 10^{-20}\text{cm}^2, \quad \Omega_6 = 0.615 \times 10^{-20}\text{cm}^2.
\]

According to Jorgensen and Reisfeld [36], due to covalency between rare earth ions and ligand anions, \(\Omega_2\) is strongly affected and is responsive to the local structure of the RE\(^{3+}\) site where as \(\Omega_4\) and \(\Omega_6\) are concerned to the rigidity and viscosity of the host medium where the ions are present. The \(\Omega_2\) parameter in the present phosphor LaOCl:Sm\(^{3+}\) is smaller than that of other hosts which can be attributed to higher symmetry of the co-ordination structure surrounding the RE ion. In addition the presence of the Cl\(^{-}\) ions plays the important role for the reduction of \(\Omega_2\) value as the chlorine ions have higher electronegativity (around 3.5) in comparison with the other anion ions, therefore the RE-Cl bonds have the smaller covalency bond than other RE-anion bonds. This is main reason for the reduction of \(\Omega_2\) values [37]. In our case since \(\Omega_2 < \Omega_4\) we can assume that the field experienced by the Sm\(^{3+}\) ions in the host matrix (LaOCl) is centrosymmetric in nature. This implies MD transitions are dominant than that of ED transitions. The same is reflected in PL spectrum. In case of PL spectrum, as per the selection rule, 564 nm emission is completely corresponds to MD transition and 650 nm is purely ED in nature. If we observe the spectrum figure 9 we can come to conclusion that the intensity of 564 nm is greater than the intensity of 650 nm. This suggests that the emission corresponding to MD is dominant over ED transitions which are in correlation with the results obtained by JO parameters i.e. \(\Omega_2 < \Omega_4\). Furthermore, high is the \(\Omega_6\) values compared to other parameters (\(\Omega_2\) and \(\Omega_4\)) the host under consideration is rigid. In our case \(\Omega_6 > \Omega_4 > \Omega_2\) indicates the host is fairly rigid. The spectroscopic quality of the material is determined by
the ratio $\Omega_4/\Omega_6$ \cite{38}. The present nanophosphor exhibits the highest $\chi = \Omega_4/\Omega_6$ value = 0.79, indicating the LaOCl:Sm$^{3+}$ phosphor display good performance as a host for luminescence activators.

These values of J-O analysis were utilized to compute the line strength of the absorption band by equation (8) and data is available in table 3 which also consists of the mean wavelength ($\bar{\lambda}$), reduced matrix elements, band sum ($\Gamma$) related to the integrated absorption cross section.

For a shift from ground level to higher energy level, The sum of ED and MD probabilities give rise to the radiative transition probability $A (J \rightarrow J')$ which is written as

$$A (J \rightarrow J') = \frac{64\pi^4\hbar^2}{3\hbar^3(2J + 1)} \left\{ \frac{n(n^2 + 2)^2}{9} S_{ED}(J \rightarrow J') + \frac{n^3 S_{MD}(J' \rightarrow J)}{9} \right\}$$ \hspace{1cm} (10)

Where $n^3$ denotes the MD transition and $\frac{n(n^2 + 2)^2}{9}$ is the local field correction for the ED transition.

Figure 12. (a) CIE (b) CCT chromaticity diagram of La$_{1-x}$Sm$_x$OCl (0.01 $\geq x \geq$ 0.09) nanophosphors.
Table 3. Comparison of measured and calculated line strength in La$_1$,Sm$_{0.5}$OCl ($x = 0.05$).

| Transition (From) | $[U^{(2)}]_0$ | $[U^{(4)}]_0$ | $[U^{(6)}]_0$ | Range (nm) | $\lambda$ (nm) | $\Gamma$ (cm$^{-1}$) | $S$ (cm$^2$ rad$^{-1}$ nm$^{-2}$) | $S$ (cm$^2$ rad$^{-1}$ nm$^{-2}$) | $\Delta S$ cm$^2$ |
|------------------|-------------|-------------|-------------|--------|-------------|----------|-----------------|-----------------|----------|
| $^4G_{5/2}$      | 0           | 0.0006      | 0.0515      | 892–1004 | 948         | 2.496 $\times$ 10$^{-20}$ | 0.0795          | 0.032             | 0.0475   |
| $^4G_{7/2}$      | 0           | 0.0206      | 0.3413      | 1025–1153 | 1089       | 7.453 $\times$ 10$^{-20}$ | 0.214            | 0.219             | 0.005    |
| $^4G_{5/2}$      | 0.0020      | 0.1429      | 0.4310      | 1133–1324 | 1239       | 13.25 $\times$ 10$^{-20}$ | 0.334            | 0.335             | 0.001    |
| $^4G_{5/2}$      | 0.0332      | 0.2840      | 0           | 1324–1409 | 1367       | 6.496 $\times$ 10$^{-20}$ | 0.149            | 0.151             | 0.002    |
| $^4F_{3/2}$      | 0.1444      | 0.1364      | 0           | 1409–1518 | 1464       | 6.156 $\times$ 10$^{-20}$ | 0.131            | 0.125             | 0.006    |
| $^4F_{1/2}$      | 0.1939      | 0           | 0           | 1518–1609 | 1564       | 3.788 $\times$ 10$^{-20}$ | 0.075            | 0.079             | 0.004    |

Table 4. Predicted line strengths, branching ratio and transition probabilities in Sm$^{3+}$ doped LaOCl.

| Transitions      | $[U^{(2)}]_0$ | $[U^{(4)}]_0$ | $[U^{(6)}]_0$ | $\lambda$ (nm) | $S$ (cm$^2$ rad$^{-1}$ nm$^{-2}$) | $S$ (cm$^2$ rad$^{-1}$ nm$^{-2}$) | $\Delta S$ cm$^2$ | $A_{ED}$ (S$^{-1}$) | $A_{MD}$ (S$^{-1}$) | $\beta$ |
|------------------|-------------|-------------|-------------|---------|-----------------|-----------------|----------|-----------------|-----------------|------|
| $^4G_{5/2} \rightarrow ^{6}F_{7/2}$ | 0           | 0.000 774  | 0.000 4019 | 1316    | 0.000 29        | 0               | 0.121    | 0               | 0.009 | 0.0047  |
| $^4G_{7/2} \rightarrow ^{6}F_{5/2}$ | 0.001 5040  | 0.000 2204 | 0.000 2510 | 1113    | 0.000 88        | 0               | 0.605    | 0               | 0.007 | 0.0047  |
| $^4G_{5/2} \rightarrow ^{6}F_{3/2}$ | 0.000 8767  | 0.001 4667 | 0.000 0986 | 984     | 0.000 81        | 0.001 93        | 0.805    | 0.966           | 0.0138 | 0.0138  |
| $^4G_{5/2} \rightarrow ^{6}F_{1/2}$ | 0.005 9209  | 0.001 1367 | 0           | 908     | 0.002 96        | 0.005 78        | 3.745    | 3.683           | 0.0581 | 0.0581  |
| $^4G_{5/2} \rightarrow ^{6}F_{1/2}$ | 0.000 9949  | 0.000 0483 | 0           | 868     | 0.000 43        | 0.007 23        | 0.623    | 5.274           | 0.0461 | 0.0461  |
| $^4G_{5/2} \rightarrow ^{6}H_{15/2}$ | 0           | 0           | 0.000 1509 | 867     | 0.000 09        | 0               | 0.131    | 0               | 0.001 | 0.001  |
| $^4G_{5/2} \rightarrow ^{6}H_{1/2}$ | 0.001 0398  | 0           | 0           | 850     | 0.000 43        | 0               | 0.663    | 0               | 0.0052 | 0.0052  |
| $^4G_{5/2} \rightarrow ^{6}H_{13/2}$ | 0           | 0.000 1281 | 0.001 4782 | 768     | 0.000 98        | 0               | 2.049    | 0               | 0.0160 | 0.0160  |
| $^4G_{5/2} \rightarrow ^{6}H_{11/2}$ | 0           | 0.004 3047 | 0.001 6052 | 692     | 0.003 10        | 0               | 8.860    | 0               | 0.0692 | 0.0692  |
| $^4G_{5/2} \rightarrow ^{6}H_{9/2}$ | 0.009 5419  | 0.006 1972 | 0.001 8552 | 633     | 0.008 03        | 0               | 29.98    | 0               | 0.2342 | 0.2342  |
| $^4G_{5/2} \rightarrow ^{6}H_{7/2}$ | 0.000 0124  | 0.008 4249 | 0.007 1842 | 588     | 0.008 50        | 0.005 51        | 39.60    | 12.928          | 0.4103 | 0.4103  |
| $^4G_{5/2} \rightarrow ^{6}H_{5/2}$ | 0.000 2387  | 0.000 7346 | 0           | 0       | 0.000 45        | 0.005 50        | 2.506    | 15.429          | 0.1401 | 0.1401  |

Further $S_{ED}$ can be calculated using equation (9) and $S_{MD}$ can be found by equation,

$$S_{MD}(J' \rightarrow J) = \mu_B B_{J^*} |(S, L)| |L + 2S||S', L')|^2$$

(11)

Here, $\mu_B = \frac{h}{4\pi\epsilon_0}$ be the magnetic dipole parity [39].

Table 4 consists of the obtained values of radiative transition rates $A_{ED}$ and $A_{MD}$.

The total radiative transition probability $A_T$ is found by the addition of $A(J \rightarrow J')$ terms evaluated allover the terminal levels and is represented as,

$$A_T = \sum A(J \rightarrow J')$$

(12)

The radiative lifetime $\tau_{rad}$ of an excited state $J'$, being the reciprocal of $A_T$ and is given by

$$\tau_{rad} = \frac{1}{A_T(J' \rightarrow J)}$$

(13)

Sum of the rate of transition probabilities for all the transition results in the total transition rates which is 127.968 for $^4G_{5/2}$ ($J = 5/2$) and hence for this level the radiative lifetime is 7.81 ms.

The ratio of total photon flux from initial $J'$ to lower manifold $J$ gives the measured branching ratio amongst the manifolds which is given by equation (14)

$$\beta_{meas} = \frac{\int I_{J'}(\lambda)d\lambda}{\int I_J(\lambda)d\lambda}$$

(14)

where, $I_{J'}(\lambda)d\lambda$ is the luminescence intensity and is wavelength dependent.

Likewise calculated fluorescence branching ratios for a transitions initiating from a particular upper manifold ($J'$) which goes to a lower ($J$) [22] is as follows

$$\beta_{calc} = \frac{A(J' \rightarrow J)}{\sum A(J' \rightarrow J)}$$

(15)

Table 5 indicates the measured and computed values of branching ratio, rate of transition ($A_T$), and the percentage difference of 5 mol% Sm$^{3+}$ doped LaOCl nanophosphor for the transitions from $^4G_{5/2} \rightarrow ^{6}H_{5/2}$, $^2T_{2/2}, ^{6}H_{5/2}, ^2T_{1/2}$ and $^2T_{1/2}$ respectively. The slight difference in the measured and calculated values of branching ratios is because of the environment of ligand to metal charge transfer.
Table 5. Values of transition rates ($A_T$), Calculated and measured fluorescence branching ratio, measured Line shape function, emission cross section, gain band width and optical gain of different transition of La$_{1-x}$Sm$_x$OCl ($x = 0.05$) nanophosphor.

| Transition     | $\lambda$ (nm) | $A_T = A_{ld} + A_{ld}(S^{-1})$ | $\beta_{ok}$ | $\beta_{max}$ | Percentage difference | $g(\tau)$ cm | $\sigma(J, J'; \delta) \times 10^{-22}$ cm$^2$ | Gain bandwidth $\times 10^{-28}$ cm$^3$ | Optical gain $10^{-25}$ cm$^2$s |
|----------------|-----------------|---------------------------------|--------------|---------------|-----------------------|----------------|---------------------------------|---------------------------------|------------------|
| $^4G_{5/2} \rightarrow ^6H_{5/2}$ | 564             | 17.935                          | 0.1401       | 0.178         | 23.83                 | 0.0091         | $2.232 \times$                   | 0.815              | 17.41            |
| $^4G_{5/2} \rightarrow ^6H_{7/2}$ | 608             | 52.528                          | 0.4103       | 0.588         | 35.60                 | 0.0043         | 3.983                           | 3.457              | 31.10            |
| $^4G_{5/2} \rightarrow ^6H_{9/2}$ | 650             | 29.98                           | 0.2342       | 0.211         | 10.42                 | 0.0032         | 1.364                           | 1.712              | 10.64            |
| $^4G_{5/2} \rightarrow ^6H_{11/2}$ | 708             | 8.860                           | 0.0692       | 0.023         | 100                   | 0.0196         | 0.979                           | 0.245              | 7.636            |
Table 6. Comparison of JO parameters ($10^{-20}$ cm$^2$), branching ratio, emission cross section and quality factor $\chi = (\Omega_4/\Omega_6)$ of Sm$^{3+}$ ions in the nanophosphors with other systems.

| Phosphor            | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | $\beta_{\text{rad}}$ | $\beta_{\text{man}}$ | $\sigma$ $10^{-22}$ cm$^2$ | $\chi = (\Omega_4/\Omega_6)$ | Trend $\Omega_4$ | Related work               |
|---------------------|-------------|-------------|-------------|-----------------------|-----------------------|-----------------------------|-----------------------------|------------------|---------------------------|
| La$_{1-x}$Sm$_x$OCl | 0.408       | 0.484       | 0.615       | 0.410                 | 0.588                 | 3.98                        | 0.79                        | $\Omega_4 > \Omega_6 > \Omega_2$ | Present work              |
| Sr$_2$SiO$_4$:Sm$^{3+}$ | 0.52        | 0.28        | 0.39        | 0.35                  | 0.66                  | 3.82                        | 0.71                        | $\Omega_6 > \Omega_4 > \Omega_2$ | [22]                     |
| LaF$_3$:Sm$^{3+}$   | 1.0         | 0.5         | 1.5         | 0.376                 | 0.556                 | 14.4                        | 0.33                        | $\Omega_4 > \Omega_6 > \Omega_2$ | [19]                     |
| PZSM$_{0.5}$       | 13.3        | 5.02        | 3.62        | 0.26                  | 0.521                 | 10.3                        | 1.39                        | $\Omega_2 > \Omega_4 > \Omega_6$ | [38]                     |
| LBGS1               | 9.69        | 8.18        | 7.46        | 0.375                 | 0.642                 | 2.82                        | 1.0                         | $\Omega_4 > \Omega_6 > \Omega_2$ | [42]                     |
| PKAZLFSm           | 4.5         | 7.4         | 3.93        | 0.56                  | —                     | 9.53                        | 1.88                        | $\Omega_4 > \Omega_6 > \Omega_2$ | [31]                     |
| K$_2$YF$_5$:Sm$^{3+}$ | 0.38        | 3.55        | 2.18        | 0.506                 | 0.565                 | 0.64                        | 1.63                        | $\Omega_4 > \Omega_6 > \Omega_2$ | [37]                     |
| ZBS1                | 1.93        | 1.87        | 1.79        | 0.379                 | —                     | 9.01                        | 1.04                        | $\Omega_4 > \Omega_6 > \Omega_2$ | [41]                     |
| ZBS3                | 2.49        | 1.64        | 1.61        | 0.316                 | —                     | 10.1                        | 1.02                        | $\Omega_2 > \Omega_4 > \Omega_6$ | [41]                     |

PZSM$_{0.5}$: 0.5 mol% Samarium doped magnesium zinc sulfophosphate glass.
LBGS1: Samarium doped lanthanum borogermanate glass.
PKAZLFSm: Samarium doped zinc fluorophosphates.
ZBS1 & ZBS3: Samarium doped bismuth borate glasses.

High gain and low threshold laser applications expects for higher stimulated emission cross section and also is used for continuous wave laser action [40]. Table 5 also includes the values of emission cross section, Measured Line shape function, optical gain and gain band width of different transition of La$_{1-x}$Sm$_x$OCl ($x = 0.05$) nanophosphor. With the help of equation (16), the room temperature emission cross section of the transition from $^4$G$_{5/2}$ to $^6$H$_{7/2}$ ($J = 5/2, 7/2, 9/2, 11/2$) of 5 mol% Sm$^{3+}$ doped LaOCl nanophosphor are determined

$$\sigma (J, J'; \nu) = \frac{\lambda^2}{8\pi a^2} \frac{\beta_{\text{rad}}(J' \rightarrow J)}{\tau_{\text{rad}}} g(\nu)$$

(16)

where $\lambda$ is the wave number, $\tau_{\text{rad}}$ is radiative lifetime of upper manifold $^4$G$_{5/2}$, $\lambda$ is the fluorescence peak wavelength, $\beta_{\text{rad}}$ be the fluorescence branching ratio, and $g(\nu)$ is line shape function which is resolved by numerical integration of the respective fluorescence spectrum from figure 5. [22].

$$g(\nu) = \frac{I(\nu)}{\int I(\nu) d\nu}$$

(17)

Table 1 gives the asymmetric ratio as measured for various mol % of La$_{1-x}$Sm$_x$OCl ($x = 0.01, 0.03, 0.05, 0.07$ and 0.09). The obtained J-O parameter values indicate that the ions are occupying asymmetric sites and the crystal field is satisfying lack of inversion symmetry, which is evident from the asymmetric ratio values. Equation (18) represents the fraction of integrated intensity of the ED ($I_{\text{ED}}$) to the MD transition ($I_{\text{MD}}$) called the asymmetric ratio using which we get to know the behaviour of crystalline field around the trivalent 4f ions.

$$A = \frac{\int I_{\text{ED}} d\lambda}{\int I_{\text{MD}} d\lambda}$$

(18)

In table 6, gives the comparison of the parameters $\Omega_2$, $\Omega_4$, $\Omega_6$, branching ratios, quality factor and emission cross section for $^4$G$_{5/2} \rightarrow ^6$H$_{7/2}$ in samarium doped matrix [19, 22, 38, 41, 44]. In the present work, the synthesized nanophosphor follows the trend of $\Omega_4 > \Omega_6 > \Omega_2$ and exhibits a branching ratio of 59% for the transition $^4$G$_{5/2} \rightarrow ^6$H$_{7/2}$ which serves to be a critical parameter for laser design due to its characteristic possibility of stimulated emission. The optical gain ($\sigma_\text{g} \times \tau$) and gain bandwidth ($\sigma_\text{g} \times \Delta\nu_{\text{eff}}$) are the factors required to foretell the intensification of the medium where the rare earth ions were located. An optical amplifier should possess greater values of gain bandwidth, emission cross section and optical gain which in our case are found to be 3.457 $\times$ 10$^{-28}$ cm$^2$, 3.983 $\times$ 10$^{-22}$ cm$^2$ and 31.10 $\times$ 10$^{-25}$ cm$^2$ respectively for the transition $^4$G$_{5/2} \rightarrow ^6$H$_{7/2}$ which are presented in table 5. Also the higher values of $\chi = 0.79$ indicates that the present material is optically good as active laser media [41].

4. Conclusion

A series of La$_{1-x}$Sm$_x$OCl ($x = 0, 1, 3, 5, 7$ and 9 mol %) phosphors were prepared via conventional solid state route. The XRD pattern shows that the phosphors are indexed with space group P4/mn (No. 129) to the tetragonal phase. The band gap is obtained as 4.23 eV. An intense orange red emission was monitored at 608 nm
for an optimized 5 mol% Sm$^{3+}$ ion concentration for 408 nm excitation. Optical absorption data for the optimized sample was utilized to determine J-O factors. The obtained J-O parameter value reveals that the ions are occupying asymmetric sites and the crystal field is satisfying lack of inversion symmetry, which is evident from the asymmetric ratio values. The non-radiative energy transfer mechanism is responsible for quenching effect beyond 5 mol% through dipole–dipole interaction. The prepared phosphors were suitable for laser applications due to its high branching ratio of 59% and 3.983 $\times$ 10$^{-22}$ cm$^2$ of emission cross section that corresponds to $^5G_{5/2} \rightarrow ^7H_{7/2}$. The values obtained for optical gain and gain band width indicate the phosphor exhibits the quality of being a better optical amplifier. The results also concludes that the prepared phosphor LaOCl:Sm$^{3+}$ is capable of being a feasible candidate for red element for white LED’s in solid state lighting applications.

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**References**

[1] Kort K R and Banerjee S 2011 Shape–controlled synthesis of well-defined matlocite LnOCl (La, Ce, Gd, Dy) nanocrystals by a novel non-hydrolytic approach Inorg. Chem. 50 5539–44
[2] Du M L, Guo B C, Lei Y D, Liu M X and Jia D M 2008 Carboxylated butadiene–styre rubber/halloysite nanotube nanocomposites: interfacial interaction and performance Polymer 49 4871–6
[3] Marsal A, Rossinyol E, Bimbela F, Tellez C, Coronas J and Cornet A 2005 Characterisation of LaOCl sensing materials using CO$_2$-TPD, XRD, TEM and XPS Sens. Actuators. B 109 38–43
[4] Huayna T and Claudia W 2015 UV, blue, green, yellow, red, and small: newest developments on Eu$^{2+}$/ Eu$^{3+}$-doped phosphors J. Rare Earths 33 1019–21
[5] Jin M, Zhaohao F, Zhaohui H, Yangai L, Chao T and Hekai Z 2014 Preparation and luminescent properties of orange emitting phosphor LaMgAl11O19:Eu$^{3+}$+Opt. Mater. 37 110–4 (2014)
[6] Jia G, You H P, Song Y H, Jia J, Zheng Y Z, Zhang I H, Liu K and Zhang H J 2009 Facile chemical conversion synthesis and luminescence properties of uniform Ln$^{3+}$ (Ln = Eu, Tb)-doped NaLuF$_4$ nanowires and LuBO$_3$ micro disks Inorg. Chem. 48 10193–201
[7] Judd B R 1962 Optical absorption intensities of rare-earth ions Phys. Rev. 127 750–62
[8] Ofelt G S 1962 Intensities of crystal spectra of rare-earth ions J. Chem. Phys. 37 511–20
[9] Walsh B M, Di Bartolo B and Forte O (ed) 2006 Judd ofelt theory: principles and practices Advances in Spectroscopy for Lasers and Sensing (Netherlands: Springer) 403–33
[10] Gorlitz–Warland C and Binnemans K 1999 Ch 167 Spectral intensities of f-f transitions Handbook on the Physics and Chemistry of the Rare Earths ed K A Gschneidner Jr and L Eyring 26 (Amsterdam: North–Holland) 101–264ISBN: 978–0–444–50185–1
[11] Park S and Cho S H 2014 Spectral–converting study of La$_{1–m}$–Eu$_m$Yb$_{0.5}$OCl (m = 0.001–0.2, n = 0.01) phosphors J. Lumin. 153 90–5
[12] Zak A K, Majid W H A and Darroudi M 2012 Facile synthesis and characterization of lanthanum (III) oxychloride nanoparticles using a natural polymeric matrix Mater. Chem. Phys. 136 705–9
[13] Wei Z X, Wang Y, Zhang X Y and Hua C W 2010 Combustion synthesis and effect of LaMnO$_3$ and LaOCl powder mixture on HMX thermal decomposition Thermochim. Acta. 499 111–6
[14] Lee J, Zhang Q and Saito F 2001 Mechanochemical synthesis of LaOCl (X = Cl, Br) and their solid state solutions J. Solid State Chem. 160 469–73
[15] Kim S W, Jyokko K, Masui T and Imanaka N 2012 Green-emitting (La, M, TbOCl (M = Mg, Ca, Sr)) phosphors Opt. Mater. 35 280–284.
[16] Lee S S, Park H I, Joh C H and Byeon S H 2007 Morphology dependent photoluminescence properties of LnOCEu (Ln=La and Gd) J. Solid State Chem. 180 3529–34
[17] Kong Q, Wang J, Dong X, Yu W and Liu G 2013 Synthesis and luminescence properties of LaOCl:Eu$^{3+}$ nanomaterials via the combination of electrospinning with chlorination technique J. Mater. Sci., Mater. Electron. 24 4753–56
[18] Choubey A, Som S, Biswas M and Sharma S K 2011 Characterization of optical transitions of Eu$^{3+}$ in lanthanum oxychloride nanophosphor J. Rare Earths 29 495–8
[19] Hoang M H, Hoa T T Q, Vu L V and Long N N 2016 Optical properties and Judd–Ofelt analysis of Sm ions in Lanthanum trifluoride nanocrystals J. Mater. Sci., Mater. Electron. 28 884–91
[20] Nallamala K, Baker A P and Wang G G 2017 Synthesis and luminescence properties of MgO: Sm$^{3+}$ phosphor for white light-emitting diodes J. Mol. Struct. 1129 211–5
[21] Do I V, Tuyen V P, Quang Y K, Thanh N T, Ha V T T, Khaidukov N M, Lee Y and Huy B T 2012 Judd–Ofelt analysis of spectroscopic properties of Sm$^{3+}$ ions in KYF$_3$ crystal J. Alloys Compd. 520 262–5
[22] Manjunath C, Rudresha M S, Walsh B M, Hari Krishna R, Panigrahi B S and Nagabhushana B M 2018 Optical absorption intensity analysis using Judd–Ofelt theory and photoluminescence investigation of orange-red Sr$_2$SiO$_4$:Sm$^{2+}$ nanophosphors Dyes Pigm. 148 118–29
[23] Cullity B D 1956 Elements of X-ray Diffraction 2nd edn (California: Addison-Wesley Publishing Company Inc) 501–3
[24] Khorasani Z, Abd W H and Darroudi M 2012 Synthesis and characterization of lanthanum (III) oxychloride nanoparticles using a natural polymeric matrix Mater. Chem. Phys. 136 705–9
[25] Rossini P and Holmgren A 2009 A fourier transform infrared (FTIR) and thermogravimetric analysis (TGA) study of oleate adsorbed on magnetite nano-particle surface Appl. Surf. Sci. 255 3901–5
[26] Dhananjaya N, Shivakumara C, Saraf R, Behera S and Nagabhushana H 2015 Comparative study of Eu$^{3+}$–activated LnOCl (Ln=Lm and Gd) phosphors and their Judd–Ofelt analysis J. Rare Earths 33 946–53
[27] Carnall W T, Fields P R and Rajnak K 1968 Electronic energy levels in the trivalent lanthanide aquo ions. I. Pr3+, Nd3+, Pm3+, Sm3+, Dy3+, Ho3+, Er3+, and Tm3+ J. Chem. Phys. 49 4424–4442.

[28] Blase G 1968 Energy transfer in oxidic phosphors Phys. Lett. 28 444–5

[29] Worawut N, Worawat W, Wantana K and Thanawat R 2017 Effect of local structure of Sm3+ in MgAl2O4:Sm3+ phosphors prepared by thermal decomposition of triethanolamine complexes on their luminescence property J. Alloys Comp. 701 1019–26

[30] Van Uitert L G 1967 Characterization of energy transfer interactions between rare earth ions J. Electrochem. Soc. 114 1048–53

[31] Lim K S, Vijaya N, Kesavulu C and Jayasankar C 2013 Structural and luminescence properties of Sm3+ ions in zinc fluorophosphate glasses Opt. Mater. 35 1557–63

[32] Rasool S N, Moorthy L R and Jayasankar C 2013 Spectroscopic investigation of Sm3+ doped phosphate based glasses for reddish-orange emission Opt. Commun. 311 156–62

[33] Raju G S R, Jin Y P, Hong C J, Pavitra E, Moon E B K, Jung H J and Hwan K J 2011 Excitation induced efficient luminescent properties of nano crystalline Tb3+/Sm3+Ca2Gd8Si6O26 phosphors J. Mater. Chem. 21 6136–9

[34] Krupke W F 1971 Radiative transition probabilities within the 4f3 ground configuration of Nd:YAG IEEE J. Quantum Electron. QE-7 153–9

[35] Krupke W F 1974 Induced-emission cross sections in neodymium laser glasses J. Quantum Electron. QE-10 450–7

[36] Jorgensen C K and Reisfeld R 1983 Judd–Ofelt parameters and chemical bonding J. Less Common Met. 93 107–12

[37] Do P V, Tuyen V P, Quang V X, Thanh N T, Ha V T T, Khaidukov M N, Lee Y I I and Huy B T 2012 Judd–Ofelt analysis of spectroscopic properties of Sm3+ ions in K, YF3 crystal J. Alloys Compd. 520 262–5

[38] Tanko Y A, Ghoshal S K and Sahar M R 2016 Ligand field and Judd–Ofelt intensity parameters of samarium doped tellurite glass J. Molecular Struct. 1117 64–8

[39] Ahmadi F, Hussin R and Ghoshal S K 2016 Judd–Ofelt intensity parameters of samarium-doped magnesium zinc sulfophosphate glass J. Non-Crystalline Solids. 448 43–51

[40] Jayasimhadri M, Cho E J, Jung K W and Lee H S 2008 Spectroscopic properties and Judd–Ofelt analysis of Sm3+ doped lead–germanate–tellurite glasses J. Phys. D: Appl. Phys. 41 175101–12

[41] Agarwal A, Pal I, Sanghi S and Aggarwal M P 2009 Judd–Ofelt parameters and radiative properties of Sm3+ ions doped zinc bismuth borate glasses Opt. Mater. 32 339–44

[42] Rajaramakrishna R, Knorr B, Dierolf V, Anavekar R V and Jain H 2014 Spectroscopic properties of Sm3+-doped lanthanum borogermanate glass J. Lumine. 156 192–8