Yellow Luminescence from LaAlO₃:Sm³⁺ Nano-Phosphors Prepared by Sol-Gel Technique

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Abstract: LaAlO₃:Sm³⁺, nano-phosphors with varying dopant concentrations of Sm³⁺ from 1 to 20 mol% were prepared by Sol-Gel Synthesis and the samples were further heated to 600,700, and 1000 °C to improve the crystallinity of the materials. The advantages of gel combustion base process have been applied to obtain nano particles in the pure homogeneous form . Finally the phosphor was characterized by XRD, SEM, PL measurement to check the crystallinity, particles size and luminescence intensity of the phosphor respectively. XRD results reveal that the sample begins to crystallize at 600 °C, and pure LaAlO₃ phase can be obtained at 700°C. SEM images indicate that the Sm³⁺ -doped LaAlO₃ phosphors are composed of aggregated spherical particles with sizes ranging from 40 to 80nm. Under the excitation of UV light (245nm) and low-voltage electron beams (1–3kV), the Sm³⁺ -doped LaAlO₃ phosphors show the characteristic emissions of phosphor consist of five emission peaks, which are attributed to the transitions from ⁴G₅/₂ state to ⁵H₇/₂ (J=5/2, 7/2, 9/2, 11/2, 13/2) states of Sm³⁺ ions with Yellow, Orangish-Yellow, Orangish-red and red color having emission peak located at 565, 598, 615, 633, 707 nm respectively. Among these emission peaks, the transition emission ⁴G₅/₂→⁵H₇/₂ (J=5/2, 7/2, 9/2) for peak at 565, 598, 615nm is strongest for Yellow, Orangish-Yellow and Orangish-red emission is due to the magnetic dipole transition of Sm³⁺ ion having a magnetic dipole (MD) allowed one and also an electric dipole (ED) dominated one but the other weak transition ⁴G₅/₂→⁵H₃/₂ & ⁴G₅/₂→⁵H₁/₂ (653 nm, 707nm red) is purely an ED one. Highest photoluminescence intensity is observed with 3 mol% doping of Sm³⁺ made LaAlO₃:Sm³⁺, a strong competitor for promising Yellow, Yellow-orange & also for Orange-red colored display applications.

Keywords: Sol-gel synthesis, Nano-phosphors, LaAlO₃:Sm³⁺ , Host lattices, Co-dopants , Magnetic dipole, Electric dipole.

1. Introduction

Presently the development of flat panel displays, such as field emission displays (FEDs), plasma display panels (PDPs) and thin film electro-luminescent devices (TFEL), or white light emitting diode (LED), have emerged as the principal motivation for research into rare-earth luminescence, and the present article therefore concentrates on the variety of different ways in which rare-earth luminescence has been exploited in this field[1-4]. The rare-earth ions are characterized by a partially filled 4f shell that is well shielded by 5s² and 5p⁶ orbitals. The emission transitions, therefore, yield sharp lines in the optical spectra. The use of rare-earth element based phosphor, based on “line-type” f–f transitions, can narrow to the visible, resulting in both high efficiency and a high lumen equivalent [8]. It is, therefore, urgent to find a stable, inorganic rare-earth-based phosphor with high luminescence efficiency. The phases composed by the elements with the smaller difference of electronegativity (X), corresponds to a narrower band gap of compounds, leading to higher conductivity. The difference between the electronegativities of Si and O (X = 1.54) exceeds that between Ge and O (X= 1.43)[9]. During the past decades, rare earth ions doped in various host materials have been widely studied due to their characteristic luminescence properties. Among the rare earth ions,Sm³⁺, Eu³⁺, Tb³⁺, and Dy³⁺ are important activator ions for producing visible light [10-17]. Sm³⁺ activated luminescent materials have received much attention at present [18-19]. They show bright emissions in orange and red regions to the transitions from the excited state ⁴G₅/₂ to the ground state ⁴H₇/₂ and the other state ⁵H₇/₂ (J = 7/2, 9/2 , and 11/2), which can be used in high density optical storage, temperature sensors, under sea communication, various fluorescent devices, color display, and visible solid-state lasers [20–21]. Luminescence of is especially useful to probe the local structure of luminescent centers in a host lattice because of its simple energy level structure, great sensitivity to ligand field, and similar lanthanide chemical properties to the other rare earth ions [22-23]. Growing interest recently has been focused on luminescence of trivalent rare earth ions in phosphates, tungstates, borates, molibdates, and aluminates, among which rare earth doped borates are especially attractive because of their wide UV transparency, exceptional optical damage thresholds, excellent chemical and thermal stability, and high luminescence efficiency[24-34]. The luminescence study of a series of such compounds provides much valuable information for optical applications.

It is our main interest to synthesize another family of newly developed Sm³⁺ doped phosphors via low temperature initiated gel based combustion process and investigate their photoluminescence properties in view of the commercial importance of yellow and oragnish-red color emitting phosphors. Generally, the typical Sm-activated phosphors usually show charge-transfer absorption of Sm³⁺ –O₂⁻ interaction in the UV region. However, there was no obvious charge-transfer absorption of Sm³⁺ –O²⁻ interaction or host absorption band that could be detected in the excitation spectrum. Only direct excitation of Sm³⁺ ions could be observed. It is recognized that Sm³⁺ interaction with the host lattice is very weak, and no energy transfer occurs between Sm³⁺ and host. As we know different material preparation methods such as solid state reactions, sol-gel techniques[35], hydroxide precipitation[36], hydrothermal synthesis[37], spray pyrolysis[38], laser evaporation[39] and combustion
synthesis [40- 42] has been investigated for the preparation of oxide phosphors. These methods have their advantages as well as limitations. In multi step processes like heating at high temperatures and long processing time are required. The sol-gel method is a novel technique through which a voluminous, foamy nano crystalline powder can be prepared within a few minutes. This technique is ideal for producing the fine, pure and single-phase powders. have some important effects on material microstructure and physical properties. The sol-gel method provides an interesting alternative over other elaborated techniques because it offers several attractive advantages such as: simplicity of experimental set-up; surprisingly short time between the preparation of reactants and the availability of the final product; and being cheap due to energy saving.

The main aim of the sol-gel is the rapid decomposition of the rare earth nitrate in the presence of an organic fuel. During the reaction, many gases, such as CO₂, N₂, NO₂ [43] and H₂O, as well as a large amount of heat are released in a short period of time before the process terminates with white, foamy and crispy products. Many times final products are found to be composed of nano-sized particles. This work has been carried out with the aim to prepare ,compare and investigate the high intensity photoluminescence nano sized crystalline powders of LaAlO₃ doped with Sm³⁺ sintered at 1000°C temperature.

A series of La₁₋ₓSmₓAlO₃ phosphor have been synthesized by sol-gel method with the dopant concentration ranging from 01 to 20 mol%. The crystalline structure and morphology of prepared nano-materials have also been discussed. The crystalline structure of prepared materials, morphology of particles and their photoluminescence properties are characterized by XRD, SEM and PL spectra with 245 nm lasers for excitation. The present work is mainly focused on preparation characterization & discussion on the LaAlO₃:Sm³⁺ nano phosphor showing high luminescence.

2. Experimental

All the chemicals used were of high purity (Aldrich 99.99%). High purity chemicals La(NO₃)₃, Al(NO₃)₃, Sm(NO₃)₃, in such a way that total [La₃⁺ + Sm³⁺] = 1.0 mole, and carboxyhydrate as a fuel were used to prepare Sm³⁺ doped nano crystals with general formula Laₙ₋ₓAlO₃ : Smₙ⁺ , where x is 1 to 20 mol%. This mixture was heated in a crucible on a hot plate for about half an hour to form a viscous gel. After evaporating most of the water contents, crucible was placed into a microwave oven for 5 minutes to propagate for the combustion reaction which is done in a preheated furnace maintained at 600,700, and 1000 °C to improve the crystallinity of the materials. XRD results reveal that the sample begins to crystallize at 600°, and pure LaAlO₃ phase can be obtained at 700°C. The stoichiometric amount of the fuel was calculated by using total oxidizing and reducing valences [43]. The paste was made by dissolving metal nitrates and fuel in a minimum amount of doubly distilled water. In furnace, the material had rapid dehydration followed by decomposition, generating combustible gases which burnt with a flame and producing a white solid. The solid thus obtained was again fired at 1000°C for 3h to increase the crystallinity. Finally the powder was characterized by XRD, SEM, PL measurement to check the crystallinity, particles size and luminescence intensity of the phosphor respectively.

3. Characterization & Discussion

3.1 XRD studies

The structural characterizations of compounds were done on XRD diffractometer (Rigaku Ultima IV) using Cu Kα radiation (1.541841 Å).

![Figure1: XRD spectra of LaAlO₃:Sm³⁺ phosphors showing sharp xrd peaks.](image)

The structural characterizations of compounds were done on XRD diffractometer (Rigaku Ultima IV) using Cu Kα radiation. XRD results reveal that the sample begins to crystallize at 600°C , and pure LaAlO₃ phase can be obtained at 700°C . Crystallinity, particle size, and surface roughness of the phosphor materials have strong effects on the photoluminescence. Fig1 showed the X-ray diffractograms of Sm³⁺ doped LaAlO₃ LaAlO₃:Sm³⁺ phosphors . The phase analysis demonstrated (Fig.1) that LaAlO₃:Sm³⁺ belongs to trigonal crystal system with R3m (160) space group having unit cell dimensions: a = b = 5.364 Å and c = 13.11 Å. This was in good agreement with the standard JCPDS C. NO. 031-0022. In this phosphor, trivalent lanthanum ions were replaced by trivalent samarium ions. Dopant ions (Sm³⁺) concentration variation from 1mol% to 10 mol% have no noticeable effect on the obtained X-ray diffractograms of the as-prepared LaAlO₃:Sm³⁺ phosphors, indicating that the doped ions were occupied the primordial La³⁺ sites of the LaAlO₃ lattice. All measurements were carried out at room temperature. The structural characterization was done by a high resolution X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer in the θ–2θ configuration and using Cu Kα radiation (1.5418 Å) using Scherrer equation (1).

\[
\tau = K\lambda/\beta \cos \theta
\]

where
- \( \tau \) is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;
• $K$ is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;
• $\lambda$ is the X-ray wavelength;
• $\beta$ is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is sometimes denoted as (2θ);
• $\theta$ is the Bragg angle was used to calculate the crystallite size of all materials.

At least five prominent peaks from each XRD (samples with various Sm$^{3+}$ concentration) were used for calculation and peaks belonging to different phases were also taken into consideration. Maximum and minimum values obtained for each type of lattice are reported as range of crystallite size (e.g. 40±5nm for LaAlO$_3$).

3.2 SEM micrograph and particle size analysis

The SEM micrographs were obtained by JEOL ISM6300 scanning electron microscope. SEM images indicate that the Sm$^{3+}$-doped LaAlO$_3$ phosphors are composed of aggregated spherical particles with sizes ranging from 40±5 nm.

Figure 2: SEM micrographs of phosphor particles (a,b, c, d): (a) LaAlO$_3$ lattice (b to d) LaAlO$_3$Sm$^{3+}$

Figures 2 (a to d) exhibited the surface morphologies of LaAlO$_3$, LaAlO$_3$:Sm$^{3+}$ particles. Generally non-uniformity of shape and size is associated with the non-uniform distribution of temperature and mass flow in the combustion flame. However the SEM images of LaAlO$_2$:Sm$^{3+}$ particles (fig. 2a, b) show small and coagulated particles of nearly cubical shape with larger size distribution. The surface morphology of LaAlO$_2$:Sm$^{3+}$ lattices as depicted in the picture 2a and 2b is smooth and aggregated spherical particles of different sizes are observed. The smooth surface of phosphor can reduce the non-radiation and scattering, thus beneficial to the luminescence efficiency in application[44-45]. The dense packed small particles can prevent the phosphor from aging.

3.3 Photoluminescence Properties

For the photoluminescence measurement, 0.05g powder samples were pressed into pellets and then exposed to a He–Cd laser (245nm) with an optical power of 30mW for excitation. The emitted light was analyzed by HR-4000 Ocean Optics USB spectrometer optimized for the UV–vis range. Under the excitation of UV light (245nm) and low-voltage electron beams (1–3kV), the Sm$^{3+}$-doped LaAlO$_3$ phosphors show the characteristic emissions of the Sm$^{3+}$ at $^{4}G_{5/2}$→$^{4}H_{j}$ ($j=5/2, 7/2, 9/2, 11/2$) transitions and strongest yellow, Yellow-orange & Orange-red color with $^{4}G_{5/2}$→$^{4}H_{11/2}$ ($j=5/2, 7/2, 9/2$). The room-temperature emission spectra of Sm$^{3+}$ doped LaAlO$_3$ crystals with different doping concentrations are shown in figures 3 (a to b). The emission spectra were obtained by monitoring at 245nm under an excitation of ultraviolet light. The obtained products emitted the red luminescence of varying intensities, which showed the activator Sm$^{3+}$ had successfully entered the host lattice of LaAlO$_3$. The characteristic emissions of phosphor consist of five emission peaks, which are attributed to the transitions from $^{4}G_{5/2}$ state to $^{4}H_{j}$ ($j=5/2, 7/2, 9/2, 11/2$) states of Sm$^{3+}$ ions. Among these, emission peak located at 565-577, 598, 617-619, 653-655, 708-709, are attributed to the transitions of $^{4}G_{5/2}$→$^{4}H_{5/2}$, $^{4}G_{5/2}$→$^{4}H_{7/2}$, $^{4}G_{5/2}$→$^{4}H_{9/2}$, $^{4}G_{5/2}$→$^{4}H_{11/2}$ and $^{4}G_{5/2}$→$^{4}H_{13/2}$, respectively [44-50]. Among these emission peaks, the transition emission $^{4}G_{5/2}$→$^{4}H_{13/2}$ (565nm, strongest yellow, a strong Yellow-orange located at 598nm & 615 nm for orange-red color due to the $^{4}G_{5/2}$→$^{4}H_{5/2}$, $^{4}H_{7/2}$, $^{4}H_{9/2}$ magnetic dipole transition of Sm$^{3+}$ ion having a magnetic dipole (MD) allowed one and also a electric dipole (ED) dominated one and the other transition $^{4}G_{5/2}$→$^{4}H_{11/2}$ (653 nm, 708-709nm, red) is purely an ED one. The MD transition does not appreciably depend on the chemical surroundings of the luminescent center and its symmetry; however, the ED transition belongs to hypersensitive transitions. Generally, the intensity ratio of ED to MD transitions has been used to evaluate the symmetry of the local environment of the trivalent 4f ions. The greater the intensity of the ED transition, the more the asymmetry nature [51]. The exact positions of emission peaks in various lattices are shown in table 1. The $^{4}G_{5/2}$→$^{4}H_{5/2}$, $^{4}H_{7/2}$, $^{4}H_{9/2}$ transition is well known to be mainly a magnetic dipole transition when the Sm$^{3+}$ ions locate in a high symmetric position while the $^{4}G_{5/2}$→$^{4}H_{11/2}$, $^{4}H_{13/2}$ transitions are essentially electric dipole transitions which appear only when Sm$^{3+}$ ion locates at sites without inversion symmetry [52-53]. In fig 3, the emission intensity of all peaks increased with increase of doping concentration from 1% to 3 mol % and then starts decreasing. It becomes nearly one fifth with 20 mol% doping of Sm$^{3+}$ in LaAlO$_3$:Sm$^{3+}$ phosphors. The emission and decay behaviors of the $^{4}G_{5/2}$→$^{4}H_{7/2}$ transition depend on the concentration of Sm$^{3+}$ ions. The emission intensity increases with Sm$^{3+}$ concentration up to 3 mol%, and then decreases quickly. The decay time also begins to decrease rapidly at around 3 mol%. At higher concentrations (x > 0.03), however, the observed decay were non-exponential, and the non-exponential change becomes more prominent as (Sm$^{3+}$) content increases, revealing that more than one relaxation process exists. It is expected that with the increase of Sm$^{3+}$ ions, photoluminescence should increase. However, the emission intensity tends to decrease above 3 mol% of Sm$^{3+}$ ions due to concentration quenching [54], because of non-radiative interaction between ions as the resonant energy transfer becomes stronger. As the concentration is increased, the Sm$^{3+}$ ions are packed closer and closer together, which favors the transfer of energy from
one Samarium ion to the next by a resonance process; the energy eventually reaches a sink from which it is dissipated by non-radiative processes rather than by the emission of visible light [55-56].

Table 1: The emission peaks in LaAlO₃:Sm³⁺ nano-phosphors

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Yellow (nm) Strong peak</th>
<th>Orange (nm) Strong peak</th>
<th>Red (nm) Strong peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>G₃₅₂→⁴H₅₂</td>
<td>565</td>
<td>598, 614, 625</td>
<td>655, 657, 708</td>
</tr>
<tr>
<td>La₃₁₃O₃:Sm³⁺</td>
<td>577</td>
<td>598 &amp; 615</td>
<td>653 &amp; 709</td>
</tr>
<tr>
<td>La₃₁₃O₃:Sm³⁺AlO₃</td>
<td>565</td>
<td>599, 612, 625</td>
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<td>654, 708</td>
</tr>
</tbody>
</table>

In the present case, the emission spectrum shows three strong sharp peaks at the 565, 598nm and 615nm corresponding to the magnetic dipole transition (⁴G₃₅₂→⁴H₅₂ , J=5/2 , 7/2) and electric dipole transition (⁴G₃₅₂→⁴H₅₂ , J=9/2) of Sm³⁺ emission respectively. Other weak intensity peaks are seen on right side of these three strong peaks. It may be mentioned that similar results from magnetic dipole transition (⁴G₃₅₂→⁴H₅₂ , J=5/2 , 7/2) were observed for Sm³⁺ doped LaAlO₃ host [57] and the strong yellow, yellow-orange & orange-red emission of the prepared LaAlO₃:Sm³⁺ nano-phosphors had already not been proposed for its probable utility for display applications.

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4. Conclusion

LaAlO₃:Sm³⁺ nano-phosphors with varying dopant concentrations of Sm³⁺ from 1 to 20 mol% were prepared by sol-gel synthesis and the samples were further heated to 600,700, and 1000 °C to improve the crystallinity of the materials. The advantages of gel combustion base process have been applied to obtain nano particles in the pure homogeneous form. Finally the phosphor was characterized by XRD, SEM, PL measurement to check the crystallinity, particles size and luminescence intensity of the phosphor respectively. XRD results reveal that the sample begins to crystalize at 600°C , and pure LaAlO₃ phase can be obtained at 700°C. SEM images indicate that the Sm³⁺-doped LaAlO₃ phosphors are composed of aggregated spherical particles with sizes ranging from 40 to 80nm. Under the excitation of UV light (245nm) and low-voltage electron beams (1-3KV), the Sm³⁺-doped LaAlO₃ phosphors show the characteristic emissions of phosphor consist of five emission peaks, which are attributed to the transitions from ⁴G₃₅₂ state to ⁴H₅₂ (J=5/2, 7/2, 9/2) states of Sm³⁺ ions with Yellow, Orangish-Yellow, Orangish-red and red color having emission peak located at 562, 598, 615, 653, 707 nm respectively. Among these emission peaks, the transition emission ⁴G₃₅₂→⁴H₅₂ (J=5/2, 7/2, 9/2) for peak at 562, 598, 615nm is strongest for Yellow, Orangish-Yellow and Orangish-red emission is due to the magnetic dipole transition of Sm³⁺ ion having a magnetic dipole (MD) allowed one and also an electric dipole (ED) dominated one but the other weak transition ⁴G₃₅₂→⁴H₅₂ & ⁴G₃₅₂→⁴H₅₂ (563 nm, 707nm red) is purely an ED one. Highest photoluminescence intensity is observed with 3 mol% doping of Sm³⁺ made LaAlO₃:Sm³⁺, a strong competitor for promising Yellow, Yellow-orange & also for Orange-red colored display applications. The prepared LaAlO₃:Sm³⁺ nano-phosphors had already been proposed for its probable utility for display applications and so became more attractive for further research work.

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References

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