Green Light Emitting Tb\(^{3+}\) Doped Phosphors - A Review

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Abstract

WLEDs were the potential materials for significantly improving lighting efficiency, resulting in reduction of the excitation energy and also reduction in pollution from fossil fuel power plants. To enhance the quality of white-light, the researches on single-component phosphor are very much essential. Green light emitting phosphors are widely used in solid state lighting technology. Tb\(^{3+}\) ions are doped into different hosts and they are excited by UV or NUV light to emit green light. This review presents, different hosts like silicates, oxides, phosphates and titanates based Tb\(^{3+}\) ions doped phosphor. Attempts were made to analyse preparation technique and photoluminescence characteristics of phosphors. Finally potential material among selected materials is identified for light emitting display device applications.

Introduction

Nanoparticles gained an immense interest because of its size-dependent properties; therefore research on nanoparticles gained an immense interest for materials science researchers. Rare earth ions in different host lattices like oxides, silicates, phosphates and titanates were studied widely due to its unique spectroscopic properties for the development of rare-earth luminescent materials for lamps, cathode ray tubes, radiation monitoring systems, lasers, scintillators, bio sensors and white light-emitting diodes (WLEDs). WLEDs were the potential materials for significantly improving lighting efficiency, resulting in reduction of the...
excitation energy and also reduction in pollution from fossil fuel power plants. To enhance the quality of white-light, the researches on single-component phosphor are very much essential. The efficient single component luminescent materials have wide range of applications due to their possible photonic applications, good luminescent characteristics, stability in high vacuum, biosensors and absence of corrosive gas emission under electron bombardment when compared to currently used sulfide based phosphors. Among rare earth ions, Tb$^{3+}$ were used to prepare green light emitting phosphor because, Tb$^{3+}$ doped samples can be excited using the radiation near UV regions, i.e. the emission does not require mercury for excitation$^{1}$.

Review on synthesis of green light emitting Tb$^{3+}$ doped phosphors

Tb$^{3+}$ doped in different hosts and their preparation technique, calcination temperature required to form the phosphor is given in Table 1. Mg$_2$SiO$_4$:Tb$^{3+}$ phosphors were prepared by solution combustion method at low temperature, without any further calcinations. The oxalyl di-hydrazide (ODH) fuel was used for the preparation. This method of preparation with ODH fuel saves energy as calcination is not required. Gadolinium aluminium garnet (GAG):Tb$^{3+}$ phosphors$^2$ were prepared by solvothermal method. The prepared powders were calcined at 1300 °C for 3 h, to get single phase phosphors. LaAlO$_3$:Tb$^{3+}$ phosphors$^3$ were prepared by combustion method and calcined at 800 °C for 4 h to get pure LaAlO$_3$. Lu$_2$O$_3$:Tb$^{3+}$ phosphors were prepared by combustion method without any post calcinations. MLa$_2$O$_3$(M=Sr or Ba):Tb$^{3+}$ phosphors$^5$ were successfully synthesized via tartaric acid assisted sol-gel method. The synthesized phosphors were fired at 500–900°C for 3 h to investigate the influence of heat treatment on the particle size and luminescence intensity of the nanoprophosphor. Sodium calcium multiphase silicate (SCMS):Tb$^{3+}$ phosphors$^6$ were prepared by sol-gel technique. The gels were grind and pre-fired at 500 °C for 2 h in air, then fully ground and annealed at 900 °C for 1 h in a reducing atmosphere of 5% H$_2$ in N$_2$ gas to obtain final phosphor powders. NaGd(MoO$_4$)$_2$:Tb$^{3+}$ phosphors$^7$ were prepared by hydrothermal method. As prepared phosphors were used for further characterisations without any calcination. YBO$_3$:Tb$^{3+}$ phosphors$^8$ were prepared by combustion method using urea as fuel. The prepared phosphors were annealed at 1000 °C for the comparison. Ca$_2$SnO$_4$:Tb$^{3+}$ phosphors$^9$ were prepared by solid state reaction method at high temperature 1400 °C. Zn$_3$(PO$_4$)$_2$:Tb$^{3+}$ phosphors$^{10}$ were prepared by sonochemical process. As prepared phosphors were used for characterisations without calcinations. Zn$_2$TiO$_4$:Tb$^{3+}$ phosphors$^{11}$ were prepared by combustion method using ODH fuel and the product was calcined at 1000 °C.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Phosphor</th>
<th>Preparation technique</th>
<th>Calcination</th>
<th>Reference temperature</th>
</tr>
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<tr>
<td>1</td>
<td>Mg$_2$SiO$_4$:Tb$^{3+}$</td>
<td>combustion</td>
<td>Without calcination</td>
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<tr>
<td>2</td>
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<td>solvothermal</td>
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<tr>
<td>3</td>
<td>LaAlO$_3$:Tb$^{3+}$</td>
<td>combustion</td>
<td>800 °C</td>
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<tr>
<td>4</td>
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<td>combustion</td>
<td>Without calcination</td>
<td>[4]</td>
</tr>
<tr>
<td>5</td>
<td>MLa$_2$O$_3$(M=Sr or Ba):Tb$^{3+}$</td>
<td>Sol–gel</td>
<td>500–900 °C</td>
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</tr>
<tr>
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<td>SCMS:Tb$^{3+}$</td>
<td>sol–gel</td>
<td>900 °C</td>
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<tr>
<td>7</td>
<td>NaGd(MoO$_4$)$_2$:Tb$^{3+}$</td>
<td>Hydrothermal</td>
<td>Without calcination</td>
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<td>8</td>
<td>YBO$_3$:Tb$^{3+}$</td>
<td>combustion</td>
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<tr>
<td>9</td>
<td>Ca$_2$SnO$_4$:Tb$^{3+}$</td>
<td>Solid state reaction</td>
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<td>10</td>
<td>Zn$_3$(PO$_4$)$_2$:Tb$^{3+}$</td>
<td>Sonochemical</td>
<td>Without calcination</td>
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<td>11</td>
<td>Zn$_2$TiO$_4$:Tb$^{3+}$</td>
<td>combustion</td>
<td>1000 °C</td>
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</table>
Review on photoluminescence (PL) properties of green light emitting Tb\textsuperscript{3+} doped phosphors

PL is the emission of light that follows the absorption of photons by nanomaterials. When Tb\textsuperscript{3+} doped materials were excited by UV or near UV light, it emits green light. Different materials of different structure, particle size and morphology were used to prepare phosphors. Detailed analysis of photoluminescence characteristics of Tb\textsuperscript{3+} doped materials is discussed as follows.

Mg\textsubscript{2}SiO\textsubscript{4}: \textsuperscript{5+} Tb\textsuperscript{3+} - 1 phosphors (1- 11 mol\%) are orthorhombic in structure with crystal size 15–25 nm. The phosphors were excited at 377 nm based on its excitation spectrum. In general the emission of Tb\textsuperscript{3+} ions occurs due to the transitions of 5D\textsubscript{3} and 5D\textsubscript{4} excited states to the 7F\textsubscript{J} ground states. The emission spectrum lines are separated in two groups. The blue emission group from 5D\textsubscript{3} → 7F\textsubscript{J} (J = 5, 4 and 3) below 480 nm and the green emission group from 5D\textsubscript{4} → 7F\textsubscript{J} (J = 6, 5, 4 and 3) above 480 nm. The 3 mol% doped sample showed maximum intensity thereafter it decreased due to concentration quenching. The concentration quenching occurs based on following two factors: (i) the excitation migration due to resonance between the activators gets enhanced when the doping concentration is increased, and thus the excitation energy reaches quenching centers, and (ii) the activators are paired or coagulated and are changed to quenching centers. The energy can also be transferred non-radiatively by theradiative reabsorption or multipole-multipole interaction. The Commission International De l’Eclairage (CIE) coordinates fall in green region of the CIE diagram.

Gadolinium aluminium garnet (GAG): Tm\textsuperscript{3+} phosphors\textsuperscript{2} are indexed to cubic phase with average crystallite size 92 nm. The phosphors were excited at 279 nm and emission spectra were recorded which shows blue and green emission. In this work, concentration quenching was studied separately for blue and green emission, which was different in both the cases. Blue emission quenched for 0.4 mol% whereas green emission for 5 mol%. LaAlO\textsubscript{3}: Tm\textsuperscript{3+} phosphors\textsuperscript{3} were excited by 377 nm excitation with high concentrations like 2%, 5%, 10%, 15% and 20%. In this report, they have claimed that, blue emission transition is not possible due to such high concentration. Emission intensity quenched at 10% concentration. Lu\textsubscript{2}O\textsubscript{3}: Tm\textsuperscript{3+} phosphors were excited by 16.7 eV photons at room temperature. Green emission of Lu\textsubscript{2}O\textsubscript{3}: Tm\textsuperscript{3+} arises from the 5D\textsubscript{3} → 7F\textsubscript{J} transitions in Tb\textsuperscript{3+}. They have reported a study on photoluminescence properties of Tb\textsuperscript{3+} and Eu\textsuperscript{2+} ions in Lu\textsubscript{2}O\textsubscript{3} host. MLa\textsubscript{2}O\textsubscript{4} (M=Sr or Ba): Tb\textsuperscript{3+} phosphors\textsuperscript{4} were excited at 233 and 227 nm, which show strongest emission peak at 544 nm in both host lattices. They observed that, luminescence intensity increased for samples heated from 500 °C to 900 °C in both host lattices. It was also reported that, this is mainly due to improvement in doping and crystallinity due to decrease in non-radiative recombination effects, quenching sites, and surface impurities in the crystal lattice at higher temperature. SCMS:Ce\textsuperscript{3+}, Tb\textsuperscript{3+}, Mn\textsuperscript{2+} phosphors\textsuperscript{5} were excited at 325 nm in which Tb\textsuperscript{3+} ions are co-doped at the concentration of 4 mol%. When 4 mol % of Tb\textsuperscript{3+} is co-doped with Ce\textsuperscript{3+} (green spectrum), a series of weak bands appear at 418, 436, and 445 nm, prominent blue and green bands at 488, 542 nm, and less intense bands at 583, and 620 nm. NaGd(MoO\textsubscript{4})\textsubscript{2}: Tb\textsuperscript{3+} phosphors\textsuperscript{6} were excited at 277 nm, which shows that emissions can be observed at higher concentrations also because concentration quenching was observed to be 14 at wt%. The luminescence decay time was reported as 0.323 ms for the optimum concentration.

YBO\textsubscript{3}: Tb\textsuperscript{3+} phosphors\textsuperscript{6} were excited at three different wavelengths i.e. 225, 250 and 340 nm and found that 340 nm excited phosphors emits highest intensity. It was reported that annealing the samples at 1000 oC enhances the initial luminescence intensity and afterglow time. Ca\textsubscript{3}SnO\textsubscript{4}: Tb\textsuperscript{3+} phosphors\textsuperscript{7} were also excited at 255, 274 and 334 nm and found that 255 nm excited phosphors emits highest intensity and exhibits all characteristic emission peaks of Tb\textsuperscript{3+} ions. Decay studies were carried out and found that, with increase in concentration decay time changes and 0.1% Tb\textsuperscript{3+} doped sample show biggest value of decay time. Zn\textsubscript{4}(PO\textsubscript{4})\textsubscript{3}: Tb\textsuperscript{3+} phosphors\textsuperscript{8} were excited at 350 nm and green emission characteristics were reported. It was also reported that, multi color emissions at selected wavelengths could be obtained by altering the doping concentration in the triple doped sample. Zn\textsubscript{2}TiO\textsubscript{4}: Tb\textsuperscript{3+} phosphors\textsuperscript{9} were excited at 415 nm and found that 3 mol% doped sample exhibits highest intensity. Radiative lifetime of the optimised sample was determined to be ~ 5 ms from Judd-Ofelt analysis.
Conclusions
In this review green light emitting phosphors have been analysed based on its synthesis methods and photoluminescence properties. It was observed that, different methods and conditions were applied to prepare. Different samples show different structures and particle size but it emits green light when excited by UV or visible light. Emission spectra of all Tb$^{3+}$ doped samples exhibits $^5D_{3/2} \rightarrow ^7F_{J}$ ($J = 5, 4$ and $3$) transitions for all different excitations. Among all, Mg$_2$SiO$_4$: Tb$^{3+}$ phosphors are potential material since they are prepared at low temperature 350 °C by combustion method and confirmed crystallinity without any post calcinations. Therefore in order to prepare potential Tb$^{3+}$ doped green emitting phosphor, solution combustion method can be used with ODH as fuel. These phosphors can be used for the fabrication of light emitting display devices as green component.

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References