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Review on synthesis of power saving phosphors NUV excited LED

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Abstract : Over centuries, incredible progress has been made by artificial lighting technology from kerosene lamps, tungsten filament bulbs and fluorescent lighting to today's light emitting diodes (LED). Over the last three centuries, the consumption of light per capita has increased by an order of magnitude and consumption of too much artificial light costs too much energy. Even in this era of digitization, one of the world's major problems is the shortage of electricity. This is because of the existing lighting system, which includes energy inefficient tungsten filament bulbs, and mercury-excited fluorescent lamps, which are not eco-friendly, harmful, non-disposable. In contrast the use of self-illuminating, ecofriendly, and power saving LEDs, could solve this problem to a great extent. For solid state lighting, one of the most studied devices is the light emitting diode. Here, a brief review of various power saving materials for near UV excited LED applications and their synthesis methods is discussed. The samples under study are synthesized by solid state method, combustion method, andwet chemical. The prepared phosphors were then characterized by XRD, SEM and photoluminescence (PL) study.

Key Words:Luminescence; lamp phosphors; solid state lighting, photoluminescence; phosphor; synthesis of phosphor; LED; power saving material; eco-friendly.

I. INTRODUCTION

Light-emitting diodes (LEDs) are presently the most predominant of the light-based technologies, which involve the direct conversion of electrical energy into light**[1].**Lighting devours over 20% of all electricity produced with an accompanying 410 million tons of carbon releases. Conventional lighting sources comprise incandescent lamps and fluorescent lamps, which are quite inefficient at converting electricity to light. Solid-state lighting sources are in the course of significantly altering the way humans produce light for general lighting applications. It is assessed that over $120 billion in energy savings could be achieved by 2020 if an efficiency mark of 200 lumens per watt can be accomplished. This will also facilitate a noteworthy reduction in the generation of green house gases. Solid-state lighting (SSL) has the ability to meet this target,by employing light emitting diodes (LEDs) with a theoretical limit of ~ 300 lm/W. It is expected that solid-state lighting could achieve 80% energy efficiency, with a corresponding luminous efficacy of approximately 300 lumens/watt, and it will be able to operate entirely on sustainable energy sources such as either solar or wind. In addition, solid-state lighting sources offer almost an infinite field lifetime (e.g., 25- 50 years). LEDs also satisfy the essential requirements of current generation displays, i.e., reproduction of decent light quality, brightness, contrast,low power consumption, high resolution, enhanced color variation, low weight, reduction in thickness, reduction in cost. These are extremely thin, flexible, and available in various shapes, colors and sizes. LED based lighting as well as display devices show 80-90% less power consumption in comparison to all earlier lighting and display devices.

Solid-state light sources enjoy two highly attractive features, which put them apart from most other light sources: (i) the properties of light, such as temporal modulation and spectral composition, can be controlled to a degree that is impossible with conventional light sources such as incandescent and fluorescent lamps and (ii) they have the potential to produce light with essentially unit power efficiency. The proposals are enormous and, as a consequence, many positive advances are to be anticipated including a decrease in global energy consumption, reduction of global-warming-gas and pollutants and a multitude of new functionalities promoting numerous applications.

Nowadays, LEDs are fabricated with a phosphor coating to improve the luminescence efficiency of the unit. The phosphors are pumped with a UV or blue LED to emit a light in the visible wavelength region. However, search for new luminescent materials for plasma display panel (PDP) and mercury free lamp, has been giving increasing attention on the vacuum ultraviolet (VUV) spectroscopic characteristics of phosphors activated with rare-earth ions since last decade**[2-5]**. The f–f, f–d and charge-transfer transitions of rare-earth ions in addition to the host related absorption are main spectroscopic bands in VUV range. The f–f transitions of rare-earth ions in vacuum ultraviolet (VUV) region have been well understood and the Dieke diagram was extended to about 65,000 cm^{-1}. However, further investigations on the f–d transitions of

the rare-earth ions in different host lattices was felt necessary since various factors like the nature of the coordinating anions, the site symmetry,coordination number and the nature of the nearest cation neighbors show influence on the position of 4f-5d states.

Rare-earth doped phosphors have gained immense attraction due to their high luminescence efficiency, color purity and long emission lifetimes. Numerous rare earth doped phosphors were investigated to improve the qualities of the existing phosphors.

Our approach is to describe the possible classes of rare earth activated inorganic based phosphors, which are characteristically associated with its luminescence study. The aim of the present work is to personify some inorganic based RGB phosphors, using various synthesis and characterization of the prepared phosphors for solid state lighting for the purpose of lamp industry.

Thisreview paper focuses on the synthesis and properties of some power saving LED phosphors.

II. STRATEGIES FOR SYNTHESIS:

With the advent of advanced scientific technologies on materials, several chemical synthesis techniques, such as solid state reaction, microwave, co-precipitation, sol-gel, and combustion synthesis methods, have been applied to prepare rare earth ions activated phosphors. All of these methods, with the exception of solid state reaction, were conducted in liquid phases for accurately controlling and uniformly mixing each component. The demand for phosphors in high-definition television and field-emission displays has triggered several studies to find new kinds of phosphors with strong chemical bonding.

(a) SolidState reaction:

Typically, phosphors with sub-micron size are considered to be most suitable for solid state lighting. Phosphors are, generally, needed in the form of particles for enabling facile coating on LEDs and lamps. Conventional solid state route involves grinding of precursors, in the form of metal oxides or carbonates, in a mortar pestle followed by heat treatment at very high temperatures ~ 1000^{o}C for a duration of several hours.

(b) Sol-Gel:

Sol-Gel method is generally implemented to produce nano/ micron – sized phosphors with uniform particle size distribution. This method involves the mixing of solutions of precursors (in the form of metal nitrates) in distilled water along with a chelating reagent and a surfactant. The resultant solution is then kept for stirring at about 80 ^{o}C, and after some time condensation takes place to yield a polymeric network leading to the formation of sol and later on gel. The resultant yield is then subjected to heat treatments to remove the organic content from the phosphor.

(c) Combustion:

Combustion method is often considered as the easiest of all methods for synthesizing phosphors. This method is an exothermic reaction that requires no additional heat treatment or further calcinations. It is a self-propagating high temperature synthesis that requires low processing cost and time. The basic requirement for this synthesis method is selection of appropriate fuel and oxidizer. The stoichiometric proportion of the fuel and the oxidizer must be chosen in such a way that maximum heat could be generated during the synthesis.

(d) Co-Precipitation:

Co-precipitation methods are best suitable for producing halide or oxide phosphors. Mostly, chloride precursors are preferred for carrying out the synthesis. Nitrate precursors are also considered in several cases. The precursors are dissolved in a solvent (preferably distilled water) which are then mixed together and a precipitating agent is kept on adding slowly to this solution along with constant stirring. The precipitated phosphor particles are washed several times in distilled water to remove any water-soluble impurity content present in the yield.

III. SOME POWER SAVING MATERIALS:

$Sr_5SiO_4Cl_6:Eu^{3+}$ phosphor:

Recently, Yerpude and Dhoble**[6]**reported thephotoluminescence (PL) excitation spectra of $Sr_5SiO_4Cl_6:Eu^{3+}$ phosphor(monitored at 616 nm)synthesized by the modified solid state method. The PL spectrashows excitation peaks at $^7F_0\rightarrow{}^5D_4$ (362 nm), $^7F_0\rightarrow{}^5G_2$ (385 nm) and $^7F_0\rightarrow{}^5L_6$ (395 nm). The prominent excitation band observed at 395 nm (NUV) due to the transition of Eu^{3+} ($^7F_0\rightarrow{}^5L_6$) ion. Under 395 nm excitation wavelength, the emission spectrum consists of sharp emission lines at 590 nm, 597 nm and 616 nm. The prominent peak observed at 616 nm due to the electric dipole $^5D_0\rightarrow{}^7F_2$ transition under 395 nm excitation in the red region of spectrum. Prepared $Sr_5SiO_4Cl_6:Eu^{3+}$ phosphor shows the characteristics are favorable for near UV excited LED application. Hence, the results indicate that $Sr_5SiO_4Cl_6:Eu^{3+}$ phosphors may be used as a potential candidate for LED application.

$NaAlSiO_4:Tb^{3+}$phosphor :

$NaAlSiO_4$:Tb phosphor prepared by sol-gel method shows a strong green luminescence, under an ultraviolet excitation reported by Zhang et al.**[7].**The corresponding emission spectra of $NaAlSiO_4:Tb^{3+}$ indicate narrow emissions that arise from 4f-4f transitions within Tb^{3+} ions**.** Zhang et al **[7]** reported the excitation spectra consist of a number of peaks extending from 275 to 425 nm. The transitions in the wavelength range of 320–400 nm arise due to the characteristic forbidden 4f-4f transitions of Tb^{3+}. The emission spectra of $NaAlSiO_4:Tb^{3+}$ phosphors above 480 nm, the emission peaks are originated from $^5D_4$ excited state. These results

reveal that this material is an important candidate as a green emitting phosphor for solid state lighting technology.

$Y_3Al_5O_{12}:Ce^{3+}$phosphors :

Aluminate phosphors have extensively been investigated because of their bright emission characteristics in the visible region as well as their high chemical stability.Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) is known to be the most common among the host materials used for solid state lighting. The YAG phosphors doped with various rare earth elements are suitable for anumber of display applications including backlight source, cathode ray tubeand low voltage field emission display. Among them, cerium doped YAG is a widely studied phosphor which is used as a yellow-emitting component. YAG: Ce exhibit efficient yellow luminescence when pumped with a blue-LED.Currently, $Y_3Al_5O_{12}$:Ce powders are commercially used in white light emitting diodes (w-LED)**[8].**

$MgAl_2O_4$phosphor :

Omkaram et al. reported **[9]** a green-emitting phosphor Tb^{3+}-doped $MgAl_2O_4$ phosphor was synthesized by solid state reaction method and its luminescence properties have been investigated. The PL emission in Tb^{3+} activated $MgAl_2O_4$ phosphor is observed in the green region due to transition $^5D_4 \rightarrow {}^7F_5$ at 543 nm, which may be attributed to the Tb^{3+} ion in the host matrix. The additional three peaks are observed at 488 nm ($^5D_4 \rightarrow {}^7F_6$), 586 nm ($^5D_4 \rightarrow {}^7F_4$) and 623 nm ($^5D_4 \rightarrow {}^7F_3$), with anear UV excitation at 350 nm. Emission intensities from $^5D_3$ excited state decrease with increase of the terbium concentration and show a maximum intensity at 543 nm.

Rare-earth orthosilicates phosphors:

Dy^{3+} ions exhibit two prominent emission peaks around 486 nm (blue emission) and around 573nm (yellow emission), which are capable ofgenerating in white-light emission**[10].** Dy^{3+} doped mixed rare-earth orthosilicates phosphors, namely $LaGdSiO_5:Dy^{3+}$, $LaYSiO_5:Dy^{3+}$ and $GdYSiO_5:Dy^{3+}$ were efficaciously prepared by urea-assisted combustion method. The structural, chemical and optical properties of these phosphors were observed by Ogugua et al.**[11]**. The phosphors showed only line emission peaks, associated with the f-f transitions of Dy^{3+},when they were excited with the monochromatized xenon lamp. The PL intensity from $LaGdSiO_5:Dy^{3+}$ was reasonably higher than that from $LaYSiO_5$: Dy^{3+} and $GdYSiO_5$: Dy^{3+}. It is, therefore, safe to conclude that $LaGdSiO_5$ is a good host of Dy^{3+}.

Strontium aluminate phosphors:

Strontium aluminate ($SrAl_{12}O_{19}$) is ansuitable host lattice for rare-earth and transition metal dopants. $SrAl_{12}O_{19}$:Mn is a good green-emitting phosphor for display panels. Recently, luminescence of Eu^{2+} in a few strontium aluminates hosts (e.g., $SrAl_2O_4$, $SrAl_2B_2O_7$, $SrAl_4O_7$,$SrAl_{12}O_{19}$, $Sr_3Al_2O_6$, and $Sr_4Al_{14}O_{25}$) sensitized with other rare-earth ions have engrossedgreatcourtesy due to their special long afterglow phenomenon **[12,13]**.

$LiNa_3P_2O_7:Eu^{3+}$phosphor :

Munirathnam et al.**[14]** reported a new series of $LiNa_{3-x}P_2O_7$:xEu(x = 0.01 to 0.09) phosphors were synthesized by the solid-state method in crystallized in the orthorhombic structure.Under 395-nm light irradiation, the Eu^{3+}-doped $LiNa_3P_2O_7$ phosphors show red emission around 613 nm. Therefore, the obtained results advise that these phosphors may have probable application as a red phosphor in the lighting devices. The CIE diagram is shown in Fig. 1.

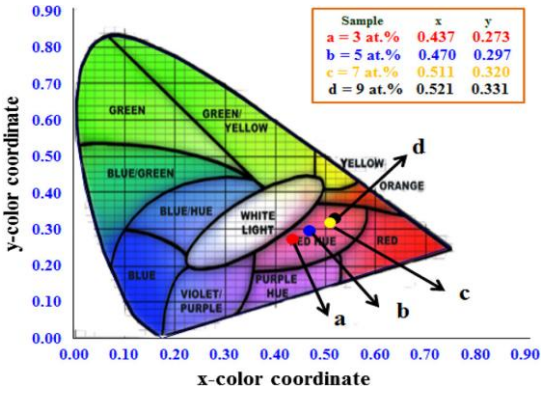

Fig. 1CIE chromaticity diagram of $LiNa_{3-x}P_2O_7:xEu^{3+}$(x = 0.03–0.09)**[14].**

$Na_2CaP_2O_7:RE^{3+}$phosphor :

Recently, we have reported $Na_2CaP_2O_7:RE^{3+}$ (RE = Ce^{3+}, Eu^{3+}, Tb^{3+}, Sm^{3+}) phosphors that were positively synthesized through well known solid state diffusion method. Ce^{3+}, Eu^{3+}, Tb^{3+} and Sm^{3+} occupy symmetric/non-symmetric sites in $Na_2CaP_2O_7$lattice**[15].** Absorption in NUV region for $Na_2CaP_2O_7$: RE^{3+} phosphors suggest that they could be effectively excited by LEDs emitting in the near-UV region. The CIE coordinates of $Na_2CaP_2O_7$: RE^{3+} fall in the white region. The entire PL results indicate that $Na_2CaP_2O_7$: RE^{3+} phosphors may be candidate for phosphor-converted white LEDs. Since the excitation wavelengths (314,380, 396 nm & 405 nm) of $Na_2CaP_2O_7$: RE^{3+} are quite distant from mercury excitation, therefore, these phosphors will turn out to be eco-friendly.

Eu^{2+}activated $Sr_5(PO_4)_3Cl$ blue phosphors

$Sr_5(PO_4)_3Cl$:Eu phosphor prepared by solid state diffusion technique at 800^0C. The formation of $Sr_5(PO_4)_3Cl$:Eu was confirmed by taking XRD pattern and comparing with the standard data. The XRD data of prepared material well matched with standard data of JCPDs file no, 16-666.Fig.2(curves a, b, c and d) shows PL emission spectra of various concentrations of Eu in $Sr_5(PO_4)_3Cl$. The prominent emission is observed at 446 nm (excitation wavelength is 350 nm). These correspond

to transition $^6P_j \rightarrow {}^8S_{7/2}$ levels of Eu^2. The maximum PL intensity in $Sr_5(PO_4)_3Cl$ is observed for 2 mol% of Eu. Fig.2, curve (e) shows the corresponding excitation spectra (excitation wavelength is 350 nm)**[16].**.

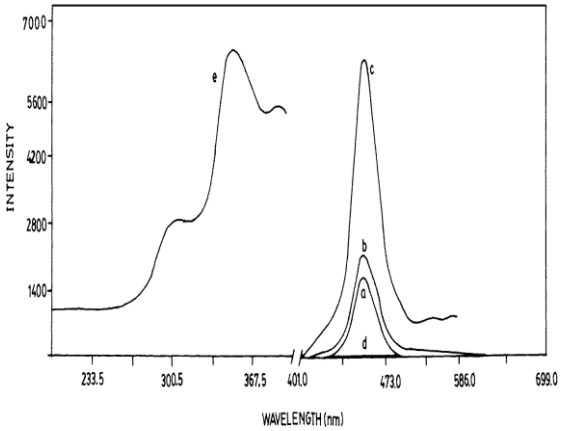

Fig. 2 The PL spectra for various concentrations of Eu in $Sr_5(PO_4)_3Cl$ phosphor. The emission spectra (excitation wavelength was 350 nm) are shown in curves (a) 0.05 mole%, (b) 0.2 mole%, (c) 2 mole% and (d) 0 mole %. The excitation spectra of $Sr_5(PO_4)_3Cl:Eu^{2+}$ (2 mole%) (Emission wavelength was 446 nm) is shown in curve (e)**[16]**.

IV. CONCLUSIONS

In conclusion, a list of power saving materials for near-UV LEDs has been reviewd in this paper. The list, by no means can be complete, includes YAG:Ce, $Sr_5SiO_4Cl_6:Eu^{3+}$,$NaAlSiO_4:Tb^{3+}$, $LaGdSiO_5:Dy^{3+}$, $LaYSiO_5:Dy^{3+}$, $GdYSiO_5:Dy^{3+}$, $SrAl_{12}O_{19}$:Mn, etc. A large number of researchers have reported that use of novel power saving materials for LEDs can save a huge amount of energy and hence, focus should be on fabricating devices using these materials. Hence, we conclude that the phosphors reviewed here may be suitable for application in green technology based solid state lighting and near-UV excited white LEDs.

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