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Luminescence characterization of blue emitting aluminates based lamp phosphors

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Abstract
In this paper we have present our recent work on Eu^{2+}/Ce^{3+} activated $SrMg_2Al_{16}O_{27}$, $Zn_{0.865}Mg_{0.730}Al_{10.270}O_{17}$, $BaMg_8Al_{18}Si_{18}O_{72}$ aluminates based phosphors. All the phosphors were prepared by combustion synthesis at 550^0C. These prepared phosphors shows isolated broad blue emission band under near UV excitation. An efficient blue emission in Eu^{2+} and Ce^{3+} ions observed due to 5d-4f emission transition in the aluminates based materials. Also spin orbit splitting difference in $^2F_{7/2}$ and $^2F_{5/2}$ ground state level is studied by using curve fitting analysis.
Keywords: Blue phosphors; PL;Spin Orbit Splitting; solid state lighting

1. INTRODUCTION

The applications of phosphor materials in various fields have resulted in its tremendous growth. An improved performance of display devices and lamps requires high quality phosphors with sufficient brightness and long term stability. To enhance the luminescent characteristics of the phosphors, extensive research has been carried out on rare earth-activated oxide-based phosphors due to their promising luminescent characteristics and better chemical stability[1–3] . They are highly stable and provide satisfactory performance even in high vacuum, inertness against the degradation in chemical and thermal properties and absence of corrosive gas emission under electron bombardment when compared to currently used sulfide-based phosphors [4]. In addition to this, rare earth doped oxide phosphors have superior emission properties compared to phosphors doped with transition metal ions, which has attracted the attention of researchers and industrialists. Therefore, rare earth doped oxide-based phosphors are likely to emerge as the potential choice for the field emission display (FED) phosphors. These find enormous applications as light emitting diodes (LEDs), field emission displays (FEDs), cathode ray tubes (CRT), temperature sensors, plasma display panels (PDPs), fluorescence imaging of cells and bacteria, latent fingerprint detection, X-ray imaging scintillators, etc [5–8]. White light-emitting diodes (LEDs) have enormous potential in replacement of traditional lighting such as incandescent and fluorescent lamps due to their superior features of long lifetime, small size, desirable chromaticity, high efficiency, energy saving, and environmental-friendliness [9–15]. Currently, available commercial white LEDs are fabricated by the combination of the blue-emitting InGaN-based LED chip and the yellow-emitting YAG:Ce^{3+} phosphor [16]. However, the white light, produced by the complementary blue and yellow emissions, shows high thermal quenching and a poor color rendering index (CRI) due to the lack of red light contribution [17]. Such deficiencies have limited the possible application of white LEDs in general illumination. An alternative approach to attain efficient white light with higher CRI is to combine a near-ultraviolet (n-UV) LED chip with red, green, and blue-emitting phosphors. However, the three-converter system has poor blue emission efficiency due to the strong re-absorption of the blue light by the red or green-emitting phosphors [18]. Thus, it's particularly essential to develop a single-phased white light-emitting phosphor by the mechanism of the energy transfer from a sensitizer (energy donor) to an activator (energy accepter) in a single host lattice for n-UVLEDs.

2. EXPERIMENTAL

All the mentioned phosphors were synthesized by combustion methods at 550^0C. The starting materials were used as follows, $Sr(NO_3)_2$, Ba(NO3)2, $Mg(NO_3)_2.6H_2O$, $Zn(NO_3)_2$ $6H_2O$, $Al(NO_3)_3.9H_2O$ (99.99% purity; Merck), SiO_2 (A.R.),

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$(NH_4)_2Ce(NO_3)_6$ Merck (99.99% purity), urea (NH_2–CO–NH_2, Merck) was used as fuel and europium oxide (Eu_2O_3, REI 99.9%). The flame with the foamy powder was formed, and that powder was collected and analyzed by and photoluminescence measurement. Photoluminescence (PL) emission and photoluminescence excitation (PLE) were measured using a Shimadzu RF5301PC spectro flurophotometer at room temperature.

3. RESULTS AND DISCUSSION

3.1 $SrMg_2Al_{16}O_{27}:Eu^{2+}$ (SAM II: Eu^{2+})

Wanjun et al recently reported SAM I ($SrMg_2Al_{16}O_{27}:Eu^{2+}$) phosphor as a blue emitting phosphor[19], in this paper we are developed same phosphors and quoted by SAM II.[20]. The PL excitation and emission spectra of the SAM II: Eu^{2+} phosphor are shown in Fig. 1(a, b) [20]. The PL emission spectra, which have been compared with BAM:Eu^{2+} phosphor, were excited at the same excitation wavelength and were prepared by the same method. Both compounds have the same excitation wavelength at 324 nm, but the emission of SAM II:Eu^{2+} appears at 465 nm and at 451 nm. The spectral position of the Eu^{2+} emission bands depends on the crystal field splitting of the $5d^1$ level and on the energy difference between the $^8S_{7/2}$ state and centre of the gravity in 5d level . The excitation spectrum observed at 324 nm was attributed to the $4f^7(^8S_{7/2})$–$4f\ ^65d^1$ (t_{2g}) transitions .The Sr^{2+} and Eu^{2+} ions are very similar in their ionic size (i.e. 1.21 and 1.20 Å, respectively). Consequently, when occupied by Eu^{2+} ions, the two different Sr^{2+} sites will have a quite similar local distortion, so that the Eu^{2+} ions located at the two different Sr^{2+} sites will have very similar local environments. Thus, Eu^{2+} ions mainly occupy Sr^{2+} sites in the conduction layer and form the corresponding emission centre, shows a strong blue emission, with a peak at 465 nm, as a consequence of $4f\ ^65d^1 \rightarrow 4f^7$ electron transition of Eu^{2+} ions. Such broad emission band in Eu^{2+} activated aluminates materials may shows potential application for lamp phosphors.

3.2 $Zn_{0.865}Mg_{0.730}Al_{10.270}O_{17}:Eu^{2+}$ phosphor

Fig.2 shows PL excitation and emission spectra of $Zn_{0.865}Mg_{0.730}Al_{10.270}O_{17}$: Eu^{2+} phosphor [21]. The emission band observed at 446 nm by monitoring excitation wavelength at 329 nm, it also gives weak emission at 619 nm due to Eu^{3+} ions, The broad blue emission corresponding to $4f^65d \rightarrow 4f^7$ transition, this broad luminescence band of Eu^{2+}

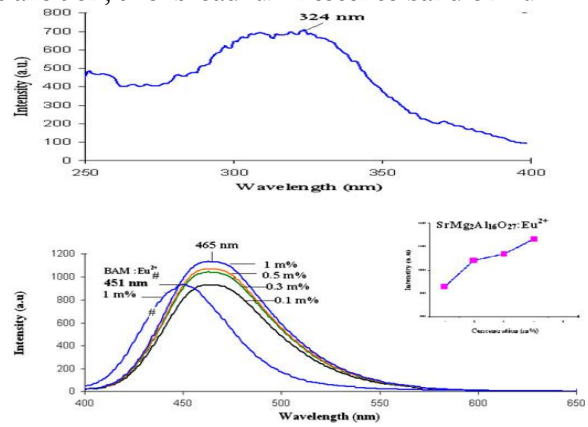

Fig. 1 (a): Excitation spectra for SAM II:Eu^{2+} and BAM:Eu^{2+}, λem = 465 nm.
Fig. 1 (b): Emission spectra for SAM II:Eu^{2+} and BAM:Eu^{2+}, λex = 324 nm [20]

ion, is an allowed electrostatic dipole transition and weak emission in red region corresponds to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion. Depending on th e ionic radii ,for Eu^{2+} (1.20 A^0) which is too large to substitute for Zn^{2+} (0.74 A^0) in a tetrahedral site and therefore it would have a greater tendency to locate in interstitial octahedral site . However as Eu^{2+} ion is divalent , it will have seek an environment of yet higher coordination balanced by an occasional Zn^{2+} vacancy and form emission center. Weak emission in red region is due to Eu^{3+} (0.95 Å), its ionic radii is much larger than that of Al^{3+} (0.54 Å) and Zn^{2+} (0.74 Å) , thus Eu^{3+} ions may enter into the host lattice to substitute Al^{3+} or Zn^{2+} or locate on the surface of the crystal, the second possibility is more feasible. Thus Eu^{3+} is more stable than Eu^{2+}, but the emission occurs in Eu^{3+} is quite weak as compare to Eu^{2+} ion, the possibility for the occurrence of Eu^{3+} may due to the oxidation of Eu ions, it because of synthesis process carried out in open atmosphere. Therefore, most of the Eu^{3+} ions are located at the surface of $Zn_{0.865}Mg_{0.730}Al_{10.270}O_{17}$ with few of them may entering into the host lattice. The peak occurred at 619 nm can be reduced if we place the materials in C/N atmosphere. Such promising blue phosphor may be useful for the SSL—NUV-LEDs technology.

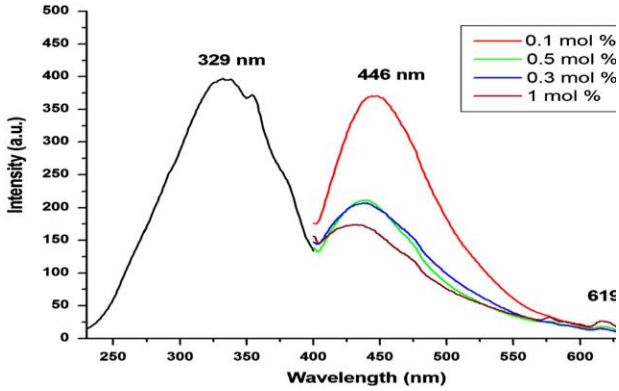

Fig.2: PL excitation and emission spectra of $Zn_{0.865}Mg_{0.730}Al_{10.270}O_{17}$: Eu^{2+} phosphor [21]

3.3 $Zn_{0.865}Mg_{0.730}Al_{10.270}O_{17}$:$Ce^{3+}$ phosphor

The PL excitation and emission spectra of $Zn_{0.865}Mg_{0.730}Al_{10.270}O_{17}$: Ce^{3+} phosphor is shown in fig.3, extending broad band excitation from 230–400 nm due to the 4f–5d transition of Ce^{3+} ions[21]. The PL emission exhibits broad band extending from 400-650 nm and peaking at 431 nm, which is due to the transition from 5d level to the ground state of the Ce^{3+} ion. From emission spectra it observed that the characteristic emission of Ce^{3+} in the blue- region originates from parity allowed electric dipole transitions between excited 5d and ground 4f states. The 5d orbital's have their energy levels split by crystal field effects into at least two sublevels, ^2E and $^2T_2$. Due to spin–orbit coupling the lowest sublevels of 5d can be further split into new components, as it is also the case for the ground state level 4f, split into the $^2F_{5/2}$ and $^2F_{7/2}$ components. The energy structure of Ce^{3+} is such that localized multiphonon non-radiative relaxation and transfer cross relaxation quenching to other like ions are highly improbable, then invariably 5d Ce^{3+} luminescence will be strong and highly efficient. Ce^{3+} gives maximum emission at 1 mol % and it decreases for higher concentration. Thus broad emission band appears is due to spectral overlap of two energy level. Doublet band of Ce^{3+} ion is not clearly observed in emission band as those observed in many aluminates based phosphor, but in our reported work it can be resolved by Gaussian fit as shown in fig 4. Fitted curve shows two emission bands peaking at 424 nm (23,584 cm^{-1}) and 466 nm (21,459 cm^{-1}), corresponding to the transitions of 5d states to $^2F_{5/2}$ and $^2F_{7/2}$ of Ce^{3+} ion, respectively. The corresponding energy difference between these two fitted emission band was observed at 2125 cm^{-1} which is consistent with theoretically calculated energy level difference in $^2F_{5/2}$ and $^2F_{7/2}$ level (2000cm^{-1}) . The stokes shift ΔS is observed at around 7128 cm^{-1} , which is larger than the values obtained for many Ce^{3+}- doped aluminates compounds [22]. The larger Stokes shift is due to the strong electron-lattice coupling in lattice . On the basis of configurational coordinate diagram, the excitation band of Ce^{3+} ion is followed by expansion, and the equilibrium of the ground state is displaced ,this displacement causes Stokes shift. Recently, X. Zhang et al [23], reported that in the case of the rigid lattice where the impurity ion is strongly coupled with the surrounding host lattice, there is less tolerance to endure such sudden expansion and cause large displacement, thus Stokes shift becomes larger.

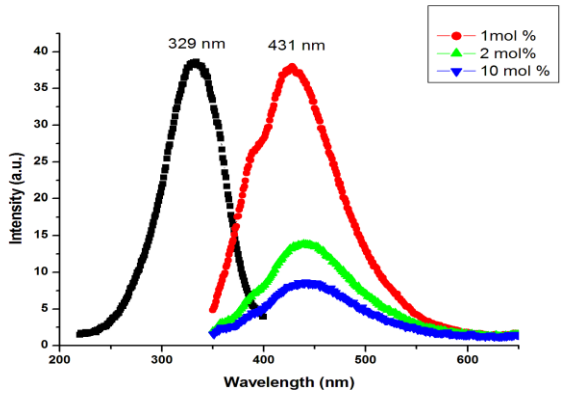

Fig. 3: PL excitation and emission spectra of $Zn_{0.865}Mg_{0.730}Al_{10.270}O_{17}$:$Ce^{3+}$ phosphor, λ_{em}=431nm.[21]

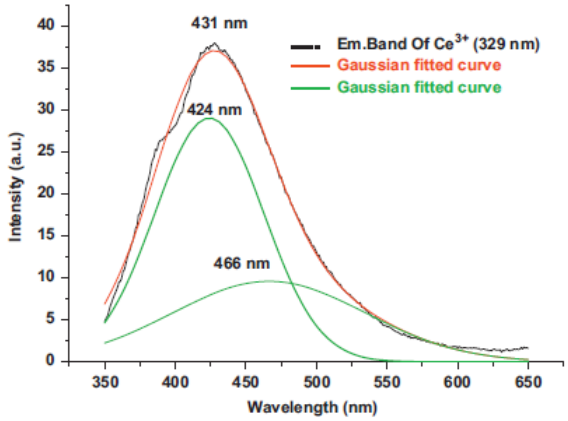

Fig.4: Gaussian fitted curve for $Zn_{0.865}Mg_{0.730}Al_{10.270}O_{17}$:$Ce^{3+}$ phosphor, λ_{ex}=329 nm.[21]

Table.1: Comparison on excitation and emission wavelength of blue emitting phosphors.

Our Work	λ_{ex}	λ_{em}
SAM II:Eu^{2+}	324 nm	465 nm
ZAM:Eu^{2+}	329 nm	446 nm
ZAM:Ce^{3+}	329 nm	431 nm
BMAS:Eu^{2+}	337 nm	437 nm

Some Published work	λ_{ex}	λ_{em}	Ref.
SAM:Eu^{2+}	314 nm	460 nm	(19)
BAM:Eu^{2+}	355 nm	450nm	(25)
$Sr_3Al_2O5Cl_2$:Ce^{3+},Li^{+}	340	445nm	(26)
$Ca_{2.95}Al_2Si_2O_8Cl_4$:Eu^{2+}	365 nm	431nm	(27)

3.4 $BaMg_8Al_{18}Si_{18}O_{72}$:$Eu^{2+}$ phosphor

The PL excitation and emission spectra of Eu^{2+} activated $BaMg_8Al_{18}Si_{18}O_{72}$ phosphor shows in Fig. (5,6)[24]. From emission spectra $BaMg_8Al_{18}Si_{18}O_{72}$:$Eu^{2+}$ phosphor shows broad emission band centered at 437 nm keeping excitation at 334 nm near UV region. The luminescence of Eu^{2+} ion consists of the $4f^65d^1 \rightarrow 4f^7(^8S_{7/2})$ broad-band emission, which belongs to electric dipole allowed transition and has the properties of large absorption of UV light and broad emission ranging from ultraviolet to visible light depending on different crystal-lattice environment. The Eu^{2+} can stay in the sites of Ba^{2+} without a large change of lattice parameters. This means that Eu^{2+} can substitute for Ba^{2+} to form solid-state solution in $BaMg_8Al_{18}Si_{18}O_{72}$ host to some extent. This indicates that one of the Ba^{2+} sites is preferentially occupied by the Eu^{2+} ions and that the second site is filled only with higher dopant concentrations. According to the crystal structure, the first Ba^{2+} site (2a) has the multiplicity of two and a site symmetry of C_3 while the second one (6c) has six and C_1. Both Ba^{2+} sites have nine coordination and the sites are similar in average size (d(Ba-O) Ave - 2.86 and 2.87 Å). However, the lower symmetry site has also shorter Ba-O distances (2.69 Å) corresponding to those typical of Eu^{2+} -O (2.68 Å).

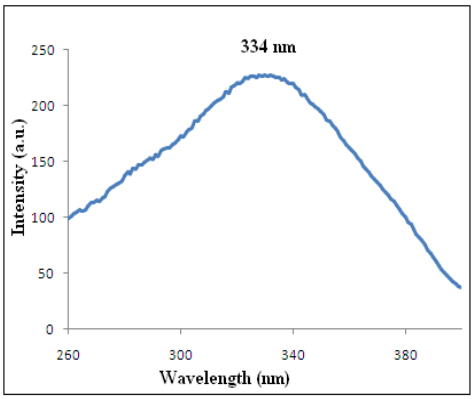

Fig.5: PL exc. spectra of $BaMg_8Al_{18}Si_{18}O_{72}$: Eu^{2+} phosphor λ_{ex}=334 nm [24]

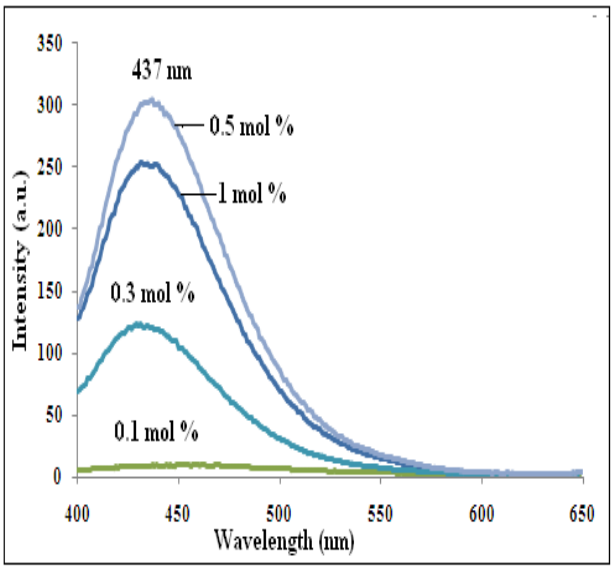

Fig.6: PL emi. spectra of $BaMg_8Al_{18}Si_{18}O_{72}$: Eu^{2+} phosphor λem = 437 nm [24]

It would therefore seem reasonable that this 6c site is filled preferentially. As Al^{3+} ion was added and substituted for Si^{4+} ion, the local negative charge was produced . Al^{3+} is closer to Ba (II) in space, the local negative charge made the electron cloud density around Ba (II) denser than that of Ba (I), which means that the blue peak increases with the increase in the concentration of Al^{3+} ion.

The overall emission extends on the whole visible spectrum which explains the blue fluorescence perceived with naked eyes under UV illumination. The strong excitation band at 260-380 nm range indicates that phosphor be excited only by the UV-LED chip, which is essential for improving the efficiency and quality of white light-emitting diodes. Table.1 shows the comparison on excitation and emission wavelength observed in our reported work and those previously published work on same family of the phosphors compound.

4.CONCLUSION

The emission characteristics of Eu^{2+} and Ce^{3+} activated phosphors facilitate the search for new oxides based blue emitting phosphors for use in tricolor devices and production of white- LEDs. Thus our reported result suggests that combustion synthesis is a promising technique for the preparation of potential blue emitting hexa aluminates and alumonisilicates based phosphors for field emission display and for the development of white-LEDs. In future we have tried to study the energy transfer mechanism and long after glow properties in reported materials.

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