Ce and Eu activated Na$_2$Zn$_5$(PO$_4$)$_4$, a new promising novel phosphor

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Abstract. A new efficient phosphor, Eu^{2+}/Eu^{3+} and Ce^{3+} activated Na$_2$Zn$_5$(PO$_4$)$_4$ has been synthesized by solid-state reaction technique at high temperature. X-ray powder diffraction analysis confirmed the formation of Na$_2$Zn$_5$(PO$_4$)$_4$ host lattice. Scanning electron microscopy indicated that the microstructure of the phosphor consisted of irregular fine grains with a size of about 0·5–2 μm. Photoluminescence excitation spectrum measurements of Ce^{3+} activated Na$_2$Zn$_5$(PO$_4$)$_4$ show that the phosphor can be efficiently excited by UV-Vis light from 280 to 310 nm to realize emission in the visible (blue) range due to the 5d–4f transition of Ce^{3+} ions which is applicable for scintillation purpose, whereas Eu^{2+}/Eu^{3+} activated Na$_2$Zn$_5$(PO$_4$)$_4$ phosphor emits blue, green and red emission spectrum shows at 487 nm, 546 nm with a dominant peak at 611 nm respectively, due to Eu^{2+}/Eu^{3+} ions which is promising candidate for solid state lighting. Therefore, newly synthesised, by low cost and easy technique prepared, novel phosphors may be useful as RGB phosphor for solid state lighting application.

Keywords. Photoluminescence; phosphor; solid state lighting; synthesis; phosphate.

1. Introduction

Phosphate has become an important luminescent material used for LED because of their excellent thermal stability and charge stabilization. Up to now, the most convenient way to generate white light from LEDs is using a blue LED and a yellow-emitting phosphor that is usually made of cerium doped yttrium aluminum garnet (YAG : Ce^{3+}). This mechanism has been investigated extensively (Yao *et al* 2001; Xia *et al* 2005; Yang *et al* 2007). However, this white LED fabricated with YAG : Ce^{3+} cannot generate warm white light due to the lack of the red light component (Hu *et al* 2005; Wang *et al* 2006). This problem can be solved by two ways: one is to compensate the red deficiency of YAG : Ce^{3+}-based LED with a separate red phosphor and the other is to combine a UV chip with tricolour (red, green and blue) phosphors (Park *et al* 2004). The luminescent effect of red phosphor is lower than that of the green and blue phosphor at UV excitation region. Thus, people are interested in the red phosphor that can be excited by blue or UV light. Europium ion (Eu^{3+}) is widely used as a luminescent centre in a number of phosphors for the exhibited characteristic red emission mainly corresponding to its $^5D_0 \rightarrow \ ^7F_2$ transition (Wang *et al* 2004a, b). Phosphates doped with trivalent europium ions have excellent efficiencies and appropriate absorption bands. A great deal of work has been done on Eu^{3+}

activation of these hosts. Ye *et al* (2008) synthesized Gd$_3$PO$_7$: Eu^{3+} nanospheres via a facile combustion method and reported its optical properties. Ternane *et al* (2001) researched the luminescent properties of Eu^{3+} in calcium hydroxyapatite. Therefore, Eu^{3+} doped in phosphate compounds has excellent luminescence. Ce^{3+} doping in phosphates results in emission spectra near ultraviolet (UV) region (Baldassare Di Bartolo 1991a). Ce^{3+} ion, which is in the 4f^1 configuration, shows efficient luminescence owing to the 4f–5d transition. The luminescent colours or wavelengths of these ions change widely from near UV to red region depending on the nature of the host lattices (Baldassare Di Bartolo 1991b). The 4f–5d transition of Ce^{3+} ions in solids is the parity allowed electric dipole transition (e–d) having large oscillator strengths and such transitions produce efficient broadband luminescence. It has larger stokes shift than that of other rare earth ions due to the extended radial wave functions of the 5d state. Because of the favourable spectroscopic properties of Ce^{3+} and the ability to incorporate Ce^{3+} into different host materials, cerium-activated materials have received renewed interest (Weber *et al* 1995). The emission spectra of Ce^{3+} ions arise from $^2D \rightarrow \ ^2F_{5/2,7/2}$ transition. Recently, Moharil and co-workers (Belsare *et al* 2009a, b) developed several fluorides incorporating Ce^{3+} prepared by simple, one-step and wet chemical synthesis.

Ji *et al* (2007) reported the new phosphate with a crystal structure which has a good thermal stability during the heating process (Ji *et al* 2007). Phosphate is a promising

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phosphor material for lamps, CRTs and plasma display panels (PDPs) because of its high chemical stability and inexpensive cost. In this study, we report the luminescence property of a new phosphate phosphor, Eu and Ce-doped $Na_2Zn_5(PO_4)_4$.

2. Experimental

The Eu and Ce-doped $Na_2Zn_5(PO_4)_4$ phosphate based phosphor synthesize by modified solid state reaction. The raw materials were analytical grade pure materials ZnO, Na_2CO_3 and $NH_4H_2PO_4$ used as starting materials. These materials were weighed in the proper molar ratio then introduced the Eu_2O_3 as a dopant. It was mixed and ground homogeneously in an agate mortar. The mixture was heated to 500°C in a silica crucible and kept at this temperature for 2 h, to allow ammonia, water, and nitrogen oxide vapours to evaporate. Then again after grinding, the powders were heated at 800°C for 24 h, to obtain the white phosphor powders. Similar procedure followed for Ce-doped $Na_2Zn_5(PO_4)_4$. Cerium was introduced in the form of $(NH_4)_3Ce(NO_3)_6$. The chemical reaction was as follows

$$10ZnO + 2Na_2CO_3 + 8NH_4H_2PO_4 \rightarrow$$
$$2Na_2Zn_5(PO_4)_4 + 12H_2O + 2CO_2 + 6NH_4 + N_2.$$
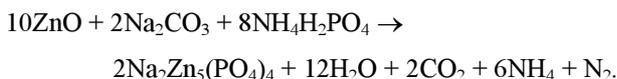
Several complementary methods were used to characterize the prepared phosphors. The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-Kα radiation) at a scanning step of 0·01°, for 20 s, in the 2θ range from 10° to 120°; the average crystallite size was calculated from the broadening of the X-ray line (311) using Scherer's equation. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample 2 g was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1·5 nm. The morphology of the products were examined by scanning electron microscopy (SEM, JEOL 6380A).

3. Results and discussion

3.1 *Structural behaviour, XRD and morphology of $Na_2Zn_5(PO_4)_4$*

The structure was solved and reported by Ji *et al* (2007). $Na_2Zn_5(PO_4)_4$ crystallizes in the orthorhombic system with space group *Pbcn*, lattice parameters a = 10·381(2)Å, b = 8·507(1) Å, c = 16·568(3) Å and Z = 4. Both Zn and P atoms are tetrahedrally coordinated by oxygen atoms. [Zn(3)O$_4$] polyhedrons link the neighbour layers by sharing apex oxygen atom with the [PO$_4$] polyhedron to form

a 3D $[Zn_5P_4O16]_n^{2n-}$zincophosphate covalent framework with channels along the b-axis in which the sodium atoms are located (figure 1). Within a radius of 3 Å, Na is coordinated by 5 oxygen atoms. Four of the 5 Na–O bond lengths are in the range of 2·278(3) Å–2·542(3) Å while the other one is 2·938(3) Å. Figure 2 shows the XRD pattern of prepared $Na_2Zn_5(PO_4)_4$ materials. The XRD pattern did not indicate presence of the constituents like, ZnO, $NaCO_3$ or $NH_4H_2PO_4$ and other likely phases which are an indirect evidence for the formation of the desired compound. These results indicate that the final product was formed in crystalline and homogeneous form. The $Na_2Zn_5(PO_4)_4$ phosphor is prepared first time; therefore the XRD standard data is not available in JCPDs files. The XRD data for $Na_2Zn_5(PO_4)_4$ is shown in table 1.

It is clearly seen that the grains have an irregular shape of particles with a size of about 0·5–2 μm. An average crystallite size is in sub-micrometre range seen in SEM images. The size of sample prepared is 0·5–2 μm, which is suitable for the solid state lighting (see figure 3).

3.2 *Photoluminescence charecterization of $Na_2Zn_5(PO_4)_4 : Eu^{3+}$*

The photoluminescence excitation spectra of the prepared Eu activated $Na_2Zn_5(PO_4)_4$ phosphor is shown in figure 4. The prominent excitation band at 407 nm may be due to the *f–f* transitions of Eu^{3+} ion. The PL excitation spectrum is broad and maximizes at 407 nm. This excitation can be ascribed to the $Eu^{3+} \rightarrow O^{2-}$ charge transfer transition (figure 4). The PL emission spectrum (λ_{exc} = 407 nm) consists of the intense peak at 611 nm (red) that can be
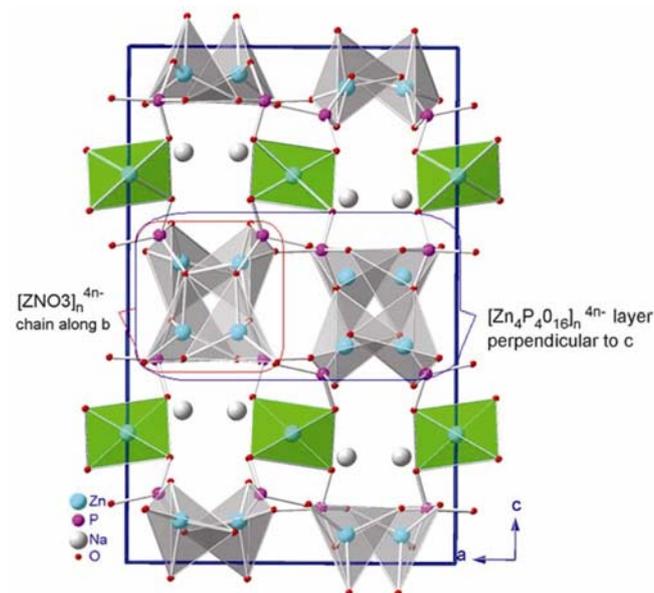
Figure 1. As per the Ji *et al* (2007), the crystal structure of $Na_2Zn_5(PO_4)_4$ lattice.

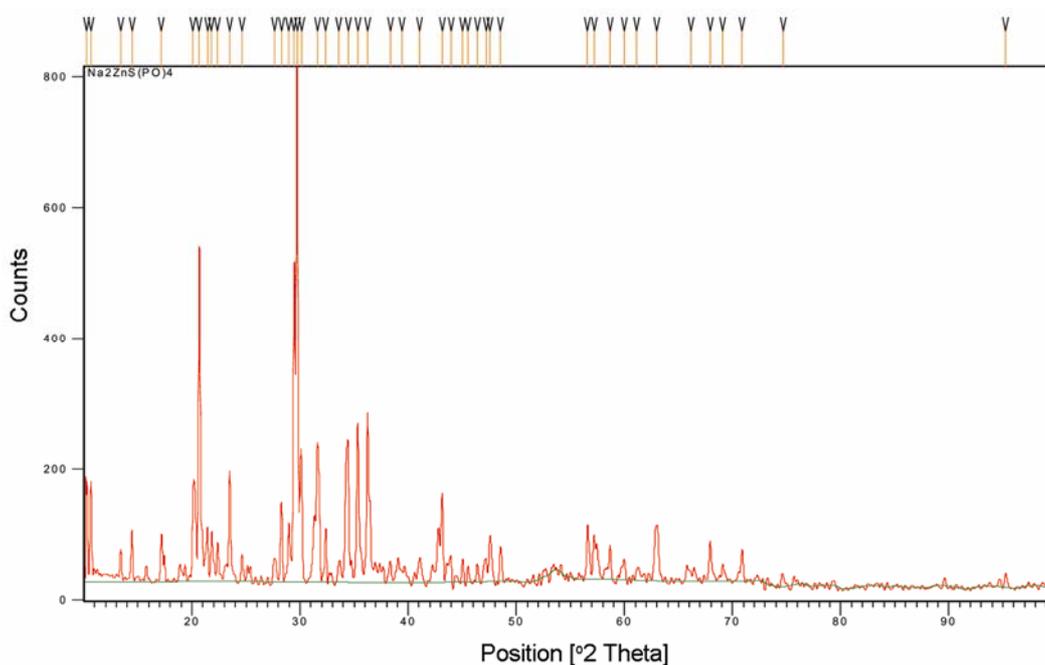**Figure 2.** XRD pattern of Na$_2$Zn$_5$(PO$_4$)$_4$.
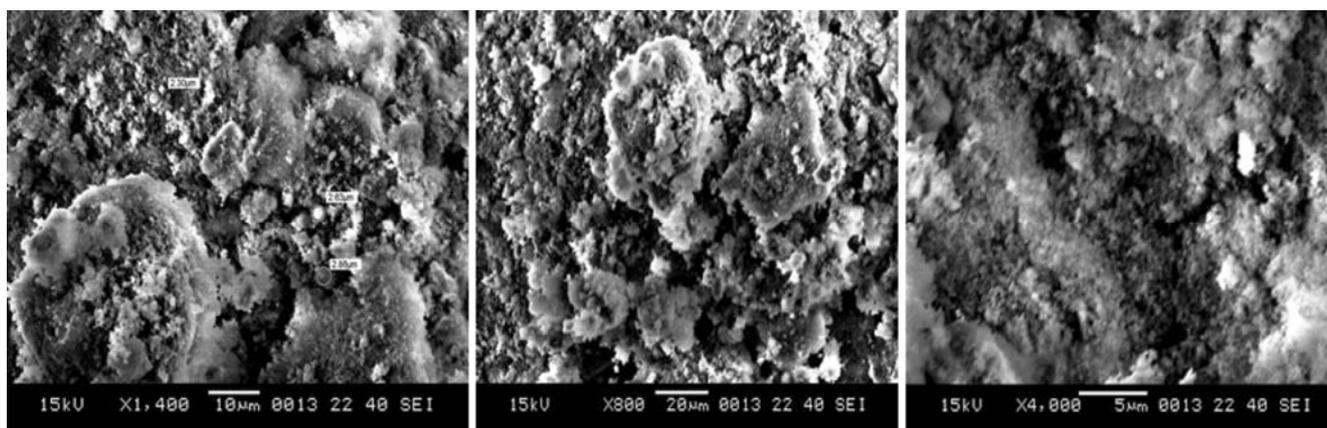
Figure 3. SEM images of Na$_2$Zn$_5$(PO$_4$)$_4$: Eu^{3+} phosphor.

ascribed to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion and other two board emission peaks are observed at 487 and 546 nm due to Eu^{2+} ions as shown in figure 5. Eu ions are shown as the emissions at 487, 546 and 611 nm in the blue, green and red region of the spectrum, respectively by 407 nm Hg free excitation. In the present case, Eu ions simultaneously shows the broad emission at 487 and 546 nm by Eu^{2+} ions and 611 nm sharp emission by Eu^{3+} ions.

The excitation of phosphor 407 nm is far away from Hg excitation, as well as this excitation is the main characteristic of LED in the lamp industry. Therefore, new synthesis by low cost and easy technique prepared novel phosphors which may be useful as RGB phosphor for solid state lighting application.

The prominent 611 nm emission of Eu^{3+} ion in Na$_2$Zn$_5$(PO$_4$)$_4$ material is very applicable as a red phosphor for the solid state lighting. The PL intensity variation with concentration from 0·1–1 mol% is observed and it decreased at more than 0·5 mol% probably due to concentration quenching effect. In the case of Eu^{3+} ion, the relative intensity of the 611 nm peak strongly depends on the local site symmetry around the Eu^{3+} ions. The transition of $^5D_0 \rightarrow {}^7F_2$ belongs to a forced electric dipole transition and its intensity is very sensitive to the site symmetry of the Eu^{3+} ions. Thus, the ratio of $R = {}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ can measure the distortion from the inversion symmetry of the Eu^{3+} ion local environment (Haque *et al* 2009; Omkaram *et al* 2009; Yadav *et al* 2009). As

**Table 1.**   Peak list of XRD pattern of $Na_2Zn_5(PO_4)_4$.

Pos. (°2Th.)	Height (cts)	FWHM (°2Th.)	d-spacing (Å)	Rel. int. (%)
10·2321	135·29	0·0612	8·63823	17·10
10·6580	153·04	0·2040	8·29397	19·34
13·4138	50·55	0·2040	6·59558	6·39
14·4482	78·77	0·2244	6·12560	9·96
17·1804	73·35	0·2040	5·15712	9·27
20·0938	132·33	0·2244	4·41549	16·73
20·6821	513·98	0·2040	4·29120	64·97
21·4284	82·21	0·1836	4·14339	10·39
21·8229	75·63	0·1836	4·06937	9·56
22·3838	59·31	0·2040	3·96865	7·50
23·4862	168·36	0·2040	3·78481	21·28
24·6132	40·38	0·2040	3·61400	5·10
27·6309	37·14	0·3264	3·22577	4·69
28·2739	122·79	0·2244	3·15385	15·52
28·9601	90·64	0·2040	3·08067	11·46
29·4472	487·00	0·1836	3·03081	61·56
29·7203	791·12	0·1836	3·00358	100·00
30·1280	187·88	0·2856	2·96386	23·75
31·5835	206·75	0·2040	2·83050	26·13
32·3858	81·92	0·2040	2·76219	10·35
33·5579	30·43	0·3672	2·66835	3·85
34·4593	199·64	0·2040	2·60059	25·23
35·3339	243·22	0·2244	2·53819	30·74
36·2358	257·32	0·1836	2·47706	32·53
38·3314	31·92	0·3264	2·34632	4·03
39·3909	20·19	0·9792	2·28561	2·55
41·0552	37·86	0·3264	2·19672	4·79
43·1471	135·33	0·2040	2·09494	17·11
43·9543	38·02	0·2244	2·05832	4·81
45·0443	36·21	0·2244	2·01101	4·58
45·4927	24·29	0·2244	1·99223	3·07
46·3944	28·30	0·2244	1·95558	3·58
47·1925	34·68	0·4080	1·92436	4·38
47·5461	68·57	0·2856	1·91087	8·67
48·5387	53·17	0·3060	1·87409	6·72
56·5868	82·71	0·2244	1·62515	10·46
57·1824	65·48	0·2448	1·60963	8·28
58·6694	53·94	0·2040	1·57232	6·82
59·9963	31·69	0·4896	1·54068	4·01
61·0957	15·13	0·4488	1·51557	1·91
62·9851	85·98	0·4080	1·47457	10·87
66·1189	16·09	0·9792	1·41207	2·03
67·9268	62·18	0·2244	1·37883	7·86
69·1098	21·96	0·4896	1·35808	2·78
70·8802	49·15	0·2244	1·32844	6·21
74·7060	13·38	0·4896	1·26960	1·69
95·2533	21·94	0·3264	1·04268	2·77

shown in figure 5, the transition $^5D_0 \rightarrow {}^7F_2$ is much stronger than the transition $^5D_0 \rightarrow {}^7F_1$, which suggests that the Eu^{3+} is located in a distorted (or asymmetric) cation environment. The sites for dopants in the host are determined by their ionic radii. The radius of Eu^{3+}, Zn^{2+} and Na^+ is 95, 74 and 95 pm, respectively. Thus, the Eu^{3+} ions can readily occupy the Na^+ sites rather than the Zn^{2+} sites. Other transitions from the $^5D_0$ excited levels to ^7F_J ground states, such as $^5D_0$–$^7F_1$ lines in the 570–600 nm range are relatively weak, which is advantageous for obtaining a phosphor with good CIE chromaticity coordinates.

In this case, the presence of a more intense red peak at 611 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition and other two peaks are observed at 487 and 546 nm by Eu^{2+} ions (figure 5). The excitation peak is 407 nm is Hg free excitation and emission at 487 nm, 546 nm and 611 nm from Eu activated $Na_2Zn_5(PO_4)_4$ phosphor. The results of Eu^{2+}/Eu^{3+} activated $Na_2Zn_5(PO_4)_4$ phosphor shows that it may be applicable to LED as RGB phosphor. Recently, more research done on the development of new solid state lighting phosphors; out of them, maximum phosphors shows the only single colour visible emission. In this paper for the first time we report the RGB emission

phosphor from newly developed host using the Eu ions as an activator. Hence, our results claim the novel phosphor for lamp industry by easy preparation techniques.

The maximum intensity is observed for the 0·5 mol% in red region (Eu^{3+}) of the spectrum while in blue region (Eu^{2+}) it is observed less. It is well known that in trivalent state, Eu ion emits a characteristic red light with a number of narrow lines due to forbidden electric dipole $4f \rightarrow 4f$ ($^5D_0 \rightarrow {}^7F_j$) transition. The luminescence spectrum of Eu^{3+} ion is slightly influenced by surrounding legands of the host material, because electronic transitions of Eu^{3+} involve only redistribution of electrons within the inner $4f$ sub-shell. The most intense transition originated from the $^5D_0$ level is observed in the luminescence spectrum, which is not split by the crystal field ($J = 0$). In accordance with Judd–Ofelt theory, transitions to even J-numbers have much higher intensity than those to odd J-number (Riwotzki *et al* 1998). The most intense luminescence lines correspond to the $^5D_0 \rightarrow {}^7F_2$ transitions. From the luminescence spectrum of samples (figure 5), Eu^{3+} or Eu^{2+} can be identified from the characteristic photoluminescence they exhibit. Eu^{2+} emission arises from the lowest band of $4f_65d_1$ configuration to $^8S_{7/2}$ state of $4f_7$ configuration. Due to the allowed nature of the transition, PL is intense. Spectral positions of these bands vary a great
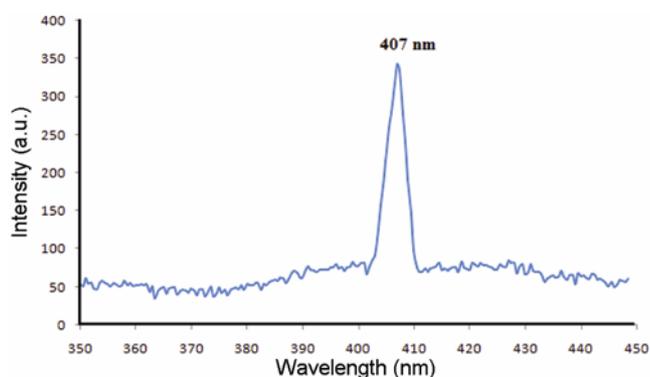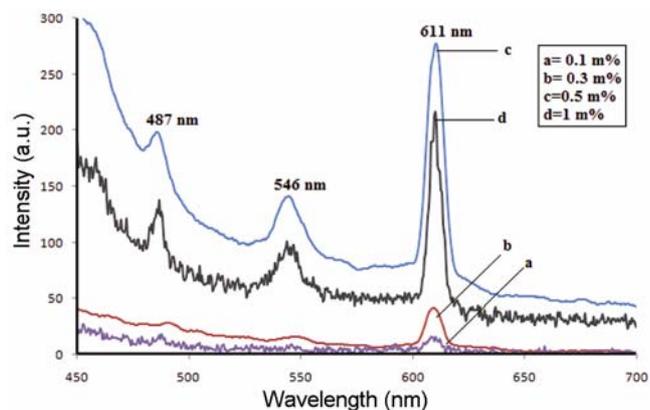
deal from lattice to lattice. Emission lines are obtained around 611 nm corresponding to $^5D_0 \rightarrow {}^7F_2$ transition. The peaks of emission were not significantly shifted with the increasing concentrations of doped rare earth ions. All the samples showed superior $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+} to the phosphor $Na_2Zn_5(PO_4)_4 : Eu^{3+}$. When a trivalent metallic ion, such as Eu^{3+}, is incorporated into a host lattice and substitutes for a divalent metallic ion, a positive centre is produced. The charge compensation route has been revealed. For $Na_2Zn_5(PO_4)_4 : Eu^{3+}$ phosphor, the incorporation of alkali metal ions can neutralize the charge generated resulting from Eu^{3+} substitution for Zn^{2+}, and thus stabilize the structure and enhance the luminescence. As all samples are prepared in open atmosphere, the atmospheric oxygen get react with samples and unwanted emission at 487 and 546 nm were observed, i.e. total Eu^{2+} was not converted into Eu^{3+} ions.

3.3 *Photoluminescence charecterization of Na₂Zn₅(PO₄)₄:Ce³⁺*

Figure 6 shows excitation spectrum of Ce^{3+}-activated $Na_2Zn_5(PO_4)_4$. Emission colour of $Na_2Zn_5(PO_4)_4$ containing 2 mol% Ce is blue (figure 7). The excitation spectrum contains several bands around 285, 294 and 300 mm. The one at 285 nm is the most prominent. The manifold splitting of the band corresponding to $4f^0$–$5d^1$ configuration suggests non-cubic environment for Ce^{3+}. The emission and excitation maxima are at much longer wavelengths. These differences in the PL spectra may be understood in terms of effect of crystal structures on Ce^{3+} energy levels. The spin–orbit split $^2D_{3/2}$ and $^2D_{5/2}$ states of the $5d$ configuration of free Ce^{3+} are located 49,700 and 52,100 cm⁻¹ above the $4f^{1 .2}F_{5/2}$ ground state of Ce^{3+} (Dorenbos 2000). When Ce^{3+} is introduced in a compound, the average energy of the $5d$ configuration is lowered and the $^2D_{3/2}$ and $^2D_{5/2}$ states are further split by the crystal field. Depending on the site symmetry, five distinct $5d$ states may form. The trivalent Ce^{3+}-ions have an electronic structure containing one $4f$-electron and as an activator,

Figure 4. Excitation spectra of $Na_2Zn_5(PO_4)_4 : Eu^{3+}$ monitored at 611 nm.

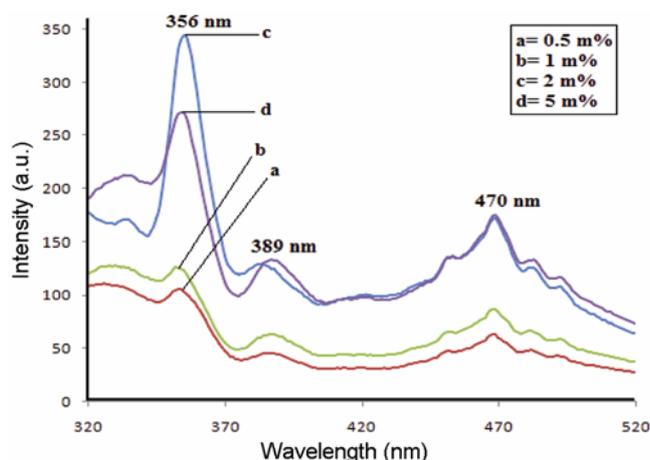**Figure 5.** Emission spectrum of $Na_2Zn_5(PO_4)_4 : Eu^{3+}$ when excited at 407 nm.
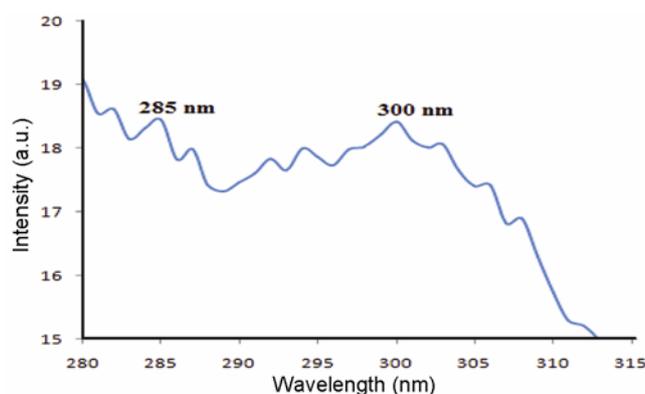
Figure 6. Excitation spectra of $Na_2Zn_5(PO_4)_4 : Ce^{3+}$ monitored at 470 nm.

Figure 7. Emission spectrum of $Na_2Zn_5(PO_4)_4 : Ce^{3+}$ when excited at 285 nm.

they generally result in phosphors having broadband UV emission. In the rare earth phosphates, the emission bands of Ce^{3+} are not like those found in other materials (Ropp 1968). The broad band is observed at around 300 nm with prominent shoulder at around 285 nm at room temperature. Figure 7 shows the PL emission spectra of Ce^{3+} ions in $Na_2Zn_5(PO_4)_4$ phosphors with different concentrations under the excitation 285 nm wavelengths of light. Peaks are observed at 356 nm and 470 nm which are assigned to the $5d$–$4f$ transition of Ce^{3+} ions. The concentration of Ce^{3+} ion increases the corresponding intensity of peaks at higher concentration (2 mol%). This indicates a change of the surrounding of the Ce^{3+} ions at higher concentration in the $Na_2Zn_5(PO_4)_4$ lattice. The observed variations of PL emission intensities may be cross relaxation between Ce^{3+} ions in the case of heavy concentration of Ce^{3+}. From the measured fluorescence spectra (figure 7) of Ce^{3+}, it is clear that band corresponds to the transitions $5d$–$4f$. The emission appears more intense and broader in all Ce^{3+} phosphors. The fluorescence intensity increases with an increase in Ce concentration up to 2 mol%, beyond which, the fluorescence intensity tends to quench. It is also noticed that the peak positions of the emission bands have not changed and blue emission makes this material a candidate for the blue component of a phosphor blend for the lamp industry.

4. Conclusions

Eu^{3+} and Ce^{3+} activated $Na_2Zn_5(PO_4)_4$ phosphors are prepared by well known solid state diffusion techniques. Ce^{3+} emission are observed at 356, 389 and 470 nm by excitation 285 nm; this emission may be applicable for scintilators as well as in the lamp industry as a blue phosphor, i.e. only 470 nm emission of Ce^{3+} ion for Hg excited lamp. Eu ions are shown the emissions at 487, 546 and 611 nm in the blue, green and red region of the spectrum,

respectively by 407 nm Hg free excitation. In the present case Eu ions simultaneously shows the broad emission at 487 and 546 nm by Eu^{2+} ions and 611 nm sharp emission by Eu^{3+} ions. Therefore, newly synthesized, by low cost and easy technique prepared, novel phosphors may be useful as RGB phosphor for solid state lighting application. Recently, more research has been done on the development of new solid state lighting phosphors, out of them maximum phosphors shows only the single colour visible emission. In this paper, first time we report the RGB emission phosphor from newly developed host using the Eu ions as a activator. Hence, our results claim the novel phosphor for lamp industry by easy preparation techniques. The prepared phosphors are characterized by X-ray powder diffraction and scanning electron microscopy techniques.

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