Novel zincate phosphors: A new red emitting phosphor for LED applications

Vijay Kumar[#], Sudipta Som, Somrita Dutta, Hendrik C Swart

Department of Physics, University of the Free State, P.O. Box 339, Bloemfontein ZA 9300, South Africa

[#]Email: vj.physics@gmail.com

Abstract. A series of $CaLa_2ZnO_5$ (CLZ):xEu^{3+} (x = 0, 1, 2, 3, 4, 5, 6 and 7 mol %) have been synthesized by the combustion route. X-ray diffraction results revealed the formation of a single-phase CLZ with a tetragonal structure. The CLZ: Eu^{3+} phosphors irradiated with ultraviolet light exhibited the red photoluminescence (PL) owing to the $^5D_0 \rightarrow {}^7F_J$ transitions of Eu^{3+}. The PL emission intensity first increased up to 5 mol% of Eu^{3+} concentration and then decreased. The reduction in emission intensity was attributed to a concentration quenching phenomenon that is explained on the basis of the different coupling mechanisms. The International Commission on Illumination diagram analysis results directed the appropriateness of the studied phosphor for pure red emission in light emitting diode applications.

1. Introduction

Rare earth (RE) doped phosphors, through many years, have been explored as the most studied materials for solid state lighting applications, as replicated from the large number of spectra in the existing literature [1-5]. Currently, the requirement of materials with improved luminescent properties in multidisciplinary areas has speed up research endeavours in this area focussed towards attaining superior material properties. RE ions are considered as prominent luminescent centers in various inorganic host lattices and, categorized by a partially filled 4f shell that is enclosed by $5s^2$ and $5p^6$ electrons, are broadly integrated to produce high quantum efficiency phosphors [5]. The addition of small concentration of RE ions into host matrix came into existence as a promising method for regulating the optical and PL properties [5]. Significant volume of research has also been carried out on various materials doped with Eu^{3+} so that they can be used in solid-state lighting applications. The beauty of Eu^{3+} ions doped phosphors has attracted the research community due to their importance in red emitting diodes [6-7].

Recently, ternary oxides XY_2ZO_5 (Y_2= rare-earth, X=Ca, Ba, Z=Zn, Cu) have attracted significant attention because of their motivating structural, optical and superconducting properties along with the exceptional physical and chemical stability [8-9]. The research interest has also been directed towards the ternary oxides XY_2ZO_5 based upconversion (UC) and down conversion materials. The luminescence properties of La_2BaZnO_5 and Gd_2BaZnO_5 activated with Eu^{3+}, Tb^{3+} and Tm^{3+} were reported for the first time in 1985 [10]. After that, significant research efforts have been directed towards the luminescent properties of RE doped XY_2ZnO_5 phosphors synthesized by various methods [11]. Recent results suggest that the sol-gel derived $CaLa_2ZnO_5$ (CLZ): Er^{3+}-Yb^{3+} phosphor is an efficient green UC phosphor [12]. The researchers have also studied optical thermometry in the temperature range of 298-513 K using the FIR technique. The optical and luminescent properties of citric based sol-gel derived CLZ: Eu^{3+} phosphors have been investigated by Bandi et al. [13]. They concluded that the studied system with a higher Eu^{3+} content under the excitation of blue light could be a good orange-red-emitting phosphor for its possible utility in white LED devices.

A large number of synthesis methods have been employed in the preparation of Eu^{3+} doped phosphors. It is a well-established fact that heat treatment of light emitting materials have a straightforward effect on the luminescence properties due to the variation in the crystallite size, crystallinity, surface morphology, shape and size of particles. We have synthesized CLZ powder by the solid state reaction method by optimizing the reaction temperature to ensure the maximum luminescent intensity of the synthesized host. Later, the host matrix was doped with a different concentration of Eu ions at an optimized reaction temperature. The influence of Eu^{3+} concentrations on the photoluminescence (PL), structural and morphological properties has been investigated and explained within the scope of this article.

2. Experimental details

The ternary oxide based red phosphors namely $CaLa_2ZnO_5$ (CLZ):xEu^{3+} (x = 0, 1, 2, 3, 4, 5, 6 and 7 mol %) were synthesized by the combustion route. Analytical reagent (AR) grade lanthanum oxide (La_2O_3, 99.9%), calcium carbonate ($CaCO_3$, >99%), zinc oxide (ZnO, 97%) and europium oxide (Eu_2O_3, 99.98%) obtained from Sigma-Aldrich were used as the starting materials. Details of synthesis procedure are reported in our previous work [14].

X-ray diffraction (XRD) patterns of the as-prepared phosphors were recorded using a Bruker D8 focus X-ray diffractometer. The PL studies were performed on a Hitachi Fluorescence Spectrometer F-2500 with a 150W Xe lamp as an excitation source in the range 220-750 nm.

3. Results and discussion

3.1. Effect of Eu^{3+} doping on the crystal structure of $CaLa_2ZnO_5$ red phosphors

To investigate the structure of undoped and Eu^{3+} (1-7 mol %) doped phosphors, the influence of different Eu^{3+} doping concentrations in the crystal lattice and to detect the phase, XRD patterns of the synthesized CLZ:Eu^{3+} phosphors were recorded. XRD patterns of undoped, and Eu^{3+} (1-7 mol. %) doped CLZ phosphors are shown in Fig. 1. The diffraction peaks were indexed to a tetragonal structure of CLZ with major (h k l) peaks at (103), (113), (022), (004), (023), (114), (221), (030), (303), (134), (026), (401), (042) and (216) and lattice constants a = b = 6.547 Å and c = 3.854 Å were obtained [3]. The sharp XRD patterns of the CLZ phosphors indicate the presence of a single phase structure. Similar XRD patterns were observed for the different Eu^{3+} concentrations. The dopant concentrations do not lead to significant changes in the host structure. On the other hand, the relative intensities of the (022) and (113) diffraction peaks of the prepared phosphors has been increased with the rise in the Eu^{3+} concentration up to 5 mol% and decreased at higher doping content. The enhancement in peak intensity may be due to the improvement of the crystallinity. The maximum intensity was observed at 5 mol% Eu^{3+} concentration for the (022) diffraction peak. The highest intensity of the CLZ at 5 mol% Eu^{3+} also exhibited maximum PL emission intensity when compared to the other doping contents [13]. The XRD analysis results are in good agreement with the PL results. A small shift was also observed in the (022) peak with an increase in the Eu^{3+} concentration. This observation specifies that the Eu^{3+} ions were totally combined into the CLZ host lattice. It may be due to the addition of Eu^{3+} ions in the CLZ lattice owing to the migration of the atoms and rearranged the density of states in the CLZ unit cell. It is also evident that the peak shifts towards a higher angle up to 5 mol% of Eu^{3+} doping, subsequently no considerable peak displacement were detected for higher concentrations. This result indicates that a marginal reduction of the lattice parameters has been found after the introduction of 1 to 5 mol % of Eu^{3+} in the CLZ lattice and then saturates.

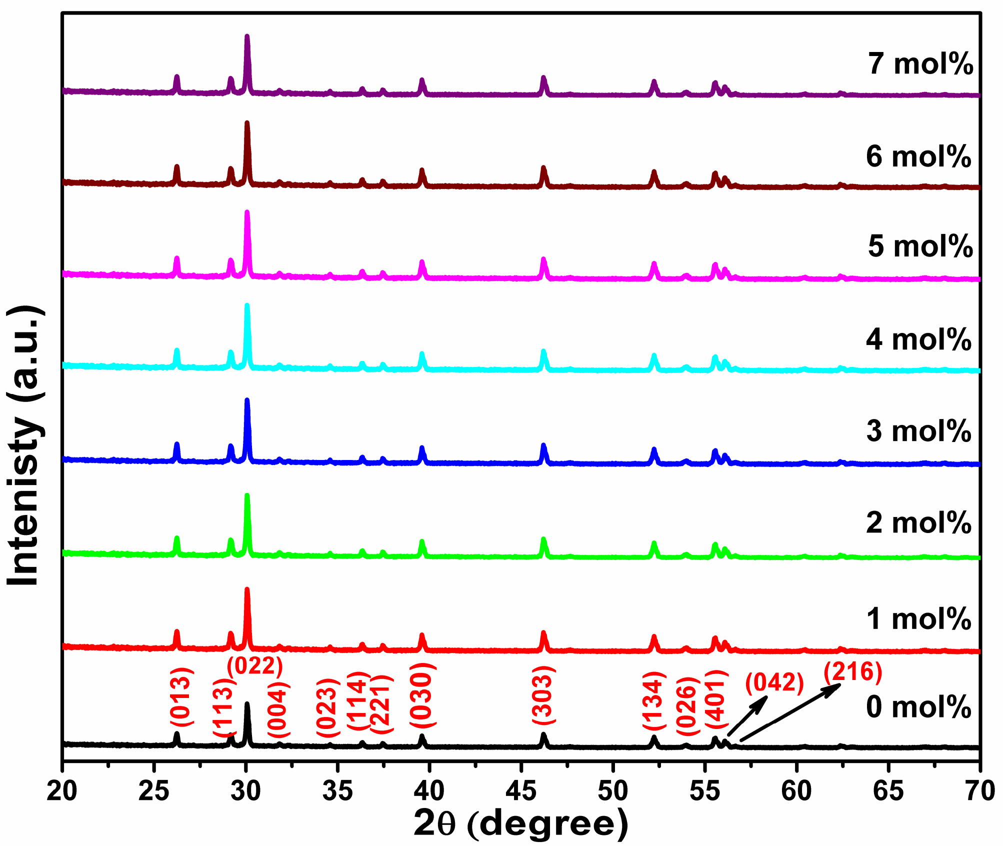

Fig.1: XRD patterns of the $CaLa_2ZnO_5$ phosphors containing different Eu^{3+} concentrations.

3.2. Photoluminescence study of $CaLa_2ZnO_5$:Eu^{3+} phosphors

The concentration of dopant has an influence on the performance of a phosphor. Hence, it is essential to ascertain the composition of CLZ: Eu^{3+} phosphors with optimum PL emission intensity. A series of CLZ: Eu^{3+} phosphors with different concentration of Eu^{3+} (1-7 mol %) ions were prepared. The emission spectra of CLZ: Eu^{3+} phosphors with different Eu^{3+} concentration are recorded at an excitation wavelength of 456 nm and are shown in Fig. 2(a). A broad emission band in the undoped sample around ~ 400 to 500 nm (as shown in the inset of Fig. 2(a)) was observed due to the presence of different intrinsic defects such as Zn vacancy or Zn interstitial in the host matrix [15-16]. After doping of Eu^{3+} this defect emission diminishes at the cost of the increment of the characteristics peaks of Eu^{3+}. The origin of the defect related emission in this host is under investigation. However, seven different emission bands extending between 500 - 750 nm were detected due to transitions from the excited $^5D_2$ to $^7F_3$ (512 nm), $^5D_1$ to $^7F_1$ (539 nm) and $^5D_0$ to the ^7F_j (j = 0-4) levels of Eu^{3+} ions [13, 17]. The presence of the luminescence from the higher excited states, such as $^5D_1$ and $^5D_2$, indicates that the nonradiative relaxation to the $^5D_0$ level was not very efficient. This may be due to the existence of stronger electron-phonon coupling. The observed bands were found to be narrow in nature which is attributed to the characteristic electron shielding effect in Eu^{3+} ions. The most intense emission peak detected at around 624 nm, which is ascribed to the electric-dipole transition ($^5D_0 \rightarrow {}^7F_2$) and found to be hypersensitive to the host structure symmetry. Most of the f–f transitions of the rare earth ions are less affected by the environment. But some are quite susceptible to the crystal environment and turn out to be more powerful. These types of transitions are termed as hypersensitive transitions. Another emission in the vicinity of 595 nm was ascribed to the magnetic dipole transition of $^5D_0 \rightarrow {}^7F_1$ and is insensitive to the site symmetry, as they are parity-allowed. It is to be noted that if the Eu^{3+} ions occupy the inversion symmetry center, only the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ is expected in the emission spectrum unless the electric-dipole transition $^5D_0 \rightarrow {}^7F_2$ will dominate. In the present case the dominance of the electric-dipole transition $^5D_0 \rightarrow {}^7F_2$ was observed. This indicates that the location of Eu^{3+} deviates from the inversion symmetry, i.e. at low balance positions with the increase in Eu^{3+} concentration [17]. A considerable enhancement in emission intensity of the phosphor with the increase in Eu^{3+} concentration was observed, and it approached the maximum at 5 mol% and then decreased. The reduction in emission intensity at a higher Eu^{3+} concentration may be due to the concentration quenching phenomena [17].

The CIE (International Commission on Illumination) chromaticity diagram of CLZ: Eu^{3+} phosphors for different Eu^{3+} content is displayed in Fig. 2(b). CIE parameters such as colour coordinates (x, y) and correlated colour temperature (CCT) were calculated to describe the colour emission of the prepared phosphors. The colour coordinates were determined using the Colour Calculator software. The colour correlated temperature (CCT) is given by the McCamy empirical formula [17].

$$CCT = -437n^3 + 3601n^2 - 6861n + 5514.31 \qquad (1)$$

where $n = (x-x_e) / (y-y_e)$ and chromaticity epicentre is at $x_e = 0.3320$ and $y_e = 0.1858$.

It is evident from the CIE diagram that the colour coordinates shifted from a light blue to a dark red region with the increase in the Eu^{3+} concentrations. The experimental results reflected that the red emission colour can be adjusted by simply varying the concentration of the dopant ions. A red emission (0.64, 0.34) was observed for the 5 mol % concentration of Eu^{3+}. The ideal red chromaticity value given by National Television Standard Committee is (0.67, 0.33), which is very close to the experiential value in the present case for the 5 mol% of Eu^{3+} [17]. At a higher Eu^{3+} concentration, the position of the colour coordinates shifted towards faded red light emission. The CCT value of the synthesized phosphors was found to vary from 1716 to 3847 K. It is well quoted in the literature that the warm white light employed for home appliances should have a CCT value less than 5000K [17]. Thus, the synthesized phosphors may be suitable for ideal red emission for home appliances. The different CIE parameters are calculated with respect to the PL data of the undoped and Eu^{3+} doped CLZ phosphors and depicted in Table 1. The ideal phosphor materials can be categorized by their most prominent wavelength and colour clarity of the radiated colour. This idea is mainly used for the narrow banded light sources. The CCT calculation is a crucial factor to be used in broad banded light sources. Thus, it is very necessary also to evaluate the colour purity of the emitted red light. To study the effect of the varied Eu^{3+} concentration on the colour purity, the colour purity was calculated using the relation given below [17]:

$$ColourPurity = \frac{\sqrt{(x_s - x_i)^2 + (y_s - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\% \qquad (2)$$

where (x_s, y_s) are the coordinates of a sample point, (x_d, y_d) are the coordinates of the dominant wavelength and (x_i, y_i) are the coordinates of the illuminated point. The calculated results are presented in Table 1. It is clearly seen from the table that the color purity increased with the rise in Eu^{3+} content and was maximum at 5 mol% of Eu^{3+}. All the emission transitions are shown in the energy level diagram of Eu^{3+} in this host as shown in Fig. 2(c).

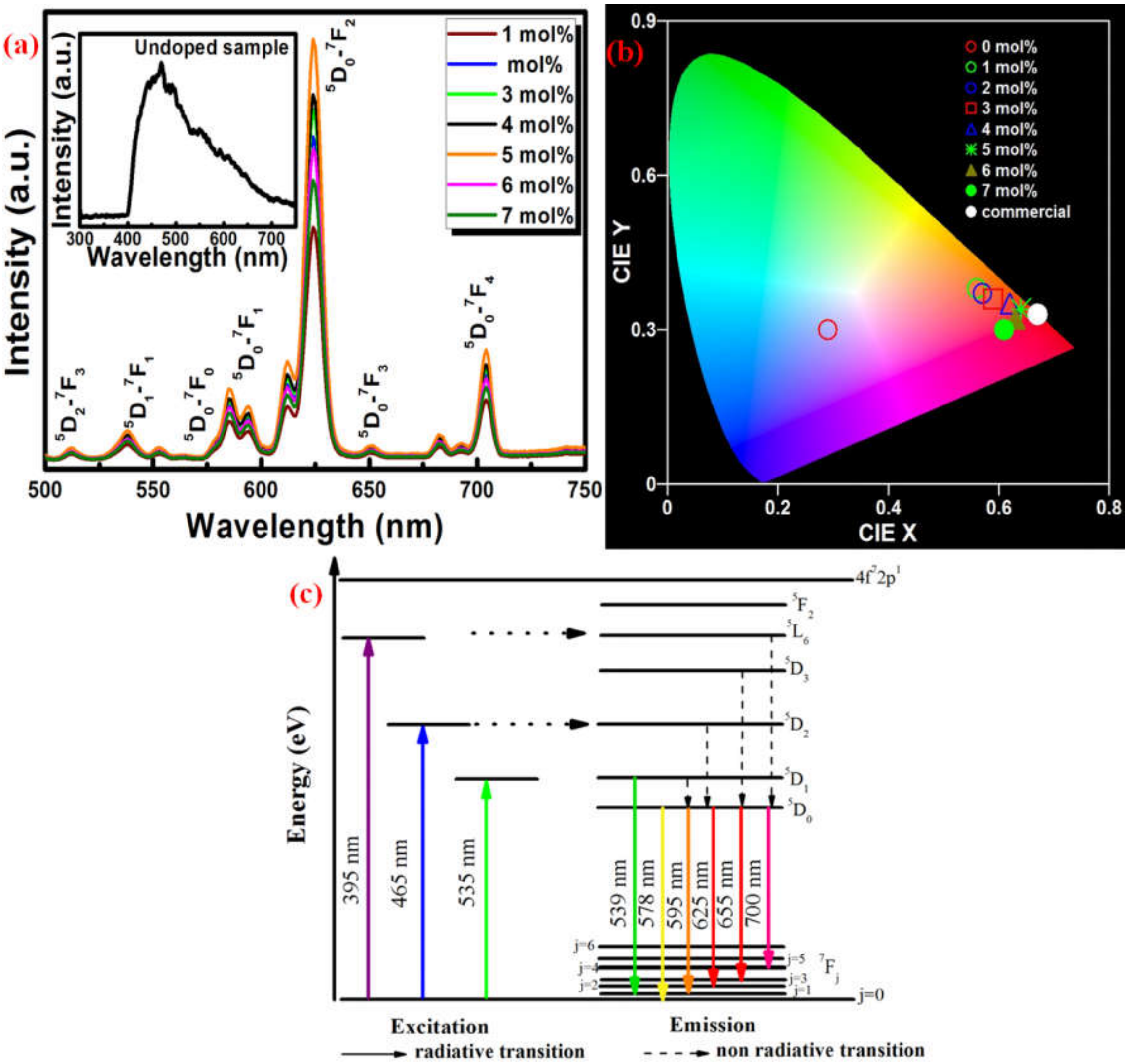

Fig. 2: (a) Effect of doping concentration on the PL emission of $CaLa_2ZnO_5$:Eu^{3+} phosphors. **(b)** The colour coordinates diagrams for $CaLa_2ZnO_5$:Eu^{3+} phosphors for different Eu^{3+}. **(c)** The energy level diagram of Eu^{3+} in the $CaLa_2ZnO_5$ host matrix.

Table 1: CIE parameters of CLZ: Eu^{3+} with different Eu^{3+} concentration.

Phosphor	**Concentration (mol%)**	**Colour Coordinates**		**CCT (K)**	**Colour Purity (%)**
		x	y		
La_2CaZnO_5: Eu^{3+}	0	0.28	0.29	-	20
	1	0.56	0.38	1716	69
	2	0.57	0.37	1718	71
	3	0.59	0.36	1831	77
	4	0.62	0.35	2200	85
	5	0.64	0.34	2694	91
	6	0.63	0.32	3250	88
	7	0.61	0.30	3847	83

4. Conclusion

In summary, a series of Eu^{3+} doped CLZ phosphors were prepared by the solid-state reaction method. The crystal system of the prepared samples was identified as a tetragonal structure, and all the peaks were indexed correctly. The Eu^{3+} doped CLZ phosphors showed a dominant red emission peak centered at 625 nm under 395 nm UV light excitation. The luminescence intensity increased with Eu^{3+} concentration up to 5 mol% and then decreased. The reduction of emission intensity with increasing Eu^{3+} is associated with a concentration quenching phenomena. The results have confirmed that the synthesized phosphors may be considered as a potential red phosphor candidate that can be utilized in solid-state lighting and display devices when combined with UV or blue chips.

Acknowledgment

The research is also supported by the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation of South Africa. The financial assistance from the University of the Free State is highly appreciated.

References

[1] Daicho H, Iwasaki T, Enomoto K, Sasaki Y, Maeno Y, Shinomiya Y, Aoyagi S, Nishibori E, Sakata M, Sawa H, Matsuishi S, and Hosono H 2011 *Nat. Commun.* **3** 1132.
[2] Luminescence. From Theory to Applications (ed Ronda, C. R.) ISBN: 978-3-527-31402-7 (Wiley-VCH, 2007).
[3] Pavitra E, Seeta R R G, Park J Y, Wang L, Moon B K and SuYu J 2015 *Sci Rep* **5** 10296.
[4] Pust P, Weiler V, Hecht C, Tücks A, Wochnik A S, Hen A K, Wiechert D, Scheu C, Schmidt P J and Schnick W 2014 *Nat Mater* **13** 891.
[5] Kenyon A J 2002 *Prog Quant Electron* **26** 225.
[6] Barnes M D, Mehta A, Thundat T, Bhargava R N, Chabra V, Kulkarni B 2002 *J Phys Chem B* **104** 6099.
[7] Gedanken A, Reisfeld R, Sominski L, Zhong Z, Koltypin Y, Panczer G, Gaft M, Minti H 2000 *Appl Phys Lett* **77** 945.
[8] Etchart I, Berard M, Laroche M, Huignard A, Hernandez I, Gillin W P, Curry R J, Cheetham A K 2011 *Chem Commun* **47** 6263.
[9] Jaffres A, Viana B, van der Kolk E 2012 *Chem Phys Lett* **527** 42.
[10] Lammers M J J, Donker H, Blasse G 1985 *Mat Chem Phys* **13** 527.
[11] Yoshida A, Ogawa H, Kan A, Kondo T 2005 *J Eur Cer Soc* **25** 2897.
[12] Li L, Guo C, Jiang S, Agrawal D K, Li T 2014 *RSC Adv* **4** 6391.
[13] Bandi V R, Grandhe B K, Jang K, Lee H S, Shin D S, Yi S S, Jeong J H 2012 *J Alloys Comp* **512** 264.
[14] Kumar V, Som S, Dutta S, Das S, Swart H C 2016 *Mater. Design* **93** 203.
[15] Pereira A S, Peres M, Soares M J, Alves E, Neves A, Monteiro T, Trindade T 2006 *Nanotechnology* **17** 834.
[16] Husain S, Alkhtaby L A, Bhat I, Giorgetti E, Zoppi A, Miranda M M 2014 *J Lumin* **154** 430.
[17] Som S, Kunti A K, Kumar V, Kumar V, Dutta S, Chowdhury, Sharma S K, Terblans J J, Swart H C 2014 *J Appl Phys* **115** 193101.