Promising blue emitting $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ nano-phosphor for near UV-excited white-LEDs

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In this paper we reported Eu^{2+} luminescence in novel $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4$ phosphors synthesized by combustion method at 550^0C furnace temperature. Phosphor was well characterized by XRD for confirmation of phase purity and PL properties of $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ shows emission wavelength at 494 nm corresponds to $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ion by keeping excitation extending broad-band from 300-400 nm centred at 345 nm. Scanning electron microscopy has been used for exploring the morphological properties of the prepared phosphors. The PL characteristics show that prepared phosphor have potential application for near UV-excited white-LEDs.

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1. Introduction

The increasing demand for fossil fuels and the environmental impact of their use are continuing to exert pressure on an already stretched world energy infrastructure [1]. Conventional incandescent and fluorescent lamps rely on either heat or discharge of gases. Both phenomena are associated with large energy losses that occur because of the high temperatures and large Stokes shifts involved [2]. Recently, new lighting device was invented by using blue InGaN LED chip coated with yttrium aluminum garnet yellow phosphor [3]. In this LED InGaN chip use as a excitation source of blue light using electroluminescence mechanism and blue light incident on the yttrium aluminum garnet yellow phosphor, than combine emit white light. Recently, we are reported new phosphors for lamp industry prepared by different root of synthesis [4-12]. The development of fine fluorescent materials with high and stable luminescence efficiencies is necessary in order to achieve much higher emission and finer resolution in innovation of a display. Eu^{2+} ions in host materials are typical blue-emission centers, which in terms of practical applications are utilized in various fields in emissive products. $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) has been widely used as a blue-color-emitting phosphor in fluorescent lamps and plasma display panels (PDPs) because of its high luminescence efficiency under vacuum ultraviolet light excitation [13,14]. Among the phosphors used for PDP applications, BAM is known to be very sensitive to manufacturing-process variables such as the baking process, irradiation of vacuum ultraviolet photons, and ion sputtering [15,16]. Therefore, appropriate phosphors for PDPs that show no degradation under these conditions are in urgent demand. The studies on halo-containing phosphors, such as halophosphate phosphors, haloborate phosphors, halosilicate phosphor and haloaluminate phosphors, become a hot issue in exploring new phosphor materials, and they have also been proved to be efficient in the application of the white LEDs light-conversion phosphors [17–19]. Recently, halide and silicate are excellent matrices for Eu^{2+} activated phosphors. The, combination of both the matrices halosilicate, has several advantages like low synthetic temperature, high chemical and physical stability. As an activated ion, Eu^{2+} ion with the 5d electron is unshielded from the crystal field by the 5s and 5p electrons, and the spectral properties are strongly affected by the surrounding environment like symmetry, covalence, coordination, bond length, site size and crystal-field strength etc. Here we repoted novel blue emitting $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ phosphor by combustion synthesis successfully.

2. Experimental

Combustion synthesis (CS) is a versatile, simple and rapid process, which allows effective synthesis of a variety of oxide –nitrates materials. This process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides). The starting materials were used for the preparation of $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4$ phosphors as $Ca(NO_3)_2.4H_2O$ (Merck's 99.9%), $Mg(NO_3)_2.6H_2O$ (Merck's 99.9%), SiO_2 (A.R.), $CaCl_2.2H_2O$ (Merck's 99.9%) and urea NH_2CONH_2 (Merck's 99.9%), Eu_2O_3(desolve in dil. nitric acids). Synthesized phosphors powders are generally more homogeneous, have fewer impurities, and have higher surface areas than powders prepared by conventional solid-state methods .XRD technique was used to identify the phase composition, structure and their crystallinity using a PAN-analytical diffractometer with Cu Kα radiation (1.5405 Å) operating voltage at 40 kV, 30 mA and scan step time at 10.3377 s . The morphology of the phosphor were examined by scanning electron microscopy (SEM, JED-2300) equipped with an energy-dispersive spectrometry attached to the JEOL 2300 was used to determine the morphology of the prepared phosphor .PL characteristics were studied using a RF-5301PC, SHIMADZU, spectrofluorophotometer fitted with a sensitive photomultiplier, at room temperature using 1.5 nm spectral slit width, for emission and excitation spectrum, same amount of sample was used in each case.

3. Results

XRD-pattern of $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4$ phosphor indicates that prepared phosphor have good crystalline nature as shown in Fig. 1. The XRD-pattern is well match with JCPDS card no. 84-1743. The particle size of the phosphor calculated from Debye Scherrer formula which comes out be approximately 39 nm. SEM analysis shows the surface morphology and the crystallite sizes in micron of the synthesized phosphor powder. It is clearly seen that the micrographs crystallite sizes at one microns. The crystallites have sharp surface morphology and have crystalline grains as shown in Fig. 2. Optical characterization is done with the help of photoluminescence (PL) technique. PL excitation spectra (Fig. 3) show the excitation peak at 345 nm is very away from Hg emission and well match in the range of excitation wavelength of solid state lighting. Therefore, we are selecting this excitation for emission characteristics of prepared phosphors. PL emission spectra of $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4 : Eu^{2+}$ shows in Fig. 4 emission wavelength at 450 nm corresponds to $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} by monitoring board-band excitation centered at 345 nm in Fig. 3. The $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4$ host matrix will be greatly affected by the occupation of Eu^{2+} ions in the lattice, which depends on the difference in electronegativity and ion radius. For Eu^{2+} (6-coordinate, 131.0 Å) and Ca^{2+} (6- coordinat, 114.0 Å) both of these parameters are quite close to each other, thus Eu^{2+} ions have a quite similar possibility to replace Ca^{2+} ions and become incorporated into the structure. However, it is well known that vacancy formation due to charge imbalance and lattice strain can self-limit the inclusion of guest ions into a host lattice. The prepared phosphor have isolated blue emission which shows it has poitential application for near NUV-white LEDs. In general, the emission from the LED chip shows a redshift when the injection current increases, which is attributed to the band-filling effect. Such instability will result in a variation in chromaticity coordination of white LED lamps. To solve this problem, n-UV LED and deep blue LED can also be used as an excitation source for light conversion phosphors, when fabricating white LEDs. The CIE chromaticity coordinates are based on the spectral luminous efficiency function for photopic vision. To study just how efficient a phosphor may be, we measure quantum efficiency (QE) by therotical calculations. The quantum efficiency is defined as: photons emitted per photons absorbed (5.61/5.60 =1) means it is an efficient phosphor.To obtain specific values, we measure total energy of emission and the total energy absorbed. It is easier to measure intensity of photons emitted as a function of wavelength. Generally, phosphors which have QE's of 80%, or greater, are considered to be efficient phosphors. Thus our prepared phosphor has application as an efficient phosphor for near UV-excited white-LEDs. The CIE chromaticity coordinates were calculated for 450 nm emission wavelength as (C_x=0.157, C_y=0.020) and triangle in Fig. 5 shows the NTSC curve (modernstandard) as shown in Fig. 5.

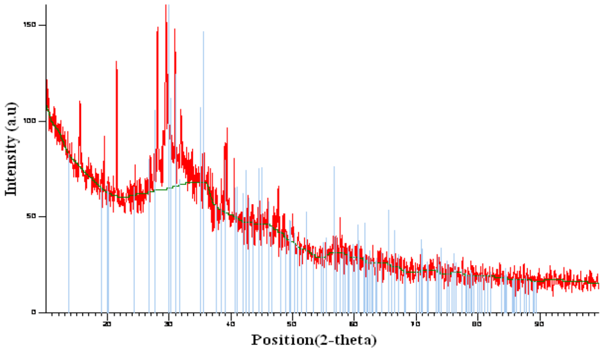

Fig. 1. XRD-pattern of $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4$ phosphor.

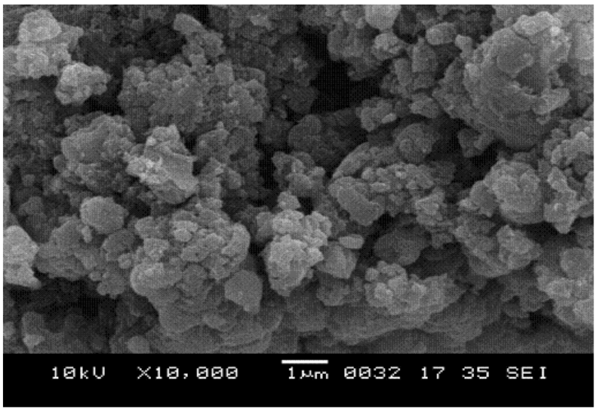

Fig. 2. Micrograph of $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4$ phosphor.

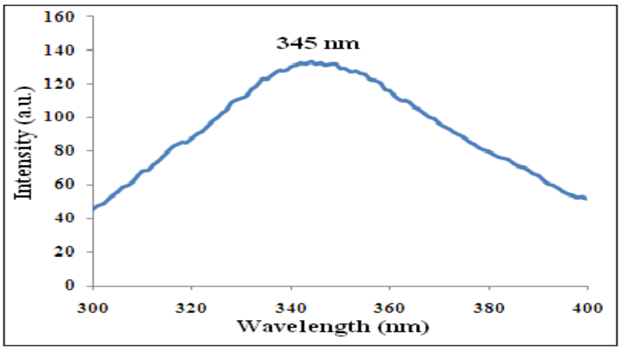

Fig. 3. Excitation spectra of $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ λ_{em}=450 nm.

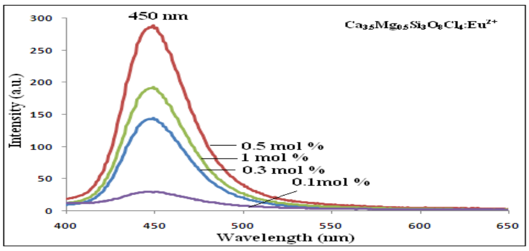

Fig. 4. Emission spectra of $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ $\Lambda ex = 345$ nm.

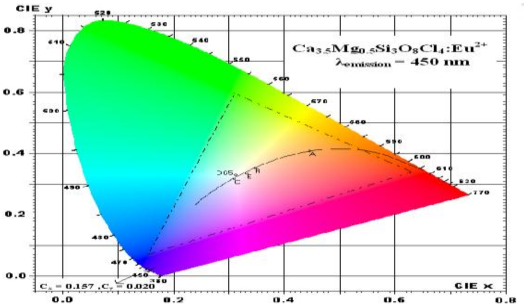

Fig. 5. CIE 1931 Chrmaticity diagram ($C_x = 0.157$, $C_y = 0.020$).

4. Discussion

In the field of research and development of luminescence materials we are trying to save the electric power by using eco-friendly solid state lighting for lamp industry. White light emitting diodes (WLEDs) are emerging as an indispensable solid state light source using the red, green and blue (RGB) emitting phosphors or blue light excited yellow phosphor for the next generation lighting industry and display systems due to their unique properties including but not limited to energy savings, environment-friendliness, small volume, and long persistence. Until now, major challenges in WLEDs have been to achieve high luminous efficacy, high chromatic stability, brilliant color-rendering properties, and price competitiveness against fluorescent lamps, which rely critically on the red, green and blue (RGB) emitting phosphors properties. A comprehensive understanding of the nature and limitations of phosphors and the factors dominating the general trends in RGB phosphors converted WLEDs or blue light excited yellow phosphor also converted WLEDs is of fundamental importance for advancing technological applications. In the present work we are preparing the $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ phosphor by low cost and time comsumming combustion method at 550 ^oC. The PL characteristics indicate the excitation peak obsreved at 345 nm it is favorable to solid state lighting and PL emission board peak boserved at 450 nm in the blue region of the spectrum due to $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ion. Very few phosphors shows the blue emission as well as very few activators shows the blue emission in the suitable host lattice. Hence, the prepared $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ phosphor shows the good characteristics for lamp industry as a blue phosphor.

5. Conclusion

Blue-emitting $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4:Eu^{2+}$ phosphor has been synthesized by combustion method sucessfully. The PLE is a broad band extending from 300 -400 nm. Emission spectra shows broad band, centered at 450 nm corresponding to the transitions of to $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}ion. SEM micrographs show the mophology of the phosphor at 1 micrometer.The efficiency of the phosphors is comes out to be 100 %. The CIE co-ordinates for emission wavelength comes out to be ($C_x = 0.157$, $C_y = 0.020$). Thus $Ca_{3.5}Mg_{0.5}Si_3O_8Cl_4 : Eu^{2+}$ phosphor seems to be a promising blue phosphor for near UV-excited white-LEDs.

References

[1] Q. F. Zhang, C. S. Dandeneau, X. Y. Zhou, G. Z. Cao, Adv. Mater. **21**, 4087 (2009).
[2] R. J. Xie, N. Hirosaki, Sci. Technol. Adv. Mater. **8**, 588 (2007).
[3] G. Fasol, S. Nakamura, The Blue Laser Diode: GaN Based Blue Light Emitters and Lasers, Springer, Berlin, 1997.
[4] N. Thejo Kalyani, S. J. Dhoble, R. B. Pode, Adv. Materials Letters (In press).
[5] Abhay D. Deshmukh, S. J. Dhoble, N. S. Dhoble, Adv. Materials Letters (In press).
[6] J. G. Mahakhode, S. J. Dhoble, C. P. Joshi, S. V. Moharil, Bull. Mater. Sci., (In press).
[7] K. N Shinde, S. J. Dhoble, Animesh Kumar, Physica B: Cond. Matter **406**(1), 94 (2011).
[8] K. N Shinde, S. J. Dhoble, Advanced Materials Letters **1**(3), 254 (2010).
[9] S. J. Dhoble, V. B. Pawade, K. N. Shinde, E. P. J. Applied Phys., **52**, 11104 (2010).
[10] N. Thejo Kalyani, S. J. Dhoble, J. S. Ahn, Ramchandra Pode, J. Korean Physical Society, **57**(4), 746 (2010).
[11] Abhay D. Deshmukh, S. J. Dhoble, S. V. Godbole, M. K. Bhide, D. R. Peshwe, Indian J. Phys., **83**(4), 423 (2009).
[12] M. S. K. Khokhar, Abhay. D. Deshmukh, D. R. Peshwe, S. J. Dhoble, R. S. Kher, Inter. J. Nanoparticles, **2**(1-6), 74 (2009).
[13] J. Koike, T. Kojima, R. Toyonaga, A. Kagami, T. Hase, S. Inaho, J. Electrochem. Soc., **126**, 1008 (1979).
[14] C. R. Ronda, J. Lumin., **49**, 72 (1997).
[15] S. Oshio, T. Matsuoka, S. Tanaka, H. Kobayashi, J. Electrochem. Soc., **145**, 3903 (1998).
[16] K. S. Sohn, S. S. Kim, H. D. Park, Appl. Phys. Lett. **81**, 1759 (2002).
[17] Z. G. Xia, H. Y. Du, J. Y. Sun, D. M. Chen, X. F. Wang, Mater. Chem. Phys. **119**, 7 (2010).
[18] Z. G. Xia, G.W. Li, D. M. Chen, H. Y. Xiao, Mater. Lett. **63**, 2600 (2009).
[19] Z. G. Xia, J. Y. Sun, H.Y. Du, W. Zhou, Opt. Mater. **28**, 524 (2006).

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