Synthesis and optical analysis of Ce^{3+} activated $Na_{21}Ma(SO_4)_{10}Cl_3$ blue emitting lamp phosphors

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Abstract - Here synthesis and photoluminescence (PL) investigation of $Na_{21}Ma(SO_4)_{10}Cl_3:Ce^{3+}$ carried out using combustion synthesis method. The structural and morphological studies and confirmation of phase and purity were done using XRD and SEM. PL spectra of Ce^{3+} due to the 4f–5d transition of Ce^{3+} ions peaking at 330 nm. The photoluminescence emission spectra of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor exhibit blue emission band centered at 442 nm. Usually, configuration of Ce^{3+} ion in ground state is divide into two levels viz., $^2F_{5/2}$ and $^2F_{7/2}$ whereas the $5d^1$ excited configuration is divide by the crystal playing field ranging from 2 to 5 components

Keywords:- Photoluminescence, XRD, SEM,CIE

I. INTRODUCTION

Because of the spectroscopic properties of Ce^{3+} with favorable response and the ability to integrate the Ce^{3+} ion into diverse host inorgnaic material which was activated with cerium ion cover transformed interest for most of the applications [1]. These materials recombine with high light capitulate, constructive emission wavelength, faster fluorescence decay with stability of temperature which make them attractive for useful in detectors for elevated energy physics [2] and also medical imaging [3]. Therefore, with the suport of outstanding luminescence properties, inorganic materials activated with Ce^{3+} ions are applied in lightings industries, detectors with display systems for ionizing radiation [3]. To calculate the 5d energies of another rare earth ion in same host lattices material trivalent cerium ion also is used as a reference ion [4]. So, the spectroscopic properties investigation of trivalent cerium ion in various host material is important for both the actual applications and the fundamental research. Generation of white light either by combination of basic fundamental colors or corresponding colors due to white light obtained from UV-blue LED by covering on LED suitable inorganic phosphors excitable by LED lights, For such inorganic phosphor transformed LED generating white light concluding development of suitable phosphor materials. Available W-LEDs has lower colors re-generation as they are frequently depends on mixting of a blue LED with yellow emitting inorganic phosphor.

Such white LEDs require red and green part of the spectrum of white color. Prepared phosphors are composition of an inert host material and an optically excited activated rare earth ion, normally 3d otherwise 4f metalic electron such as Ce^{3+}, Tb^{3+} or Eu^{3+},Cr^{3+} Oxide inorganic phosphors material have been found a appropriate for vacuum fluorescent display (VFD), electroluminescent (EL) devices, field emission display (FED) and (PDP) plasma panel display devices [5]. D. Ravichandran *etl.*, reports the luminescence study of Eu^{2+} doped alkaline earth aluminates based phosphors, but there is only some work on blue emitting trivalent cerium doped phosphor.

Due to their outstanding properties with application such as higher efficiency of luminous, energy saving capablities, longer life duration, and short of toxic mercury, white light-emitting diodes becomes considered as next generation lighting sources With the help of blue/NUVLEDs to generate white light by [1-6] different approaches are availableTo produce the white light Nichia Co., introduces initial W-LED which has been commercialized in which a blue LED is covered with a yellow color phosphor of YAG:Ce^{3+}.

Though, in the emission spectra, lack of a red component if observed so this kind of white LED suffers from the disadvantage of yellow/blue color partition and deprived color- rendering index (CRI) observed. One more approach is to combine different lights of colors emitted by diverse chips to get white light. Fabrication of white LEDs reported in 1997, by Nakamura with the help of mixing three primary usual color LEDs (i.e. green as well as blue InGaNSQ W-LEDs with a red AlGaAs LED). Though, for such type of mechanism, to balance different color degrades among the red, green and blue chips the complicated IC control system is needed. To excite two or tricolor phosphors and to

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generate white light the third loom is with the help of NUV or blue LED sources.

II. EXPERIMENTAL PROCEDURE

The blue-emitting $Na_{21}Ma(SO_4)_{10}Cl_3:Ce^{3+}$ phosphors were prepared by modified combustion method at 550^0 C. The starting materials were used as $NaNO_3$ (99.99% purity Merck),$Mg(SO_4)$,NH_4Cl (99.99% purity Merck), $(NH_4)_2Ce(NO_3)_6$ (99.99% purity Merck), and ureas (purity Merck).

The starting composition of the calcium nitrate, with aluminum nitrate and urea was depend on the total reducing and oxidising valencies of the oxidizer with the fuel with the concept of propellent chemistry. Constituent of the prepared compound were mixed according to stochiometric ratio in mortar and finally pasty solution was formed, after that solution is shifted in muffle furnace at maintained at aprox 550^0 C. The flame formed with the foamy powder was created, after that fine powder was collected and further analyzed by XRD and photoluminescence measurement.

The phase for purities of the prepared samples was checked by powder X-ray diffraction (XRD); with the help of PAN-analytical diffractometer with Cu Kα radiation (1.5405 Å) at an operating voltage at 30mA and 40 kV, and scaning step time at 10.3377's. Photoluminescence (PL) emission for partucular excitation were measured at our workplace using a Shimadzu RF5301PC spectroflurophotometer recorded at room temperature.

III. RESULT AND DISCUSSION

A. *X-ray diffraction*

Conformation of phase with purity about the formation of compound with crystal structure of the phosphor prepared by combustion synthesis method with extra heat treatment of the prepared phosphor was finalized by powder x-ray diffraction analysis method. XRD blueprint of the phosphor preapred $Na_{21}Ma(SO_4)_{10}Cl_3:Ce^{3+}$ be excellent in matched with the reported XRD pattern in *panse etl.*. [7].

A. *SEM Analysis*

SEM morphology of the prepared phosphor studied with the help of morphological analytical studies reported earlier [8], SEM study explain the morphological analysis of the prepared phosphor prepared by using combustion synthesis method suitable for the purpose of solid state lighting ranging from few micrometers to submicrometers.[9]

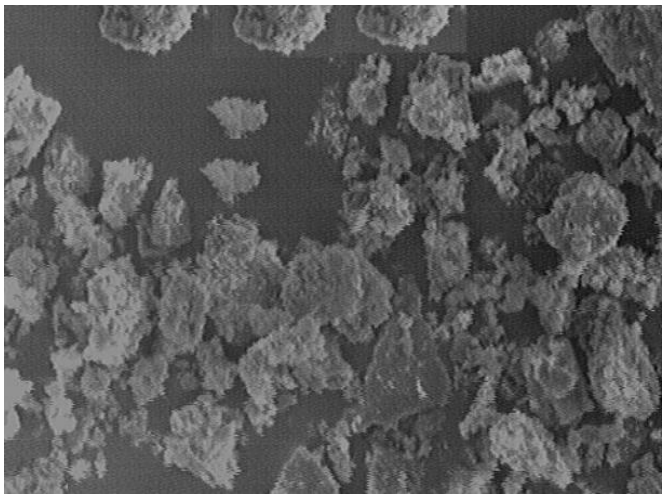

Fig. 1 : Morphology of the combustion synthesized $Na_{21}Mg(SO_4)_{10}Cl_3$ phosphors.

B. *Luminescent property of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ Phosphor*

Fig. 2 and 3 shows photoluminescence excitation and emission spectra of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphors which shows a wide absorption band in the range of 280 to 380 nm due to the 4f–5d transition of Ce^{3+} ions peaking at 330 nm. The photoluminescence emission spectra of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor as shown in fig exhibit blue emission band centered at 442 nm. Usually, configuration of Ce^{3+} ion in ground state is divide into two levels viz., $^2F_{5/2}$ and $^2F_{7/2}$ whereas the $5d^1$ excited configuration is divide by the crystal playing field ranging from 2 to 5 components.

In this research work, the emission spectra of the prepared samples shows broad blue emission band in the range of 400-650 nm peaking at 442 nm. In accordance to the literature review [10] it is recognized to the transition of electron from the excited state of ^2D_J to the Ce^{3+} ions ground states viz.,$^2F_{5/2,7/2}$ of in the prepared $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ host materials, the doublet characteristic of trivalent cerium ion not observed in the emission spectra. These photoluminescence emission spectrum resulting from the spectral overlaping of different emissions peaks connected with trivalent cerium ions substituted for five Sr sites in the T segment. The excitation takes place among the maximum ground level spliting to the 5d levels while the emission developing from the excited level i.e. lowest level toward the two spliting ground levels state. Because of this for trivalent cerium ion, there are additional 4f–5d absorption bands in the PLE spectra while the 5d-4f emission observed in the photoluminescence emission spectrum is a representative double-band profile.

The 5d-4f emission spectra of trivalent cerium ion which based strongly on the crystalographic field. The trivalent cerium ion emission frequently is in the ultra-violet or blue spectral section although shifted toward green to yellow region (eg. $Y_3A_{l5}O_{12}$:Ce^{3+}), with the manipulation of the

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crystallographic surroundings. Usually, the characteristic emission trivalent cerium ions in a specific lattice site happen as doublet bands with the transitions observed due to the relaxed lowest 5d state of excitation to the ^2F_J (J=5/2,7/2) spin–orbit spliting 4f ground state.The separation of energy of the two bands corresponding to the common spin–orbit splitting up of (2000 cm^{-1}). The peak of excitation, which was expressed by the difference of energy of the lowest 5d level of excitation of trivalent cerium ion (330 nm) in the current Sr^{2+} host material compared with the free trivalent cerium ion (6.118 eV).

In present case as explaning in fig 2and 3. .The emission spectra is clearly from the same observable site. No another emission band was observed in emission spectrum indicating that trivalent cerium ion occupies one category of sites in the host material.

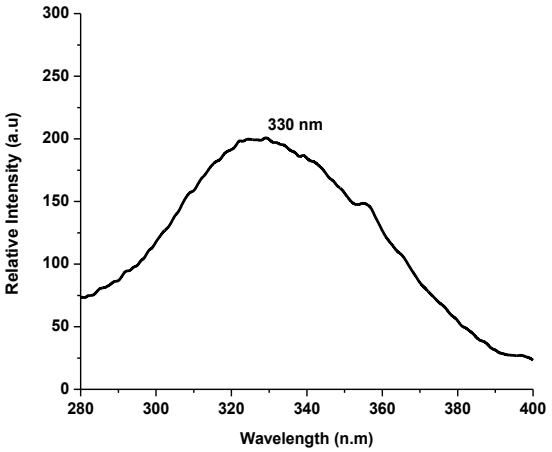

Fig.2 Excitation Spectra for $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphors, λ_{em}= 442 nm.

Thus $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ among blue emission is able to find potential applications as a blue emitting lamp phosphor. The compounds $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ was synthesized by modified combustion synthesis method and activated by alkaline earth Ce^{3+} ion , varies from 1 to 10 mol % with respects to corrosponding host material.

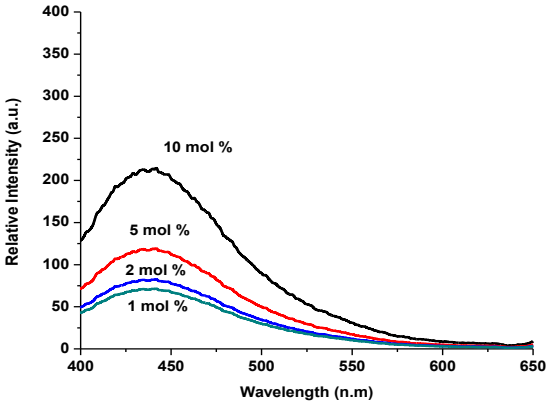

Fig.3 Emission spectra for $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor λ_{ex}=330 nm

The crest emission wavelengths of the prepared fluoride aluminates based compared with compounds prepared by high temperature reaction are summarized through emission spectrum graphical representation. It is going to investigated that, our prepared $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ blue emitting phosphor gives in the emission spectra at 442 nm exhibiting a blue shift moderately with commercial available phosphor and have prospective applications for blue lamp lighting industries.

C. Relationship between Emission Intensity and Concentration of Ce^{3+} ion in $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor

A series of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ blue emitting phosphor with various Ce^{3+} concentrations viz.,1 mol %. to 10 mol % was prepared and the effect of dopand Ce^{3+} concentration on the emission intensity of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor was investigated. While doing the study of relationships between concentration of Ce^{3+} ion and emission intensity in $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor exactness isi important. we do the representation in graphical manner of the exceeding mention samples for every concentration. In the corrosponding figure we explicate the different Ce^{3+} concentrations with emission intensity. The concentration of Ce^{3+} does not transform and disturbed the emission spectrum, excluding changes occuring in the intensity in all the cases. At lower concentrations of Ce^{3+} ion i.e.(concentration < 2 mol. %), the peak for the luminescence spectra for the strong blue emission is obtained but the emission intensity is found weak, however as we lift up the virtual concentration of Ce^{3+} ion then the emission intensity is furthermore rises, and finally reaches the maximum value for maximum concentration of 10 mol.% Ce^{3+} ion. Because of the boost up the excitation and emission properties of Ce^{3+} in $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor, the graphical representation between relative concentration of Ce^{3+} ion and intensity of emission spectra respectively is shown in fig 4 and the effect of Ce^{3+} concentration on emission spectra of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ blue emitting phosphor was also studied.

The $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ blue emitting phosphor prepared is effectively excited by 330 nm suitable for lighiting lamp phosphor; viewing strong emission in the blue region at 442 nm with observing maximum emission intensity is shown in figure 4 From the graphical representation study of Ce^{3+} we get to a closer with the result that, the emission lines spectrum intensities are improved extensively and achievement of maximum value for the high concentration and then decrease serially. As we see the examples for 10 m% of trivalent cerium concentrations the emission intensity is observed to be 216.295 nm, which is the maximum intensity shown for the as prepared $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor by using modified combustion synthesis method and the smallest amount of intensity for emission spectra is found to 69.602

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nm for 1 m% of Ce^{3+} concentration. All these excitation and emission spectra are observed at room temperature.

Figure 4 shows the graphical representative spectra of relative photoluminescence intensity related to relative concentration of trivalent cerium ion.The emission intensities of the prepared phosphors vary with the content Ce^{3+}, as with increasing the concentrations, the maximum photoluminescence intensity was observed at 10 mol % and then eafter the intensity is decreases serially. It is furthermore notified that the positions of peak of the emission spectra have not changed.

The luminescence spectrum of pawde *etl*..[11] reported that electronic transitions of ce^{3+} employ only reorganization of electrons within the inner sub-shell. Study of crystallinity of prepared phosphor might be increases because of the concentration of trivalent cerium ions. Since it is understandable that the addition of trivalent ceriumion in to $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ host which improves the crystallinity of prepared compound, in consequence with the increases in the concentration of trivalent cerium ions which increases the size of particles as well as its complexes. So, there is an increase in intensity of photoluminescence.

S. No.	Conc. of Ce^{3+} in $Na_{21}Mg(SO_4)_{10}Cl_3$ phosphor	Emission intensity (a.u.)
1	1 mol%	69.602
2	2 mol%	83.190
3	5 mol%	120.163
4	10 mol%	216.295

Fig /Table 4 (a) : Emission intensities w.r.to conc. of Ce^{3+} in $Na_{21}Mg(SO_4)_{10}Cl_3$ Blue emitting Phosphor

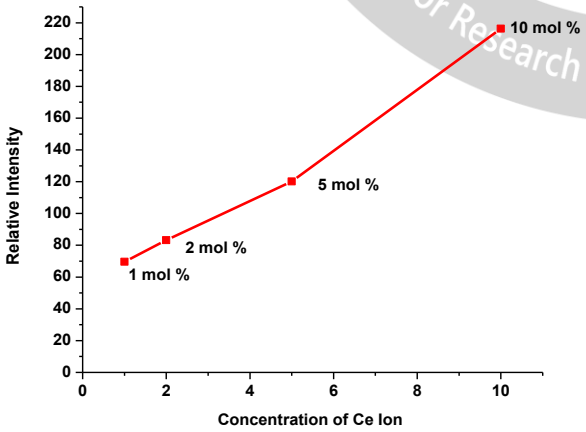

Fig 5 : Effect of conc. of dopant Ce^{3+} on emission intensity of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ Phosphor Chromatic properties of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor

Frequently, the luminescence property of prepared blue emitting phosphor is recognized as to be strongly affected by the increase in concentration of the trivalent cerium ion as a activator. The highest concentration of Ce^{3+} seems to be different with the method of taken synthesis. Zhang *etal*.[11] reported that lower concentrations of activator provide luminescence in weaker. But in our work case, as the intensity of Ce^{3+} ions is increased, intensity for emission increases prominently with the concentration from 1 to 10 mol%. As a result, the complete characteristics of Ce^{+} doped $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ reveals that, it is a promising blue emitting single-host phosphor for lamp industries. Besides it might be useful as a blue lamp phosphor and mixed with other color emission phosphors to obtain white light.

We think that as trivalent cerium ion is present with host lattice then the quantity of energy can be shifted to the activator ion, resulting from the distinctive unique emission peak of these activator ions. [12] It is renowned fact that the outcome obtained from the luminescence properties of prepared inorganic phosphors in powder form depends on the concentration of activator ion, therefore the recognition with concentration of dopant is necessary [13]. Consider the emission spectrum of Ce^{3+} which was located in blue region, was chosen for further analytical study and characterization, the luminescent properties of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ blue emitting phosphors and achieve the complete emission of color. Herewe determine the coordinate of chromaticity indexed with the help of the emission spectra of Ce^{3+}. In 1931 chromaticity coordinate illustration invented by a renowned Commission of International de l'Eclairage (CIE) .It is the two dimensional graphical pictorial illustration of any visible color by the eye system of human being on the x and y axis. [14-5]

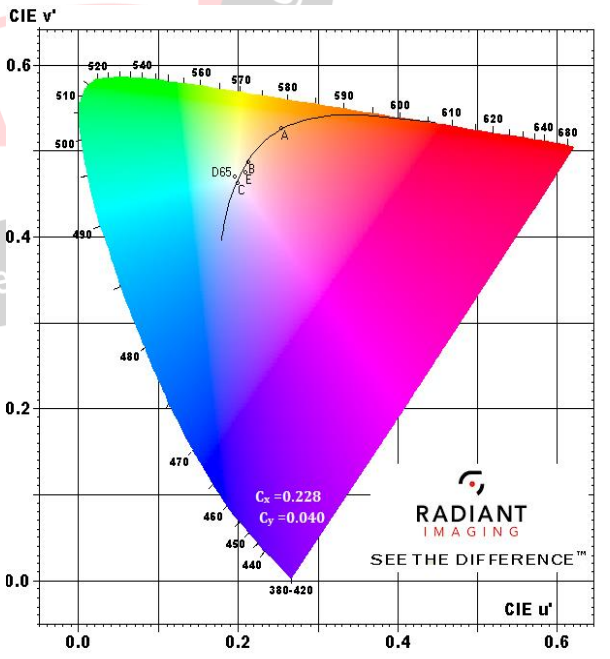

Figure 6 : CIE chromatic diagram for $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor.

Generally illumination of lighting means colors referring lighting in conditions of the chromatic color coordinate

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which recognizes by the human being visualization scheme which use 03 major colors: i.e. blue ,red and green [15].

The CIE chromaticity diagram of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ blue emitting phosphor shown in Fig 6. The color coordinates of the $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor observed,in blue region (C_x =0.228 C_y =0.040) phosphor is also in blue region shown in Fig 6.With the help of CIE diagram it is easy to explains that the $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphors are very near to the CIE graph frame, which easy to shows the utmost color clarity of prepared phosphor material. As a result observed from the emission and excitation mechanism by linking these point in the arrangement of a tri-angle [jointly with a white light (0.31 and 0.32)], the go-between arrangement be able to generate a white light between with a exacting percentage of prepared inorganic blue emitting phosphor. [16]

Because of the rising consequence of Ce^{3+} activated $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ with attractive blue emitting optical properties, which compose the prepared inorganic blue emitting phosphor become the exceptional prospective candidate for blue emitting phorphor industrial applications. The system of chromaticity coordinates (x, y) calculated with the help of the color calculator program radiant imaging. The leading wavelength of the spectrum is the singular wavelength of monochromatic light which appear to have the samilar color as the light source. Such a wavelength calculated with the help of by sketching a singular line exclusive of delay from one end of the chromaticity white illuminants (0.31, 0.32) through the coordinates of x and y axes to be calculated, in anticipation of the line intersect the outer area locus point subsequently to the boundary of the spectral region of 1931 C.I.E. chromatic graphical representation [17-18].The result indicated from the spectrum in figure 3.18 is plotted by the Commission of Internationale de l'´Eclairage (CIE) 1931 chromaticity graphical representation.

IV. CONCLUSION

The study of the photoluminescence characteristics of trivalent cerium activated blue-emitting $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphors in the near UV–vis range shows the excitation bands at 330 nm. Emission characteristics of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ shows emission band at 442 nm,because of the corrosponding energy level. The influence of activator concentration level on the photoluminescence properties of $Na_{21}Mg(SO_4)_{10}Cl_3:Ce^{3+}$ phosphor realize in conditions of a smaller changes in relativistic intensity variation of the $5d\text{-}^2F_{5/2}$ to $5d\text{-}^2F_{7/2}$ ascribed to conceit and improved spliting of crystaografic field. XRD-pattern of prepared $Na_{21}Mg(SO_4)_{10}Cl_3$ phosphor indicates the good crystalline nature. Scanning electron microscopic images shows morphology of the phosphor at microns to sub few microns.Thus modified combustion synthesis is a modified synthesis technique for the preparation of $Na_{21}Mg(SO_4)_{10}Cl_3$ phosphor. The prepared phosphors have prospective blue application for the lamp phosphor.

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