SYNTHESIS AND LUMINESCENCE PROPERTY OF $Na_2CaMg(PO_4)_2:Dy^{3+}$ PHOSPHOR

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ABSTRACT
In this work luminescence property of $Na_2CaMg(PO_4)_2:Dy^{3+}$ phosphor is presented for the first time. $Na_2CaMg(PO_4)_2:Dy^{3+}$ phosphors activated with the trivalent Dy^{3+} rare earth ion were synthesized through solid state reaction method. Phosphors were studied for the phase purity, morphology and luminescent properties. The emission and excitation spectra were followed to explore the luminescence properties. The as prepared phosphors of Dy^{3+} doped $Na_2CaMg(PO_4)_2$ emit yellowish white light as a result of intra *f-f* transitions. The study is novel as no such luminescence data are available for this compound.
Keywords: $Na_2CaMg(PO_4)_2$, Phosphor, Luminescence, Solid State Lighting.

I. INTRODUCTION

White light-emitting diodes (LEDs) offer many advantages such as long service lifetime, thermal resistance, and high efficiency [1-3]. Therefore, white LEDs are expected to be a new light source in the illumination field. Currently, the most common and simple method to produce white light is to combine a blue LED chip with a yellow light emitting phosphor YAG:Ce, however, YAG:Ce emits a greenish–yellow light and is deficient in a red spectral region, which leads to the fact that the white LED has a poor colour rendering property [1-3]. In order to solve this problem, the compensating red phosphors were introduced. Moreover, the other methods to achieve white LEDs are suggested, for example, they can be obtained by combining a tri-colour (red, green, and blue) phosphor or a single-phase white emitting phosphor with an ultraviolet or near-ultraviolet (UV) LED, and the method yields white light with better spectral characteristics and colour rendering property [1-3]. Therefore, more and more attention has been paid to the development of the new tri-colour or white emitting phosphor that can be excited in the range of UV or near-UV light due to the necessity of increasing the efficiency of white LED. Trivalent dysprosium is frequently used as an activator of white light emitting phosphor for application in fluorescent lamps, cathode ray tubes (CRTs) and field emission displays (FEDs) [1-3]. Rare earth doped phosphors have attracted much attention for their high luminescence efficiency, color purity, long emission lifetimes values, and potential applications. The luminescent properties of rare earth phosphors greatly depend on their compositions, morphologies, sizes, crystallinity, etc. As an important family of luminescent materials, phosphates have attracted much attention because of their many important chemical & physical properties [2,4]. Recently, RE^{3+}(RE = trivalent rare earth ion) doped $Na_2CaP_2O_7$ phosphates were reported [4]. There is only a single report that describes the luminescent properties of Ce^{3+} activated $Na_2CaMg(PO_4)_2$, phosphors [5]. However, to the best of our knowledge, no attention has been paid to the luminescent properties of Dy^{3+} activated $Na_2CaMg(PO_4)_2$ orthophosphate phosphor. Therefore, in the present paper, the luminescent characteristics, structural properties and morphology of Dy^{3+} activated $Na_2CaMg(PO_4)_2$ phosphor are investigated and presented for the first time. The phosphors can create the colour emission from blue to reddish yellow. They can be effectively excited by UV and near-UV, and are suitable for serving as phosphor converted white-LEDs.

II. METHODS AND MATERIAL

The samples were synthesized by solid solid state reaction method. According to the molecular formula $Na_2Ca_{1-x}Mg(PO_4)$: xDy (x=concentration of Dy^{3+} rare earth ion), the raw materials Na_2CO_3, $CaCO_3$, $MgCO_3$, $(NH_4)H_2PO_4$, and Dy_2O_3 (all materials are of analytical grade) were measured and mixed stoichiometrically in an agate mortar pestle. The raw materials were ground for more than half an hour, using mortar and pestle and heated at 350 ^oC for four hours and then furnace was switched off to allow the samples to cool to room temperature. The resulting product was crushed for 20 minutes again and fired at 600 ^oC for 20 h. After 20 h,

the furnace was switched off and the samples were allowed to cool to room temperature naturally. Finally all samples prepared in this way were pulverized for few minutes to yield a fine powder. The final phase formation of the host compound was identified by powder X-ray diffraction (XRD) (X'-pert. PRO-ANNALYTICAL X-ray Diffractometer with Cu Kα = 1.5406 Å at 40 kV and 30 mA) at a scanning step of 0.001, in the 2θ range from 10 to 60°. Excitation and emission spectra were measured using RF-5301PC Shimadzu Spectrofluoropho-tometer with slit width 1.5 nm. All the measurements were performed at room temperature.

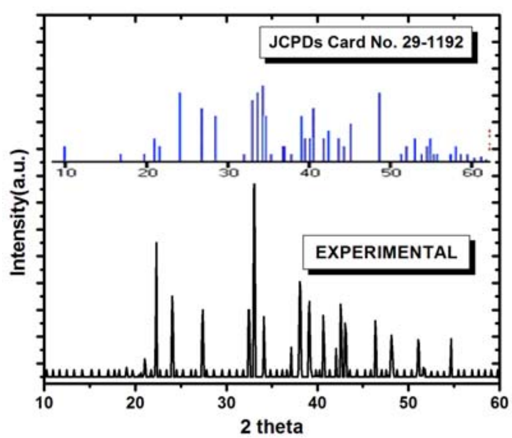

Fig.1. XRD patterns of the synthesized $Na_2CaMg(PO_4)_2$ and standard JCPDs data with file no. 29-1192.

III. RESULTS AND DISCUSSION

III.1. X-ray powder diffraction study and morphology of $Na_2CaMg(PO_4)_2$

To verify the phase formation, and crystalline nature of this compound powder X-ray diffraction test of $Na_2CaMg(PO_4)_2$ was carried out. The powder X-ray diffraction test was carried out with X'- Pert PRO ANALYTICAL X-ray Diffractometer with Cu Kα = 1.5406 angstrom. The XRD pattern of $Na_2CaMg(PO_4)_2$ reported in this work is shown in **Fig.1**.We The XRD pattern of synthesised $Na_2CaMg(PO_4)_2$ is compared with the standard JCPDs data file with card number JCPDF 29-1192. It is seen that the XRD pattern of $Na_2CaMg(PO_4)_2$ shows good match with the standard JCPDs data file. The scanning electron microscopic (SEM) image of $Na_2CaMg(PO_4)_2$ phosphor is shown in **Fig.2**. The morphological studies were carried out with the JEOL, 6380A scanning electron microscope. The SEM characterization shows that the prepared phosphor has micron size particles. These particles are identical to each other and powders of these particles seem to be homogeneous. The average particle size through SEM characterization is found to be around 1μm.

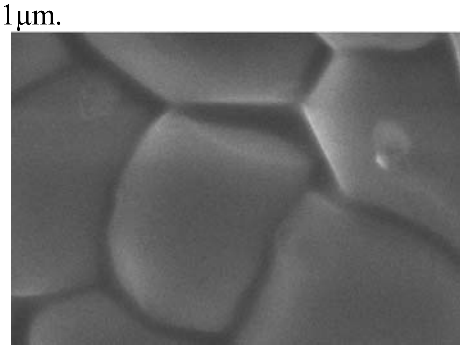

Fig.2 SEM image of $Na_2CaMg(PO_4)_2$

III.2. Spectroscopy of $Na_2CaMg(PO_4)_2$: Dy^{3+} Phosphor

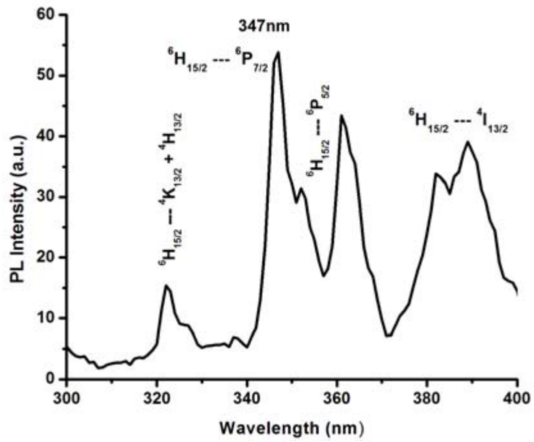

Fig.3 PL excitation spectrum of $Na_2CaMg(PO_4)_2:Dy^{3+}$ phosphor monitored at λ_{emi} **= 572nm.**

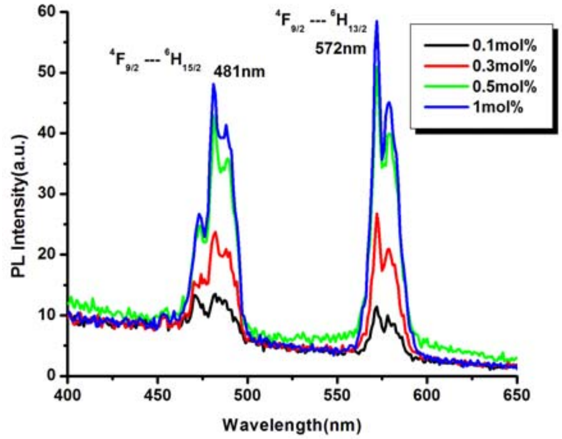

Fig.4 PL emission spectra of $Na_2CaMg(PO_4)_2:Dy^{3+}$ phosphor monitored at λ_{exc} **= 347nm.**

The excitation spectrum **(Fig.3)** monitored at yellow emission 572 nm, from Dy^{3+} activated $Na_2CaMg(PO_4)_2$ phosphor shows several lines in the wavelength region of 300-400 nm, which are due to the excitation of f–f shell transitions of Dy^{3+}. Peaks observed at 322nm, 347nm, 351nm, 361nm, and 388nm correspond to the transitions from the ground state $^6H_{15/2}$ to the excited states; $^4P_{7/2}$; $^4P_{3/2}$ and $^4F_{7/2}$ respectively[6,7]. **Fig.4** shows emission spectrum of $Na_2CaMg(PO_4)_2:Dy^{3+}$ phosphor. In the emission spectra very intense peaks are seen. These peaks cover the blue, yellow, and red regions of the visible spectrum. Therefore, it indicates that white light can be generated by using the $Na_2CaMg(PO_4)_2:Dy^{3+}$ phosphor. Fluorescence emission intensity enhances with variation in concentration of Dy^{3+} activator ions and the most intense emission was obtained at 1mol% Dy^{3+}. The yellowish white light is made up of blue (481 nm) and reddish yellow (572 nm) regions. They correspond to the emission from the $^4F_{9/2}$ excited state to the $^6H_{15/2}$ and $^6H_{13/2}$ ground states, respectively [6,7]. The CIE coordinates of $Na_2CaMg(PO_4)_2:Dy^{3+}$ phosphor were also calculated and values are x=0.303 and y=0.336. These values are very close to the standard white light values (0.33,0.33). Encircled cross in **Fig.5** locates CIE points in the CIE diagram.

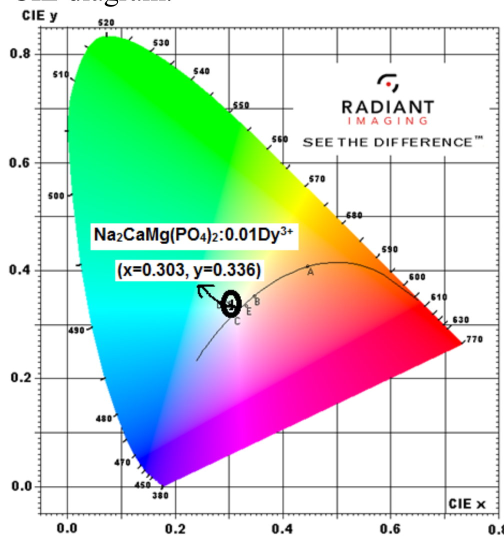

Fig.5. CIE diagram of $Na_2CaMg(PO_4)_2$: $0.01Dy^{3+}$ phosphor.

IV. CONCLUSION

Successful preparation of $Na_2CaMg(PO_4)_2:Dy^{3+}$ phosphors was achieved by using solid state reaction method at 600 °C. Typical excitation and emission spectra were observed for all concentrations of Dy^{3+} activators doped in $Na_2CaMg(PO_4)_2$ system. Both magnetic dipole as well as electric dipole transitions are involved in the luminescence property of Dy^{3+} activated $Na_2CaMg(PO_4)_2$ phosphor. Highly strong absorption in NUV region for $Na_2CaMg(PO_4)_2:Dy^{3+}$ phosphor indicates that it could be effectively excited by LEDs emitting in the NUV region. The chromaticity coordinates were found to be *(x=0.303, y=0.336),* for Dy^{3+} activated $Na_2CaMg(PO_4)_2$ phosphor. The CIE coordinates of $Na_2CaMg(PO_4)_2:Dy^{3+}$ lie in the neighbourhood of white light standard values(0.33,0.33), which in turn shows that the as prepared phosphor is suitable candidate for white light generation. The whole photoluminescence phosphor results indicate that $Na_2CaMg(PO_4)_2:Dy^{3+}$ could become an important component of pc-WLEDs for solid state lighting applications.

$Na_2CaMg(PO_4)_2:Dy^{3+}$ phosphor is environmental friendly because mercury wavelength is not involved in excitation process.

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