

Photoluminescence Characteristics of Cu^+ and Mn^{2+} in Activated Halosulphate Phosphor

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Abstract : Luminescence of Cu^+ and Mn^{2+} in NaMgF_3 and NaMgCl_3 Halo-phosphors by three different synthesis routes viz. wet chemical synthesis (WCS), solid state diffusion (SSD) and centrifuge (CS) methods, in the same atmospheric conditions are studied. Formation of compound was confirmed by taking XRDs of the samples and matched with the standered JCPDs showing the successful synthesis by different simple routes. PL emission and excitation spectra of NaMgF_3 and NaMgCl_3 when doped by Cu or Mn showed similar spectra when synthesized by different routes, moreover PL remains at the same position (wavelengths) even if halogen atom in the compound (i.e. F by Cl) is replaced.

Photo-excited luminescence from Cu-doped halophosphor showed PL emission spectra of NaMgF_3 : Cu^+ and NaMgCl_3 : Cu^+ in the ultraviolet region due to $3d^94s \leftrightarrow 3d^{10}$ transition. NaMgF_3 : Mn^{2+} and NaMgCl_3 : Mn^{2+} emission is placed in orange region (597 nm) for mercury free excitation of 380 nm due to ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. Our emphasis is not only on the characterization of the samples but on the method of synthesis of the phosphors by simple routes. All the synthesis routes are easy, worked at low temperature, low cost and least hazardous and eco friendly.

IndexTerms - Synthesis route; luminescence; phosphor; spectroscopy; wet chemical; Solid state diffusion; centrifuge route

I. INTRODUCTION

An important inorganic materials, complex metal fluorides of the type AMF_3 (A = K, Na, Li; M = divalent-metal) with interesting optical and magnetic properties have found applications as luminescent materials, radiation detectors, laser optical materials, etc. [01] and used in solid-state laser applications [02, 03]. In the series of the preparation of halophosphors, we have now made attention on NaMgF_3 and NaMgCl_3 after KMgCl_3 in view to use halide based phosphors in lamp industries; we have synthesized and characterized halophosphors doped with low cost transition metals which are not attempted much more elsewhere in the literature. Our research focus is on the different and simple preparation routes of the new halophosphors.

Luminescence in NaMgF_3 and NaMgCl_3 was also studied by adding rare earths which showed good luminescence. NaMgF_3 is reported to be orthorhombic belongs to symmetry class Pbnm. The crystal structure of NaMgF_3 is studied which is given in American Mineral data [04].

After literature survey, we found NaMgF_3 had synthesized and studied earlier by different researchers by different methods viz. N.J.M. Le Masson et al. [05] had studied the spectroscopic properties of Ce^{3+} and Pr^{3+} in NaMgF_3 . Igor Sevonkaev et al had synthesized NaMgF_3 in two stage reaction [06] Xiaoming Zhang et al had reported that NaMgF_3 as self-luminescent and its synthesis and optical property via a solvothermal method [07]. NaMgF_3 : Eu nanoparticles were produced using a modified reverse micro-emulsion method by Hua et al. [08]. M. Cao had also explained the synthesis of this compound [09]. NaMgF_3 : Eu^{2+} were prepared by melt method and are suitable for radiation dosimetry applications [10]. Single crystals of NaMgF_3 were grown via the Bridgman method in a vitreous carbon crucible in a reducing atmosphere using a high-frequency furnace and spectroscopic studies were performed with Eu^{2+} and Yb^{2+} as a dopant by S. Lizzo. [11]. Here we have discussed the simpler method of the synthesis of NaMgF_3 and spectroscopic properties with easily available transition metals, Cu and Mn.

Similar compound BaMgF_3 was investigated as host material for the luminescent rare earth (RE) or 3d transition metal ions. BaMgF_3 : Ce^{3+} crystals, grown by Czochralski technique [12]. NaGdF_4 : Eu^{3+} was synthesised by hydrothermal method [13]. M. Karbowski et al. have reported synthesis of NaGdF_4 : Eu^{3+} by co-precipitation in aqueous solution, reversed micelle method, as well as a solid-state reaction at high temperatures [14, 15]

A spectroscopic study was also performed on KMgF_3 : Eu^{2+} [16]. KMgF_3 : Ce^{3+} and has attracted interest for its possible application as scintillator [17] and as sensitive dosimeter [18, 19]. Ce^{3+} doped LiCaAlF_6 and LiSrAlF_6 have been reported as leading candidates for tunable solid-state lasers in the UV region [20, 21]. Tunable ultra-violet laser oscillations and amplification have been demonstrated in LiCaAlF_6 : Ce^{3+} [22] and LiSrAlF_6 : Ce^{3+} [23] fluorides like SrF_2 [24], SrMgF_4 [25], etc. Dorenbos [26-27] has reviewed data on several Ce^{3+} activated fluorides. Fluoride based phosphor has been investigated earlier by number of researchers but few papers are available by doping transition metals on Chloride based halophosphors. The compounds $\text{Na}_6\text{Pb}_4(\text{SO}_6)_4\text{Cl}_2$ [28] $\text{Na}_6\text{Cd}_4(\text{SO}_6)_4\text{Cl}_2$ [29], $\text{Na}_6\text{Ca}_4(\text{SO}_6)_4\text{Cl}_2$ [30,31] are few known members of the chloride group. We have also reported $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$ [32], KMgSO_4F [33], KCaSO_4Cl [34], KMgSO_4Cl [35], $\text{Na}_6(\text{SO}_4)_2\text{FCl}$ [36], NaMgSO_4F and $\text{Na}_3\text{SO}_4\text{F}$ [37] the inorganic materials as good fluoride and chloride based phosphors.

Copper (Cu) and Manganese(Mn) both belong to the group of transition metal where 3d shell is filled with electrons and outer 4s shell remains unchanged. These elements have high tensile strength, density, hardness, high melting, and boiling points. The incorporation of copper into several matrices provides them with interesting optical features, which strongly depend on the ionic state of the copper atoms [38-47]. It has been mentioned that incorporation of monovalent copper can be difficult and incorporation of monovalent copper in lattices such as halides is still considered to be difficult and thus, doping of Cu^+ has been achieved in a limited number of solids [48-51].

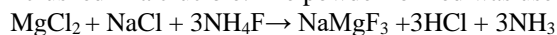
Another transition metal Mn^{2+} gives emission in the range of 500 to 700 nm depending on the host, which are mostly used in fluorescent lamps and as electroluminescent phosphor [52-54].

In this study, we have compared luminescence of NaMgF₃ and NaMgCl₃ when doped with Cu or Mn synthesizing by three different routes. They are investigated by X-ray powder diffraction methods. Excitation and emission spectra were recorded to get insight into optical properties and applicability of the compound is argued.

II. SYNTHESIS ROUTES OF HALO-PHOSPHORS

Halo-phosphor NaMgF₃ or NaMgCl₃ has been synthesized by three different routes successfully (1) Wet chemical synthesis (WCS) (2) solid state diffusion (SSD) (3) centrifuge synthesis (CS) routes.

LiBaF₃ has been synthesized using LiCl and BaCl₂ by WCS. The method for synthesis of NaMgF₃ exploits the fact that the use of chlorine ion as starting materials prevents hydrolysis. Hence, complex fluorides were prepared by dissolving the analytical reagent grade chlorides of the constituents (MgCl₂, NaCl) in the stoichiometric ratio in double distilled de-ionized water in a PTFE container and NH₄F was added drop wise. NaMgCl₃ is synthesized by dissolving MgCl₂ and NaCl in the stoichiometric ratio in double distilled de-ionized water. Then for doping stock solution of water-soluble sulfate salt of Copper or Manganese was prepared and added drop wise to the solution of NaMgF₃ and NaMgCl₃, then stirred for half an hour. The solution was heated off at 80°C, dried samples were then crushed in a crucible. The powder formed was used in further study. All components are reacted by the following reaction.



In the second method, SSD route same amount of material were taken and are crushed for half an hour and heated for an hour at 100°C, it was taken out and again crushed for half an hour and heated at 300°C overnight in a furnace and then allowed to cool overnight.

In the third method, CS route, same amount of material was taken and Cu or Mn were added and stirred for about 10 hours with the help of magnetic stirrer in ethanol. The resulting solution was centrifuged for 2-3 min at 4500 rpm to separate the sample. The samples were washed and filtered and then ethanol was allowed to evaporate from the compound at 60°C to get fine white powder.

Formation of the compounds synthesized by the three different routes is confirmed by taking the x-ray diffraction (XRD). Photoluminescence spectra were recorded in the range 220–700 nm on a Fluorescence spectrometer (Shimatzu RF-5301) with spectral slit width of 1.5 nm.

III. RESULTS AND DISCUSSION

3.1 Phase formation of NaMgF₃ and NaMgCl₃

Figure 1 and 2 shows X-Ray diffraction pattern (XRD) of NaMgF₃ and NaMgCl₃ respectively prepared by a) WCS, b) SSD and c) CS routes. All the XRD patterns are matched with the standard ICSD file 075291 of NaMgF₃ and JCPDS file 15-0295 of NaMgCl₃ which is a direct evidence for the formation of the desired compound. Some unexpected lines are appeared at few positions that may be due to unwanted impurities. However, most prominent lines are matching with standard file. These results indicate that the final product was formed in homogeneous form.

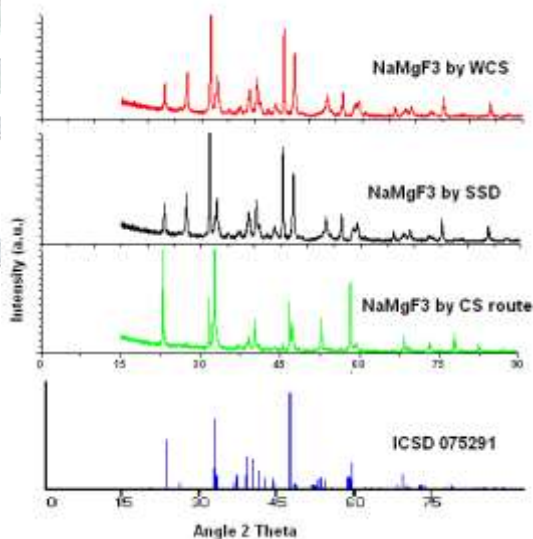


Figure 1: X-Ray diffraction pattern (XRD) of NaMgF₃ by WCS, SSD and CS routes compared with standard XRD pattern.

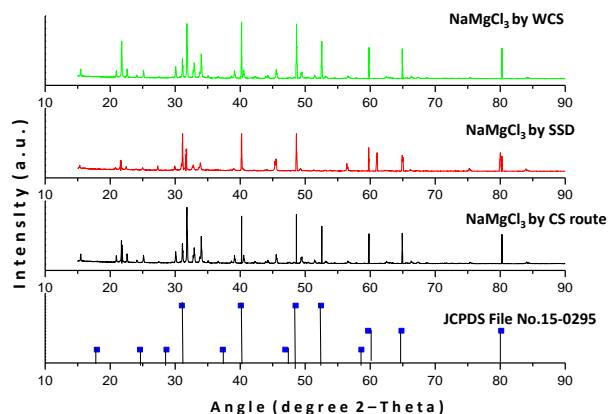


Figure 2: X-Ray diffraction pattern (XRD) of NaMgCl₃ by WCS, SSD and CS routes compared with standard XRD pattern.

3.2 PL emission in NaMgF₃ and NaMgCl₃ (Pure)

The photoluminescence (PL) of pure NaMgF₃ and NaMgCl₃ prepared by all the three different routes are studied. Excitation and emission spectra of pure NaMgF₃ are indicated in Figure 3 and Figure 4 respectively, it shows emission at 366 nm 389 and 388 nm when monitored at the excitation wavelength of 358nm when synthesized by WCR, SSD and CS routes respectively. Photoluminescence by SSD and CS routes of the pure sample of NaMgCl₃ shows very low intensity, hence not shown in figure; however peaks of excitation and emission are situated on the same places.

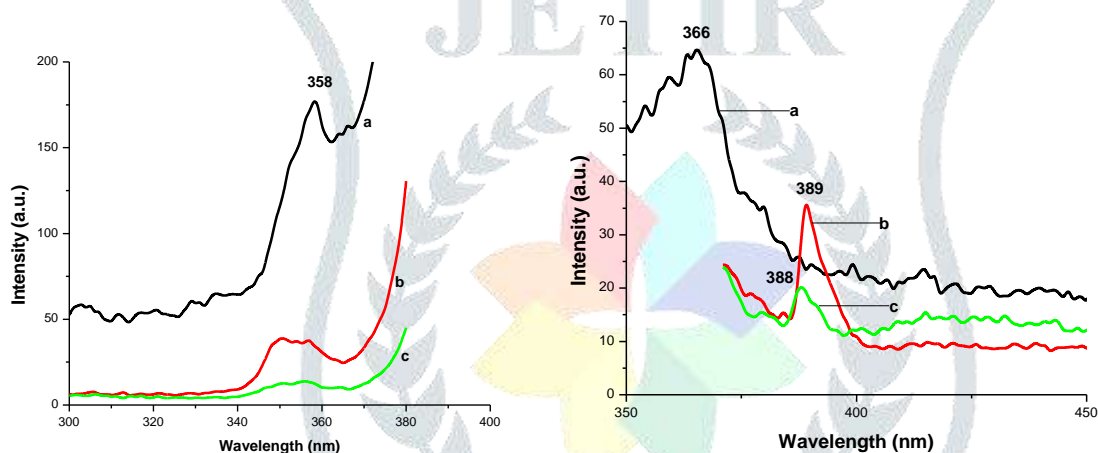


Figure 3: Excitation spectra of NaMgF₃ at $\lambda_{em}=388\text{nm}$ when synthesized by a)WCS, b)CS and c) SSD

Figure 4: Emission spectra of NaMgF₃ at $\lambda_{ex} = 358 \text{ nm}$ when synthesized by a) WCS, b) CS and c) SSD

Figure 5 and Figure 6 shows the excitation and emission spectra obtained by WCS route. The excitation spectrum shows two peaks at 326 nm and 346nm, there is emission band with maximum at 374 nm when excited by 346nm wavelength. The spectra show both compounds NaMgF₃ and NaMgCl₃ are self-luminescent. Since there are no activated ions present, so the emission has to be caused by some kinds of defects or electronic centers. [55, 56].

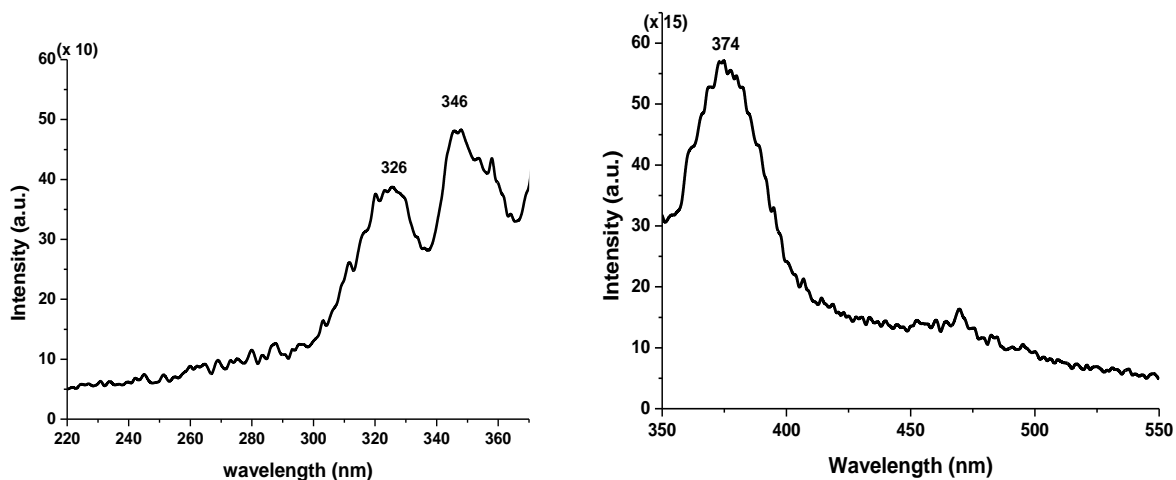


Figure 5: Excitation spectra of NaMgCl₃ at $\lambda_{em}=367\text{nm}$ when synthesized by WCS

Figure 6: Emission spectra of at $\lambda_{ex} = 348 \text{ nm}$ when synthesized by

IV. PHOTOLUMINESCENCE (PL) STUDY

4.1 Photoluminescence in NaMgF₃: Cu⁺0.05m% and NaMgCl₃: Cu⁺0.05m%

Figure 7 and **Figure 8** shows the excitation and emission spectra of NaMgF₃: Cu_{0.05m%} when synthesized by a) WCS b) SSD and c) CS route respectively. The excitation peak is observed at 265 nm when monitored at emission wavelength of 358 nm. The halophosphor for 0.05mole% of Cu⁺ shows double hump at 357nm and 368nm when excited at 265nm wavelength. NaMgF₃: Cu_{0.05m%} excitation and emission is observed at the same position when synthesized by WCS, SSD or CS route.

Figure 9 and **Figure 10** shows the excitation and emission spectra of NaMgCl₃:Cu_{0.05m%} synthesized by a) WCS b) SSD and c) CS route respectively. The excitation peak is observed at 271 nm when monitored at emission wavelength of 357 nm and it shows emission at 345nm and 357nm when excited by wavelength of 271 nm when synthesized by WCS, SSD or CS route.

The ionic radius of Cu⁺ ion is almost equal to Mg²⁺ ion. Hence, there may be possibility of replacing Mg²⁺ ion by Cu⁺ ion when enters into NaMgF₃ or NaMgCl₃ host.

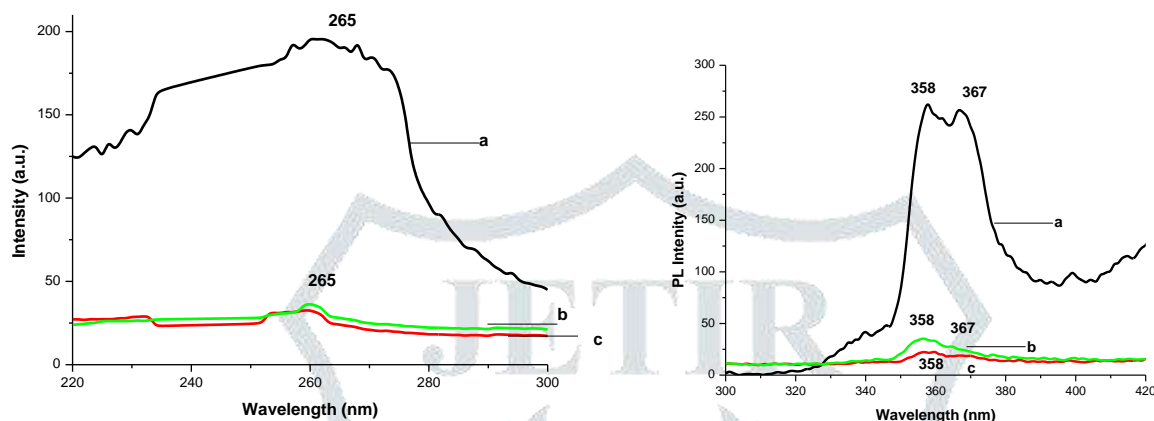


Figure 7: Excitation spectra of NaMgF₃: Cu⁺ 0.05mole% at λ_{em}=374nm synthesized by a) WCS, b) CS and c) SSD route

Figure 8: Emission spectra of NaMgF₃: Cu⁺ 0.05mole% at λ_{ex}=265 nm synthesized by a) WCS, b) CS and c) SSD route

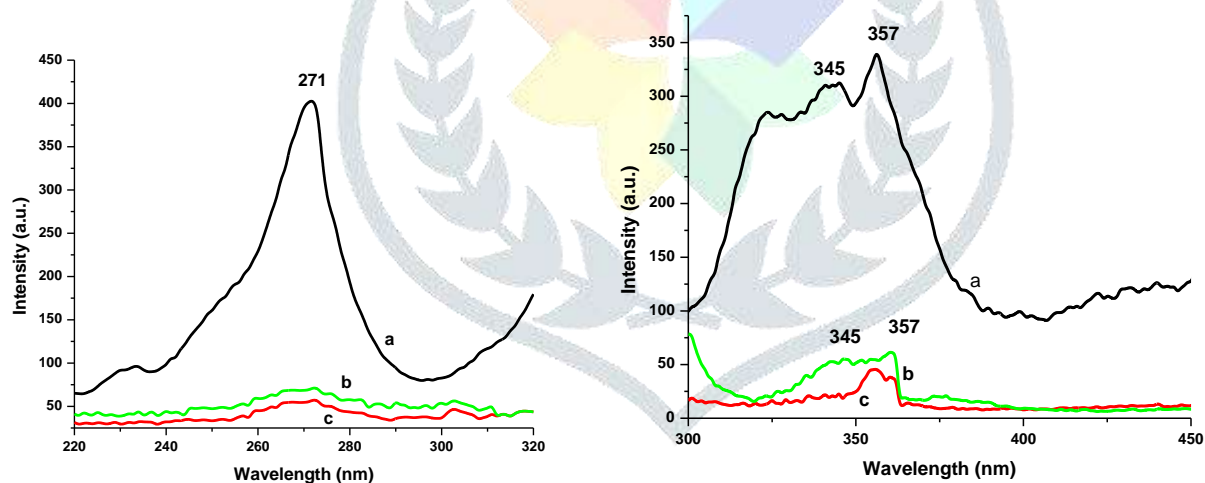


Figure 9: Excitation spectra of NaMgCl₃: Cu⁺ 0.05mole% monitored at λ_{em}=357nm synthesized by a) WCS, b) CS and c) SSD route

Figure 10: Emission spectra of NaMgCl₃: Cu⁺ 0.05mole% monitored at λ_{ex}=271 nm synthesized by a) WCS, b) CS and c) SSD route

According to energy level model, the luminescence process and the transition probabilities for Cu⁺ ions state that the system is first excited from the ground state, 3d¹⁰ to the singlet state of the 3d⁹4s¹ configuration and then, the electrons pass to the triplet state, mainly to level 2 because of symmetry reasons. The ground state of a free Cu⁺ ion is of 3d¹⁰ configuration, while the lowest excited states are populated due to the 3d¹⁰ ↔ 3d⁹ 4s and 3d¹⁰ ↔ 3d⁹ 4p transitions and the singlet state does not affect the luminescent process.

Non-radiative transitions may occur between the two energy levels of the triplet state, with probabilities p_{23} and p_{32} . The filling of the 3d orbital is irregular, since for copper (3d¹⁰4s) an electron from the 4s shell is promoted to a 3d orbital. Cu⁺ is known to exhibit characteristic luminescence corresponding to 3d⁹4s ↔ 3d¹⁰ transitions [57]. In particular, the presence of Cu⁺ ions in this matrix activates luminescent emission in the ultraviolet (UV) and visible (VIS) range of a spectrum that may arise potential applications for the realization of tunable lasers and other optical devices.

4.2 Photoluminescence in NaMgF₃: Mn²⁺_{0.05m%} and NaMgCl₃: Mn²⁺_{0.05m%}

The electrical, magnetic and mechanical properties of Mn²⁺ ions are widely investigated in the luminescent materials, [58-63]. Figure 11 and Figure 12 shows the excitation and emission spectra of NaMgF₃: Mn²⁺_{0.05m%}. The excitation peaks are observed at 328, 345 and 396 nm when it is synthesized by WCS and SSD route and CS route monitored at emission wavelength of 597 nm. In the excitation spectrum of Mn²⁺, the peaks centred at 328, 345 and 396 nm are assigned to the transitions from ⁶A₁(6S) to 4E(4D), ⁴T₂(4D) and ⁴A₁(4G), ⁴E(4G) levels, respectively.

Emission spectra are observed at the same position 597nm monitored at excitation wavelength of 396nm when synthesized by different routes respectively. The emission spectrum consists of single band in the orange range. The Mn²⁺ ions exhibit yellow luminescence if emitting level is ⁴T_{2g}(4G), while orange when ⁴T_{1g}(4G) level is involved. The emission band centred at 597 nm corresponds to the ⁴T₁(4G) → ⁶A₁(6S) (⁴T_{1g} → ⁶A_{1g}) transition of Mn²⁺. Since these transitions are spin and parity forbidden, both the excitation and emission intensities are relatively weak. The nature of excitation and emission spectra does not vary with the synthesis route and small change in luminescence intensity is observed.

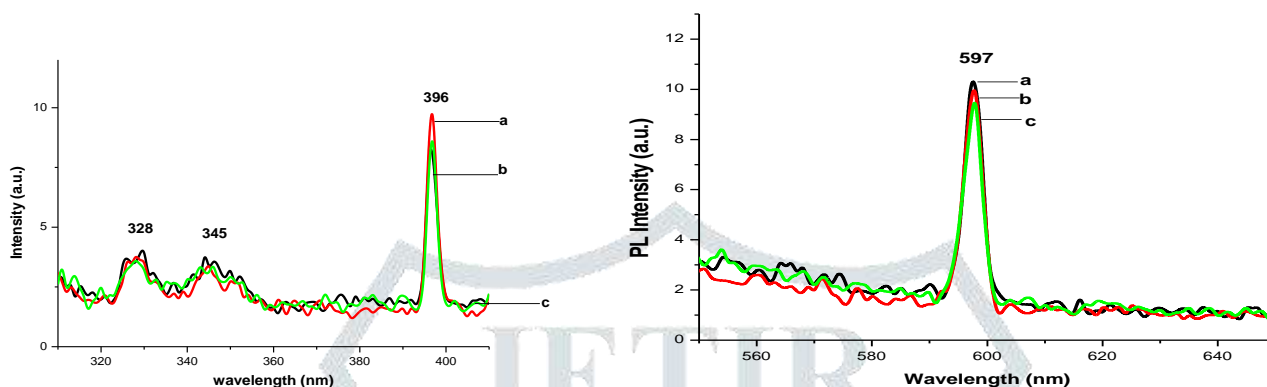


Figure 11: Excitation spectra of NaMgF₃: Mg²⁺_{0.05mole%} at $\lambda_{em}=396$ nm synthesized by a) WCS, b) CS and c) SSD route

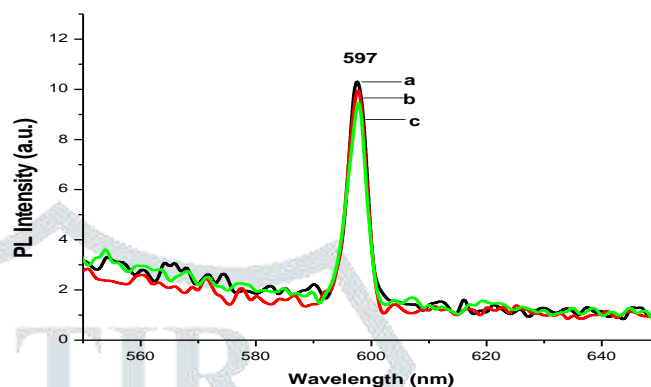


Figure 12: Emission spectra of NaMgF₃: Mg²⁺_{0.05mole%} at $\lambda_{ex}=597$ nm synthesized by a) WCS, b) CS and c) SSD route

Figure 13 and Figure 14 shows the excitation and emission spectra of NaMgCl₃:Mn_{0.05m%} synthesized by a) WCS b) CS and c) SSD route respectively. The excitation and emission peaks are observed at the same position that of NaMgF₃:Mn_{0.05m%}, only slight change in intensity is seen.

Mg²⁺ is well suited for Mn²⁺ doping due to the matching ion sizes and charge configurations.

Hence, there may be possibility of replacing Mg²⁺ ion by Mn²⁺ ion when enters into NaMgF₃ or NaMgCl₃ host.

Literature stated that, Mn²⁺ in tetrahedral coordination usually gives a green or yellow emission, whereas Mn²⁺ with octahedral coordination gives orange-red emission. This gives a wide usage of Mn²⁺ doped compounds for fluorescent lamps, cathode ray tubes and white light-emitting diodes (LEDs).

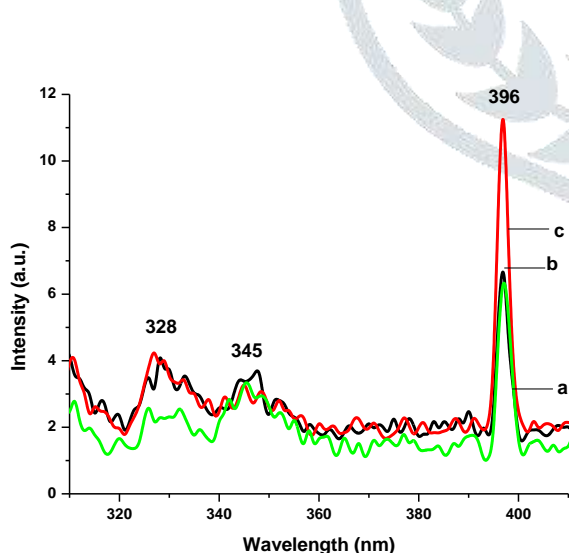


Figure 13: Excitation spectra of NaMgCl₃: Mg²⁺_{0.05mole%} monitored at $\lambda_{em}=397$ nm synthesized by a) WCS, b) CS and c) SSD

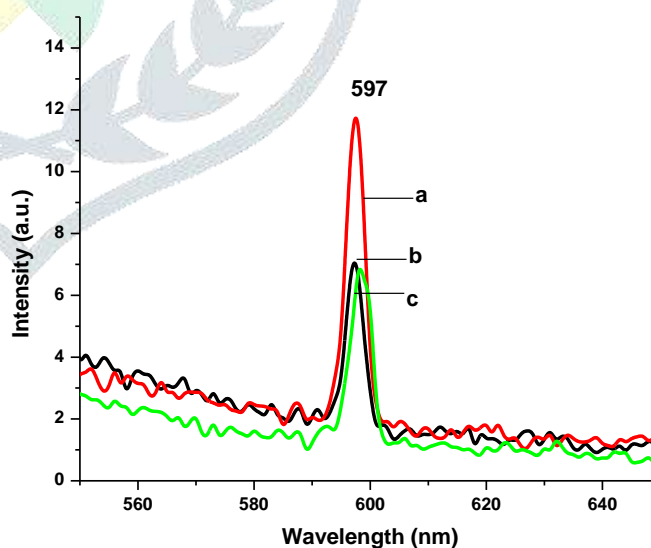


Figure 14: Emission spectra of NaMgCl₃: Mg²⁺_{0.05mole%} monitored at $\lambda_{ex}=597$ nm synthesized by a) WCS, b) CS and c) SSD

Following Table shows the comparison between the Photoluminescence of NaMgF₃ and NaMgCl₃ when doped by Cu⁺ and Mn²⁺

Phosphor	Synthesis Route	λ excitation (nm)	λ emission (nm)	Max. PL emission Intensity (a. u.)
NaMgF ₃ : Cu ⁺	WCS	265	358, 367	234
	CS	265	358, 367	39
	SSD	265	358, 367	32
NaMgCl ₃ : Cu ⁺	WCS	271	345, 357	344
	CS	271	345, 357	66
	SSD	271	345, 357	53
NaMgF ₃ : Mn ²⁺	WCS	396	597	11
	CS	396	597	10
	SSD	396	597	10
NaMgCl ₃ : Mn ²⁺	WCS	396	597	12
	CS	396	597	08
	SSD	396	597	08

V. CONCLUSION

The following conclusions are drawn from this study

1. Phosphors NaMgF₃ and NaMgCl₃ are successfully prepared by simple WCS, SSD and CS routes without using any inert atmosphere. NaMgF₃ and NaMgCl₃ both material have self luminescence.
2. An impurity of transition metal ions like Cu⁺ or Mn²⁺ in NaMgF₃ and NaMgCl₃ shows photoluminescence emission spectra. Cu⁺ emission is observed at 358 nm and 367 nm in NaMgF₃ and at 348nm and 357nm in NaMgCl₃, in UV region. While Mn²⁺ emission is seen at 597 nm (orange region) when excited by wavelength of 396nm.
3. Photoluminescence studies by three routes (WCS, SSD and CS) showed there is no much change in the wavelength of emission. The intensity of PL spectra is maximum when phosphor is synthesized by WCS.
4. No notable difference is seen in the PL spectra of Cu⁺ or Mn²⁺ doped NaMgF₃ and NaMgCl₃, this suggests if halide F is replaced by Cl, PL emission spectra remains at the same position.
5. Mn²⁺ doped NaMgF₃ and NaMgCl₃ phosphor in orange-red region when excited by wavelength of 397nm which is mercury free excitation so this can be used in solid state lightings.

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