COMPARATIVE STUDY OF PHOTOLUMINESCENCE OF Mn^{2+} IN A MIXED ALKALINE CHLOROSULPHATE NANOMATERIAL $KMgSO_4Cl$ USING DIFFERENT ROUTE METHOD

S.R.Choubey*[a], L.P.Damodare[b] and S.C.Gedam[c]

[a] PGTD,Department of Physics,VMV/JMT/JJP College, Nagpur 440008, India

[b] PGTD,Department of Physics,VMV/JMT/JJP College, Nagpur 440008, India

[c] Department of Physics, K. Z. S. College, Kalmeshwar, District Nagpur, India

ABSTRACT

To prepare $KMgSO_4Cl$ different methods have been attempted such as wet chemical synthesis (WCS) and solid state diffusion (SSD) methods. XRDs of the sample prepared by these two methods have been placed at the same position, phase and matched well with standard data. $KMgSO_4Cl$: Mn showed improved photoluminescence (PL) which may be used as efficient lamp phosphors. Photoluminescence of $KMgSO_4Cl$: Mn^{2+} synthesized by WCS and SSD route is placed in yellow region (576 nm) where as orange region shifting (593 nm) is observed for an excitation of 380 nm. Shifting of peak positions and intensity may be due to Nano particle size of the $KMgSO_4Cl$ host. X-ray diffraction and PL characterization of phosphors has been reported in this sample. All the synthesis routes are easy, worked at low temperature, low cost and least hazardous and eco friendly.

Keywords: Wet Chemical Synthesis, Solid State Diffusion, X-Ray Diffraction, Photoluminescence, Emission Spectra

1. Introduction

In view to use alkaline Chlorine halides based phosphors used in lamp industries; we have synthesized and characterized halophosphors which are not attempted much more elsewhere in the literature. Our research focus is always on the preparation of the new halo- phosphors. In the same series of the preparation of halophosphors, we have now made attention on $KMgSO_4Cl$ host. The phosphors are synthesized and characterized by doping transition metals manganese (Mn^{2+}). Phosphors synthesized by using transition metals are essential for its low cost, less hazardous and being eco friendly. It has wide applications in scintillation ,lighting, imaging, and display devices. 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 as per J. Ferguson, H.J. Guggenheim [1]; M.D. Shinn, J.C. Windschleif; D.K. Sardar[2] and G. U Caldiño [3]. We have reported KZnSO4Cl, KMgSO4F, KCaSO4Cl, NaMgSO4Cl, KCaSO4Cl, inorganic materials as good phosphors by doping transition metals as per A. Poddar, S.C. Gedam, S.J. Dhoble[4], S.C. Gedam, S.J. Dhoble, R.B. Pode [5] and P.S. Thakre, S.C. Gedam, S.J. Dhoble, R.G. Atram [6]. However, we could not find any information on luminescence in $KMgSO_4Cl$ compound after doping with transition metals. In this paper special attention has been paid to photoluminescence study of manganese doped in chloride based material

$KMgSO_4Cl$ by synthesizing it by different routes. We have successfully used the technique in doping Mn^{2+} in $KMgSO_4Cl$ host which could be interesting for several reasons.

2. Experimental

In this study $KMgSO_4Cl$ is synthesized by WCS and SSD routes and incorporation of Mn have been done successfully without using any inert atmosphere. The details of synthesis routes are explained as follows-

For wet chemical synthesis (WCS) route $MgSO_4$ and KCl of AR grade were taken in a stoichiometric ratio and they are dissolved separately in double distilled de-ionized water and mixed together, resulting in a solution of $KMgSO_4Cl$. Then water-soluble sulphate salt of manganese was added to obtain $KMgSO_4Cl:Mn^{2+}$. The solution was evaporated at 80 °C. Compounds are formed by this route are hygroscopic and catch moisture if left in the open, so they are heated at 350 °C. The resultant polycrystalline mass was crushed to fine particle in a crucible. The powder was used in further study.

For solid state diffusion (SSD) route same amount of material is taken then crushed for half an hour and heated for an hour at 100°C then temperature has been increased in steps up to 350 °C and heated for 12 hour in furnace and cooled slowly. All the compounds reacted by the following reaction:

$$MgSO_4 + KCl \rightarrow KMgSO_4Cl$$

$$KMgSO_4Cl + Mn_2(SO_4).2H_2O \rightarrow KMgSO_4Cl:Mn^{2+}$$

Formation of (both methods) compounds were confirmed by taking x-ray diffraction (XRD) and reported earlier [11] Photoluminescence (PL) spectra were recorded in the range 220–700 nm on a Fluorescence spectrometer (Shimatzu RF-5301) with spectral slit widths of 1.5 nm. Samples were also found to be stable against UV irradiation that was used for the PL measurements.

3. Results and Discussion:

3.1. Photoluminescence (PL) study of Mn^{2+} emission in $KMgSO_4Cl$:-

Mn^{2+} ions have been widely investigated in the luminescent materials, for the electrical, magnetic and mechanical properties as per C.C. Diao, C.F. Yang (2010) [12]. The typical luminescence of Mn^{2+} $(3d^5)$ is attributed to the $^4T_1 \rightarrow {}^6A_1$ transitions. From the Tanabe–Sugano diagram, the emission transition of $^4T_1g(G) \rightarrow {}^6A_1g(G)$ in Mn^{2+} ions depends on the crystal field strength of the substituted sites, C.C. Diao, C.F. Yang (2010) [12]. For example, the Mn^{2+} in tetrahedral coordination usually gives a green or yellow emission, whereas Mn^{2+} with octahedral coordination gives a red emission. This gives a wide usage of Mn^{2+} doped compounds for fluorescent lamps, cathode ray tubes and white light-emitting diodes (LEDs). As described in the Sugano–Tanabe diagram the ground state of Mn^{2+} has six manifold spin degeneracy[13]. However, no excited states of Mn^{2+} have sextet spin degeneracy. As a result, all the absorption transitions to the excited state are spin-forbidden with low transition probabilities.

Fig. 1 shows the excitation spectra of $KMgSO_4Cl:Mn^{2+}$ 0.02 mol % by a) WCS b) SSD route The excitation peaks are observed at 330, 347 and 383 nm when it is synthesized by WCS and SSD route. In the excitation spectrum of Mn^{2+}, the peaks centred at 330, 347 and 383 nm are assigned to the transitions from $^6A_1(6\ S)$ to $4E(4D)$, $^4T_2(4D)$ and $^4A_1(4\ G)$, $^4E(4\ G)$ levels, respectively.

Figs. 2–3 shows emission spectra of $KMgSO_4Cl:Mn^{2+}$ halophosphor for different concentrations of Mn^{2+} (0.02 mol%, 0.05 mol% 0.1 mol%) by two different synthesis routes respectively. The emission spectrum consists of single band in the yellow or orange range with maximum peak at about 576 nm (yellow, for WCS and SSD route). The Mn^{2+} ions exhibit

yellow luminescence if emitting level is $^4T_{2g}$ (4 G), while orange when $^4T_{1g}$(4 G) level is involved. Shifting of peak position (from yellow to orange- red region) and intensity of Mn in $KMgSO_4Cl$ matrix may be due to nano particle size. The emission band centered at 576 nm corresponds to the $^4T_1$(4 G) — $^6A_1$(6 S) transition of Mn^{2+} while the emission band centered at 593 nm corresponds to the $^4T_1$(4 G) — $^6A_1$(6 S) ($^4T_{1g}$— $^6A_{1g}$) transition of Mn^{2+} (Fig. 4).Since these transitions are spin and parity forbidden, both the excitation and emission intensities are relatively weak. The nature of emission spectra does not vary with the Mn^{2+} concentration but the luminescence intensity changes by changing concentration and the synthesis route. It has been found that the emission intensity of Mn^{2+} increases first when Mn concentration increases. The change in PL intensity of the emission peak may be due to a higher concentration of defects that generates non radiative states within the forbidden gap, which is consistent with the previous work reported for other phosphors. Mg^{2+} is well suited for Mn^{2+} doping due to the matching ion sizes and charge configurations.

Comparison of PL in $KMgSO_4Cl$: Mn^{2+} synthesized by different routes.

Phosphor	Synthesis Route	λ excitation (nm)	λ emission (nm)	Max. PL emission Intensity (a. u.)
$KMgSO_4Cl$: Mn^{2+}	WC	383	576	42
	SSD	383	576	65

4. Conclusion:

The following conclusions have been made by doping successfully transition metal ions like Mn in $KMgSO_4Cl$.The samples $KMgSO_4Cl$:-Mn^{2+} are prepared by simple WCS and SSD without using inert atmosphere. PL emission spectra of the of the phosphors of Mn^{2+} emission at 576 nm (yellow region) or at 593 nm (orange region) is observed. Photoluminescence studies $KMgSO_4Cl$:-Mn^{2+}suitable. The concentration quenching takes at 0.1 mol% of Mn^{2+} in $KMgSO_4Cl$. The notable differences observed due to the effect of nanosize particle materials. $KMgSO_4Cl$:-Mn^{2+}gives emission in UV region; this may arise its potential applications for the realization of tunable lasers and in other optical devices while $KMgSO_4Cl$:-Mn^{2+}might find a possible application in yellow LEDs for lamp industries.

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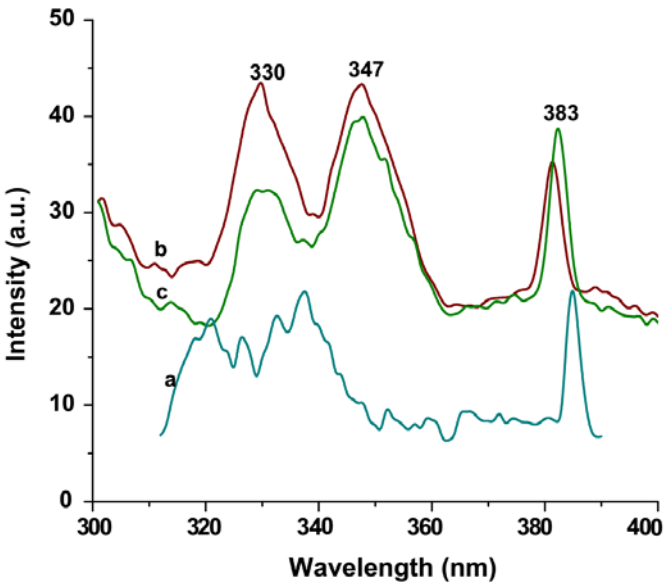

Fig 1. Excitation spectrum of $KMgSO_4Cl:Mn^{2+}$ Mn 0.02 mol% by (a) WCS (b) SSD (c) CS

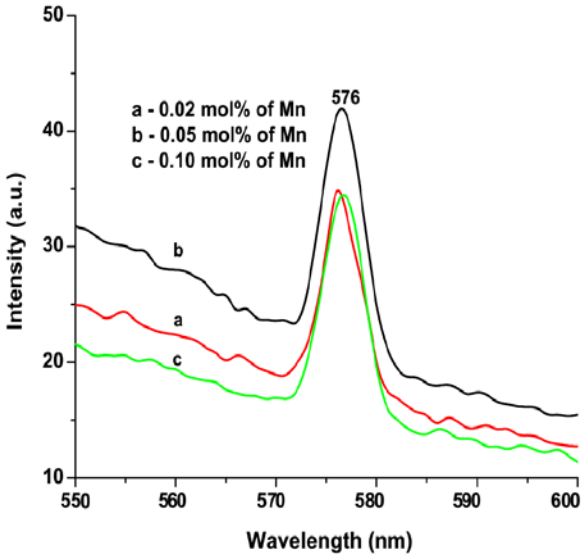

Fig 2. Excitation spectrum of $KMgSO_4Cl: Mn^{2+}$ Mn 0.05 mol% by (a) WCS (b) SSD

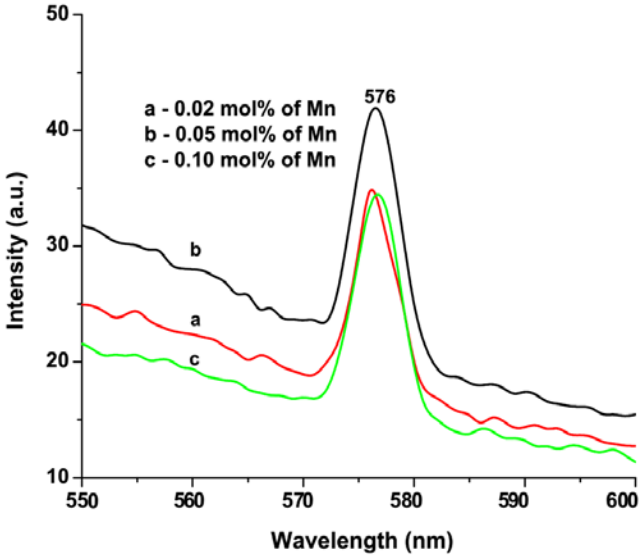

Fig 3. PL emision spectra $KMgSO_4Cl: Mn^{2+}$ forAn excitation of 383 nm synthesized by SSD route

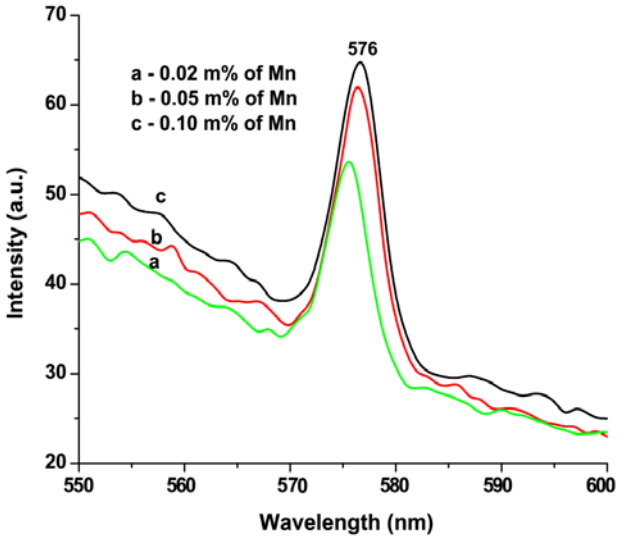

Fig 4. Excitation spectrum of $KMgSO_4Cl: Mn^{2+}$: Mn 0.05 mol% by (a) WCS (b) SSD

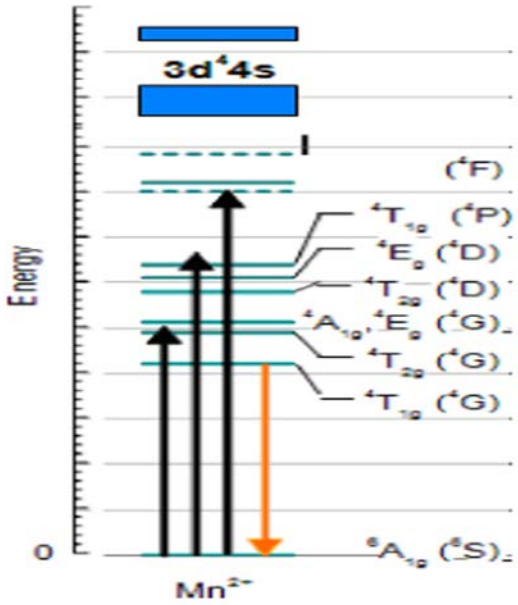

Fig. 5: Energy level diagram showing the states involved in the luminescence process and the transition probabilities in Mn^{2+}