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Comparative Photoluminescence Study of Nanomaterial Kmgso4cl :Cu with Different Synthesis Route for Lamp Application

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ABSTRACT

To prepare KMgSO4Cl different methods have been adopted such as wet chemical synthesis (WCS) and solid state diffusion (SSD) methods. XRDs of the sample prepared by these methods matched well with standard data.

KMgSO4Cl: Cu showed improved photoluminescence (PL) which may be used as efficient lamp phosphors. Ultraviolet photo-excited luminescence from Cu-doped halophosphor has been investigated. PL emission spectra of KMgSO4Cl: Cu has been observed at 357 nm . X-ray diffraction and PL characterization of phosphors has been reported in this article. The article discusses the luminescence of metal transition ion such as Cu. All the synthesis routes are easy, worked at low temperature, low cost and least hazardous and eco friendly.

Keywords: Nanomaterial, Luminescence, Phosphor, WCS, SSD, Photoluminescence (PL), XRD

I. INTRODUCTION

In order to use alkaline halosulphate phosphors in lamp and lighting industrial application ; we have synthesized and characterized alkaline halophosphors which are yet not reported in existing literature. Our focus is always on the preparation of the new alkaline-halo- sulphate based phosphors doped either with the rare earth impurity or metal transition ion impurity.

In the same series of the preparation of mixed alkaline sulphate based halophosphors, we have now made attention on KMgSO4Cl host. The phosphors are synthesized and characterized by doping transition metals like copper. Phosphors synthesized by using transition metal Cu is essential for it low cost, less hazardous and being eco friendly. It has wide applications in lighting, imaging, and display devices. The incorporation of copper into several matrices provides them with interesting optical features, which strongly depend on the ionic state of the copper atoms [1]. It has been mentioned that incorporation of monovalent copper can be difficult and it is done without inert atmosphere. 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 [2].

II. EXPERIMENTAL

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

For wet chemical synthesis (WCS) route

potassium chloride, magnesium sulphate and copper sulphate of AR grade were taken in a stoichiometric ratio and they are dissolved separately in double distilled de-ionized water & mixed and kept for heating in oven at 80 ^{0} C for about 8 hour. 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.

In solid state diffusion method (SSD) the starting material of AR grade have been crushed to fine powder in mortar pestle. 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. The reaction is as follows:

$$MgSO_4 + KCl = KMgSO_4Cl \text{ [WCS/SSD]}$$

$$MgSO_4 + KCl + CuSO_4 = KMgSO_4Cl \text{ [WCS/SSD]}$$

Formation of compounds (in both methods) were confirmed by taking x-ray diffraction (XRD) and reported earlier [3] 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 mm. Samples were also found to be stable against UV irradiation that was used for the PL measurements.

III. RESULT AND DISCUSSION

X-Ray diffraction pattern (XRD) of $KMgSO_4Cl$:Cu prepared by wet chemical synthesis (WCS) and solid state diffusion (SSD) synthesis route and particle size have been reported earlier [4]. The particle size of 20 nm of $KMgSO_4Cl$:Cu was detected using transmission electron microscope (TEM). A well-aligned and stable TEM is operated at a fixed magnification that allows a large number of nanoparticles to be visible within the field of view, while ensuring that each individual nanoparticle is recorded with a large number of image pixels. The particle size of the pure $KMgSO_4Cl:Cu^{+}$ is found to be 20 nm, which confirms its Nano crystal form.

Figure 1 shows the excitation spectra of $KMgSO_4Cl$:Cu + by a) WCS b)SSD synthesis route. The excitation peaks are observed at 271 nm when it is synthesized by WCS and SSD route.

Figure 2-3 shows emission spectra of $KMgSO_4Cl:Cu^{+}$ halo sulphate phosphor for different concentrations of Cu^{+} (0.02 mol%, 0.05 mol% 0.2 mol% and 0.5 mol%) by WCS and SSD respectively. All emission spectra have double hump located at 357 and 368 nm in WCS and SSD route. This is assigned to electronic transitions $3d^94s^1 — 3d^{1◦}$ in Cu^{+} ions. The nature of emission spectra does not vary with the Cu+ concentration but the luminescence intensity changes more significantly by changing the synthesis routes. It has been found that the emission intensity of Cu + increases initially with an increase of concentration of do- pant. The quenching concentration is about 0.5 mol%. The ionic radius of Cu^{+} ion is almost equal to Mg^{2+} ion.

Hence, there may be possibility of replacing Mg^{2+} ion by Cu^{+} ion when enters into $KMgSO_4Cl$:Cu host. McClure et al. [5] have been reported the Cu^{+} ion as a substitutional impurity in alkali halide crystals provides a simple model system to learn in detail about the optical properties of ions in crystals. They have reported the absorption and emission spectra of the $d^{1◦}$ ions Cu^{+}in alkali halides along with the results of NaF:Cu^{+} system.

Figure 4 shows Energy level diagram indicating the states involved in the luminescence process and the transition probabilities for Cu^{+} ions. In this energy level of Cu the excitation is first from the ground state ($3d^{10}$ configurations) to the singlet state of the $3d^94$

s^1 configuration and then, to the triplet state. The ground state of a free Cu^+ ion is of $3d^{10}$ configuration, while the lowest excited states are populated due to the $3d^{10}$ -$3d^9$ 4s and $3d^{10}$ -$3d^9$ 4p transitions. The last transition may be considered instantaneous; it follows that the singlet state does not affect the luminescent process. Cu^+ is known to exhibit characteristic luminescence corresponding to $3d^94s$ – $3d^{10}$ transitions [6-7] In particular, the presence of Cu^+ ions in this matrix activates lu- minescent emission in the ultraviolet (UV) and visible (VIS) range of a spectrum that may arises potential applications for the realization of tunable lasers and other optical devices.

Table 1
Comparison of PL in KMgSo4cl:Cu synthesized by different routes.

Phosphor	Synthesis Route	λ excitation (nm)	λ emission (nm)	Max. PL emission Intensity (a. u.)
KMgSo4cl:cu	WC	271	357, 368	202
	SSD	271	357, 368	245

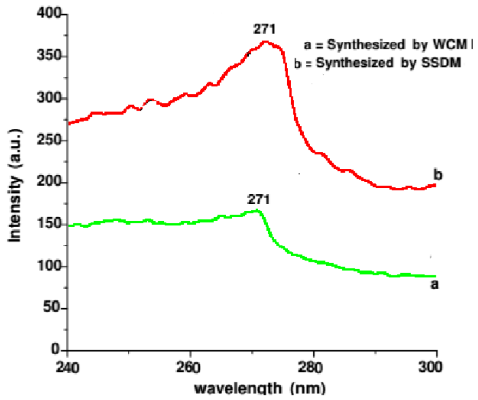

Figure 1. PL Excitation Spectra of $KMgSO_4Cl$:Cu [WCS]

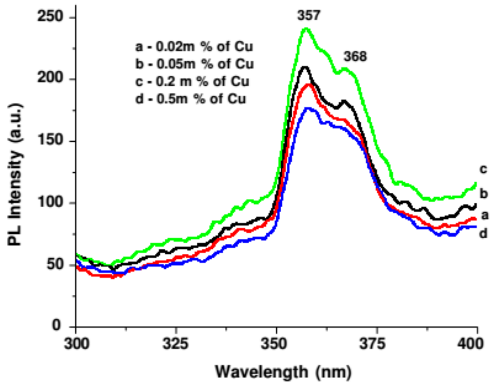

Figure 2. PL Emission Spectra of $KMgSO_4Cl$ [WCS]

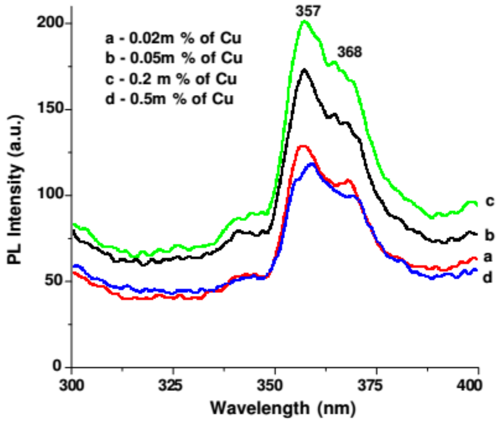

Figure 3. PL Emission Spectra of $KMgSO_4Cl$:Cu[SSD]

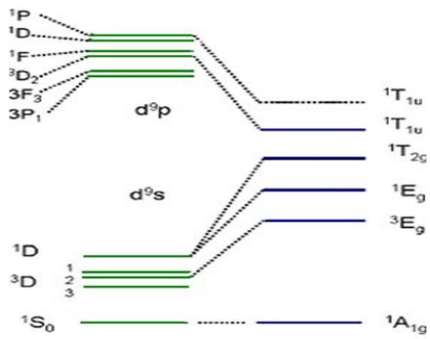

Figure 4. Energy level diagram for $KMgSO_4Cl$:Cu

IV. CONCLUSION

$KMgSO_4Cl$ have been prepared by wet chemical synthesis (WCS) and solid state diffusion (SSD) methods. XRDs of the sample prepared by these methods matched well with standard data. KMgSO4Cl: Cu showed improved photoluminescence (PL) which may be used as efficient lamp phosphors. Ultraviolet photo-excited luminescence from Cu-doped mixed alkaline halosulphate phosphor has been investigated. PL emission spectra of KMgSO4Cl: Cu has been observed at 357 nm when excited at 271nm.

V. REFERENCES

[1]. C. Pedrini, Cu + Luminescent Centre in LiCl Single Crystals, Phys. Stat. Sol. B 87 (1978) 273-277.

[2]. A. Bohun, J. Dolejsi, Mollwo-Ivey relations for emission bands in copper doped alkali halides, Czech J. Phys. B 22 (1972) 737-741.

[3]. J. Ferguson, H.J. Guggenheim, Electron-transfer states of pairs of unlike tran-sition metal ions in

perovskite fluorides, Phys. Rev. B 1 (1970) 4223-4229.
[4]. S.C. Gedam, S.J. Dhoble, R.B. Pode, 5D0-7F1 and 5D0-7F2 transition in halosulphates for mercury-free lamps, J. Lumin. 132 (2012) 2693-2696.
[5]. P.S. Thakre, S.C. Gedam, S.J. Dhoble, R.G. Atram, Luminescence of KCaSO4Cl: x, Y (X ¼ Eu or Ce; Y ¼ Dy or Mn) halosulfate material, J. Lumin. 131 (2011)1612-1616.
[6]. S.J. Dhoble, S.C. Gedam, I.M. Nagpure, S.V. Godbole, M.K. Bhide, Photo- luminescence and thermoluminescence characteristics of KXSO4Cl: Eu (X ¼ Zn or Mg) halosulphate phosphors, J. Phys. D: Appl. Phys. 40 (2007) 6039-6044.
[7]. S.C. Gedam, S.J. Dhoble, S.V. Moharil, Eu2 + and Ce3 +emission in sulphate based phosphors, J. Lumin. 128 (2008) 1-6.