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Energy Transfer in Co-doped $KMgCl_3$: Ce^{3+}-Eu^{3+} Phosphor

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ABSTRACT

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The present work discusses photoluminescence in $KMgCl_3$ singly doped by Ce^{3+} ions and Eu^{3+}ions independently and co-doped. Co-doped phosphor showed transfer of energy between a sensitizer ion Ce to an activator ion Eu and resulted into enhancement in photoluminescence emission. Phosphors have been prepared using wet chemical synthesis. XRD pattern of $KMgCl_3$ matched with the standard JCPDS file 20-0905. The PL emission spectra have been observed for Ce^{3+} at 353nm and 375nm due to 5d-4f transition at excitation wavelength of 338 nm. PL of Eu^{3+} is peaking at 596nm and 616nm at excitation wavelength of 394 nm in orange and red region due to $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_2$ transition.

$KMgCl_3$:Ce^{3+},Eu^{3+} have two peaks in PL emission spectra in orange-red region of the spectrum at 596 nm and 616nm by UV excitation at 268nm due to transitions of Eu^{3+} ion with improved luminescence properties. The energy transfer from Ce^{3+} to Eu^{3+} has been discussed based on the excitation and emission spectra.

Keywords : Photoluminescence, Phosphor, XRD, Co-doped

I. INTRODUCTION

Over the last few years, intensive research has been devoted to the development of efficient luminescent materials. In the view of developing new luminescent materials, interest in the luminescent properties and energy transfer process was developed. A number of reports have appeared describing spectroscopic properties of pure and activated sulphides and revealing applications. Gedam et al. have reported the halosulphate materials as phosphors [1–8]. Moreover mixed sulphates are also known to be good PL and TL materials. Sahare et al. [9–11] have studied mixed sulphate systems for the applications in dosing of high energy radiations using TL technique. They synthesized and characterized $K_2Ca_2(SO_4)_3$:Eu, Dy [12] and $K_2Ca_2(SO_4)_3$:Eu [13]; LiNaSO4:Eu [14] and LiNaSO4:Eu,Dy [15]. Energy transfer between pairs of rare earth ions at dilution levels below the self-quenching limits is through multi polar interactions like dipole–dipole interactions or dipole–quadrupole interactions [16–18]. The energy transfer from Ce^{3+} to different activator ions in different host lattices has been reported [19-21].

Study on crystal structure, PL, TL, TL response, fading and reusability by doping RE and transition metals as well as energy transfer from

Ce^{3+}→Eu^{2+}→Eu^{3+} in $K_3Ca_2(SO_4)_3F$ has been reported elsewhere [22-24]. We have previously studied PL characteristics of phosphor ($KMgSO_4F$:Dy/Eu) [25].

The objective of the present work is to study luminescence in the host, prepared at room environment.

According to the referred data [26] the Carnalite ($KMgCl_3$ _ 6H2O, hydrous magnesium and potassium chloride) crystal structure has the following parameters. It has orthorhombic symmetry class and usually displays granular structure. It belongs to Pbnn space group and has a hardness of 2.5, the same as the nail. It is soluble in H_2O. The Unit Cell Parameters are a=9.5980, b=16.1410, and c=22.5190. It has number of formula Unit, Z=12and Unit Cell Volume, Vc =3488.67Å3. Number of atomic position per full Unit Cell, P/U=132 and Molar Volume, Vm=175.11cm^3/mol. Its R-factor μ =108.752MU,1/cm. Mass attenuation coefficient, μ /p=68.548cm2/g. Figure 1(A) shows the crystal structure of $KMgCl_3$. Anhydro carnallite has corner and face-sharing. Carnallite minerals have 2/3 of KCl_6 octahedral face sharing networks. $Mg(H_2O)_6$ octahedral occupy the open spaces within the KCl octahedra. This face sharing creates more chance of instability according to the third rule from Pauling's rules. According to Brynestadetal, $KMgCl_3$ takes the orthorhombic structure belonging to space group D16 2h, at room temperature and undergoes a phase transition to the cubic perovskite structure as shown in Figure 1(B) at some temperature between 110°C and170°C [27]. Midorikawa et al. suggested crystalline $KMgCl_3$ undergoes phase transitions at 296,224,212 and142°C. The room temperature phase of $KMgCl_3$ is found to be monoclinic from the fact that the extinction position varies as temperature changes, though it has been reported to be orthorhombic [28]. Figure (B) shows perovskite structure of $KMgCl_3$ crystal where K^+ ions are at the center of a cube, with Mg^{2+} ions at the corners. Chlorine ions are located on the midst of each of the sides of the cube12-fold coordination around K^+ which is then in the form of a cuboctahedron. The coordination around K^+ can also be described as a tetra-capped square prism. Each Mg^{2+} ion is octahedrally coordinated. $MgCl_6$ octahedra share their corner to form a three- dimensional network. The cubic structure is not stable anymore and the cubic structure "collapses" by means of tilting of the $MgCl_6$ octahedra [29].

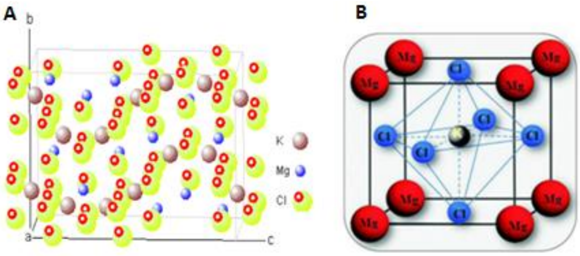

Figure 1(A). Crystal Structure of $KMgCl_3$. (B) Perovskite structure of $KMgCl_3$ crystal.

II. EXPERIMENTAL DETAILS

The sample $KMgCl_3$: Ce^{3+}, $KMgCl_3$: Eu^{3+} and $KMgCl_3$:Ce^{3+},Eu^{3+} were prepared by Wet chemical synthesis(WCS). $MgCl_2$ and KCl of AR grade were taken in a stoichimetric ratio and they are dissolved separately in double distilled de-ionized water and mixed together, resulting in a solution of $KMgCl_3$. Then water-soluble sulphate salt of Cerium, or Europium was added to obtain $KMgCl_3$:Ce^{3+} $KMgCl_3$:Eu^{3+}. $KMgCl_3$:Ce^{3+},Eu^{3+} in liquid form was synthesized by adding water-soluble sulphate salt of Cerium (2mol %) and Europium ((a) 0.05,(b)0.1,(c)0.5mol%). Then the solution was evaporated at 80°C and then slowly cooled at room temperature. Compounds formed by this route are hygroscopic and catch moisture if left in the open, so they are annealed in at 400°C for 2 hour under normal atmosphere. The resultant polycrystalline mass was crushed to fine particle in a crucible. The powder was used in further study. The formation of pure compound was confirmed by taking the X-ray diffraction (XRD). The photoluminescence (PL) emission spectra of the samples were recorded using Fluorescence spectrophotometer (Shimatzu RF-5301 PC) fitted with a sensitive photomultiplier. Emission and excitation spectra in the 250–450nm and 350-650 nm range were recorded. The spectral slit width of spectrophotometer was kept at 1.5 nm.

III.RESULTS AND DISCUSSION

A. X-ray diffraction (XRD)

The XRD of $KMgCl_3$ (Figure 2) pattern did not indicate presence of the constituents and other likely phases. The maximum lines of the XRD pattern matches with the standard JCPDS file20-0905which is a direct evidence for the formation of the desired compound. These results indicate that the final product was formed in homogeneous form.

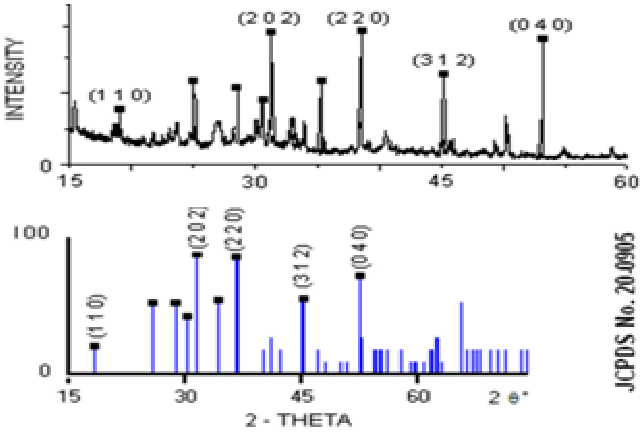

Figure 2: XRD of $KMgCl_3$

B. Photoluminescence (PL) in $KMgCl_3:Ce^{3+}$

Figure 3 shows excitation spectra of $KMgCl_3$: Ce^{3+}phosphor shows broadband at 338nm and 264nm at emission wavelength of 375nm. Figure 4 shows PL emission spectra of Ce^{3+} ions under excitation of 264nm (Figure 4 (a) 2 mol% , (b) 5 mol% , (c) 10 mol% of Ce) and 338nm (Figure 4 (d) 2 mol% , (e) 5 mol% , (f) 10 mol% of Ce) wavelength of light showed double hump at 353nm and 375nm in ultraviolet to visible region of the spectra that depends on host lattice which is close to wavelength of UVA1 phototherapy lamps. These are assigned to the 5d-4f transition of Ce^{3+} ions The double peaked spectrum is characteristic of split ground state ($^2F_{7/2}$ and $^2F_{5/2}$) of Ce^{3+}. Pl intensity increases with increase in concentration of Ce^{3+} ions observed upto 10 mol% in this study

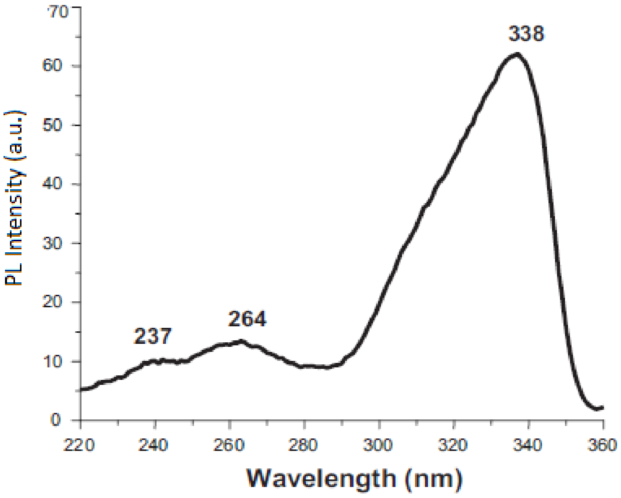

Figure 3: Excitation spectra of $KMgCl_3$: $Ce^{3+}{}_{10mol\%}$ at λ_{em}=375nm.

C. PL in $KMgCl_3$: Eu^{3+}

Figures 5 and 6 show the excitation and emission spectra of $KMgCl_3$: Eu^{3+}at λ_{em}=616nm and λ_{ex}=394nm respectively. Excitation spectrum shows peak at 394nm and at this excitation wavelength emission is observed at the wavelength of 596nm and 616nm.The intensity of the spectra is observed very low.Eu^{3+} emission usually occurs from $^5D_0$-^7F_j transitions. Usually two transitions are observed $^5D_0$-$^7F_1$ (around 596nm) and $^5D_0$-$^7F_2$ (around616nm).The first$^5D_0$-$^7F_1$ transition is forbidden as electric dipole, but allowed as magnetic dipole [30].

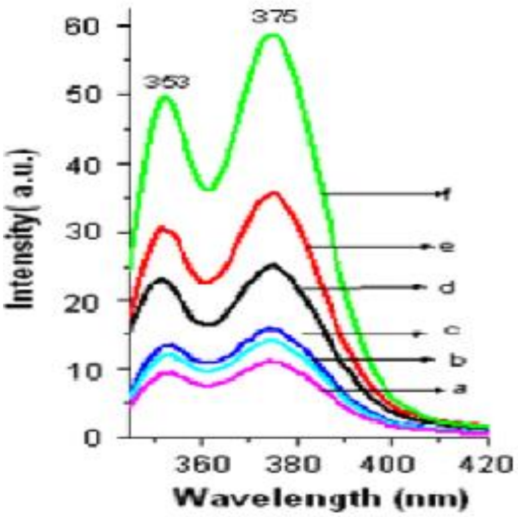

Figure 4 : Emission spectra of $KMgCl_3:Ce^{3+}$at λ_{ex}=264nm of Ce (a) 2, (b) 5, (c) 10 mol% and at λ_{ex}=338nm of Ce(d)2,(e)5, (f) 10mol%

This is the only transition when Eu^{3+} occupies as it's coinciding with a center of symmetry. When Eu^{3+} ion is situated at a site, which lacks the inversion symmetry, then the transitions corresponding to even values of J (except 0) are electric dipole allowed and red emission is observed. The prominent peaks are observed at 596nm and weak emission is seen at 616nm due to $^5D_0$-$^7F_1$ magnetic dipole transitions of Eu^{3+} ions and due to the hypersensitive $^5D_0$-$^7F_2$ electric dipole transition respectively when excited at 394nm. The luminescent properties of the phosphors occur from complex interactions among the host structure, defects, activators, and interfaces.

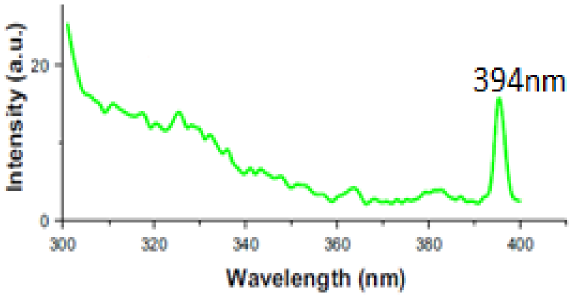

Figure 5 : Excitation spectra of $KMgCl_3:Eu^{3+}$0.1 mol% halo-phosphor monitored at λ_{em}=616nm.

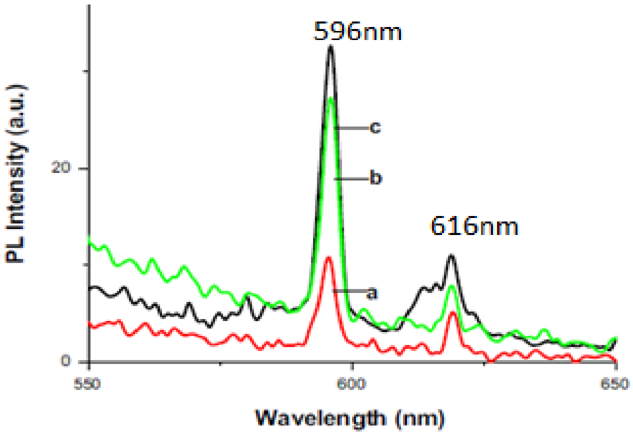

Figure 6 : PL emission spectra of $KMgCl_3$: Eu^{3+} (a) 0.05,(b)0.1,(c)0.5mol%at λ_{ex}=394 nm

D. PL in co-doped $KMgCl_3:Ce^{3+}$, Eu^{3+}

The emission spectra of $KMgCl_3:Eu^{3+}$ phosphor which showed emission at 596 nm and 616 nm with lesser intensity when excited at 394 nm. PL excitation and emission spectra of co-doped $KMgCl_3$:Ce,Eu is shown in Figures 6 and 7 for excitation of 264 nm. The excitation spectrum is monitored, recorded and plotted at 616 nm of emission wavelength. The emission spectra were recorded for the samples for different concentrations (2 mol% for Ce and 0.05, 0.1 and 0.5mol% for Eu). When this sample was excited by 268 nm, it shows emission with two broad spectra at 596 nm and 616 nm which is attributed to Eu^{3+} transitions indicating transfer of energy from sensitizer Ce^{3+} to activator Eu^{3+} .The prominent peaks are observed at 596nm and at 616nm due to $^5D_0$-$^7F_1$ magnetic dipole transitions of Eu^{3+} ions and due to the hypersensitive $^5D_0$-$^7F_2$ electric dipole transition respectively when excited at 268nm. However, $KMgCl_3:Eu^{3+}$ sample when excited by wavelength of 394 nm results in an emission band of lower intensity while $KMgCl_3$:Ce,Eu sample excited by wavelength of 268nm results in an emission band of much higher intensity maintaining the emission wavelengths. The emission intensity has increased with the increase in Eu^{3+}concentration and reached a maximum value for 0.5mol% of Eu whereas concentration of Ce was fixed at 2 mol%. This indicates that the $KMgCl_3$:Ce,Eu lattice is more suitable for higher concentrations of Eu^{3+}ions upto 0.5mol%.

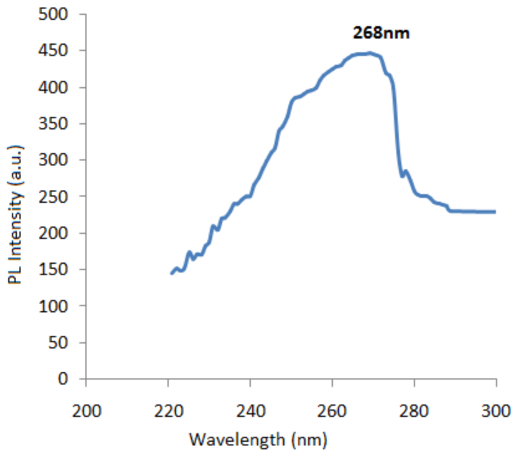

Figure 7 : Excitation spectra of $KMgCl_3:Ce^{3+}$2mole%,Eu^{3+}0.5mol% at λem=616nm.

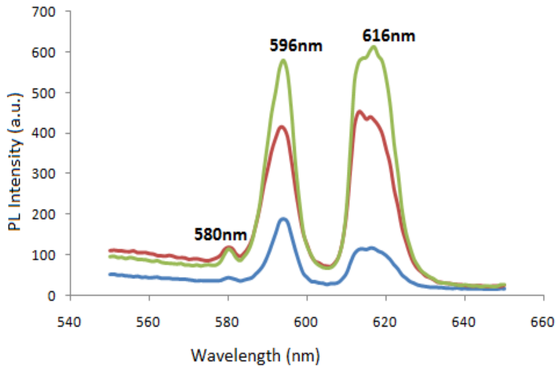

Figure 8 : PL emission spectra of $KMgCl_3:Ce^{3+}{}_{2mole\%},Eu^{3+}$ (a)0.05,(b)0.1,(c)0.5mol% at λ_{ex}=268 nm

Photoluminescence emission peak position is shown in the table 1 which shows huge increase in the PL intensity when $KMgCl_3$ co-doped with Ce^{3+} and Eu^{3+} and table also illustrates intensity increases with increase in concentration of dopants.

TABLE I. PL INTENSITY

Phosphors	λ_{ex} (nm)	λ_{emi} peak (nm)	Relative PL intensity (a.u.)
$KMgCl_3:Ce^{3+}{}_{2mol\%}$	264 and 338	353,375	9,11 and 24,25
$KMgCl_3:Ce^{3+}{}_{5mol\%}$		353,375	12,14 and 39,44
$KMgCl_3:Ce^{3+}{}_{10mol\%}$		353,375	14,16 and 44,52
$KMgCl_3:Eu^{3+}{}_{0.05mol\%}$	394	596,616	11,06
$KMgCl_3:Eu^{3+}{}_{0.1mol\%}$		596,616	28,08
$KMgCl_3:Eu^{3+}{}_{0.5mol\%}$		596,616	34,11
$KMgCl_3:Ce^{3+}{}_{2mol\%},Eu^{3+}{}_{0.05mol\%}$	268	596,616	181,112
$KMgCl_3:Ce^{3+}{}_{2mol\%},Eu^{3+}{}_{0.1mol\%}$		596,616	414,454
$KMgCl_3:Ce^{3+}{}_{2mol\%},Eu^{3+}{}_{0.5mol\%}$		596,616	559,604

The luminescence mechanism could be understood from the energy-level diagram, Figure 9. In $KMgCl_3$ co-doped with Ce^{3+} and Eu^{3+} the excitation into the Ce^{3+} band at 264 nm leads to the Eu^{3+}. This means that in Ce^{3+} can be used as sensitizer which transfers its energy to the activator Eu^{3+}. The first step of the path through which the activation energy is transferred from the sensitizer Ce^{3+} to the activator Eu^{3+} involves transfer between the 5d-4f, (Ce^{3+}) energy is transferred to a Eu^{3+} activator $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_2$ transition of Eu^{3+} ion. Moreover, an additional way of transfer energy is possible, namely, the radiation transitions in Ce^{3+} may excite directly the neighboring Eu atoms. Emission spectra of Eu^{3+} peaks, spectra in the red region significantly improve the colour rendering index. This powder may be potentially utilized in the manufacture of fluorescent lamps for advertising signs and other colour rendering devices. And excellent luminescent properties allowed recommending these phosphors as good candidates for different applications.

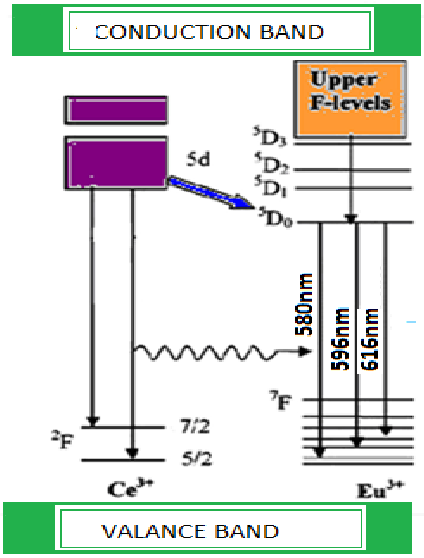

Figure 9 : Ce^{3+}-Eu^{3+} energy transfer mechanism in $KMgCl_3$ halo-sulphate phosphor

IV. CONCLUSION

PL emission spectra of Ce^{3+} ions under excitation of 338nm wavelength of light showed double hump at 353nmand 375nm which is in ultraviolet to visible region which may be useful in UVA1 phototherapy lamps. When $KMgCl_3$ is doped with Eu^{3+}ions then very low Pl intensity is observed but when the same host is co-doped significant increase in Eu^{3+} emission is observed at the same wavelength. $KMgCl_3$: Ce^{3+}-Eu^{3+}phosphors prepared by wet chemical method are good for Ce^{3+}-Eu^{3+}energy transfer. $KMgCl_3$: Ce^{3+}, Eu^{3+}shows strong emission at 596 nm and 616 nm which is in orange and red region due to $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_2$ transitions of Eu^{3+} ion.

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