ENERGY TRANSFER IN $K_2CaMg(SO_4)_3$: Ce^{3+} or Gd^{3+}, Tb^{3+} BY SINGLE STEP SYNTHESIS

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A B S T R A C T

The synthesis, X ray diffraction, photoluminescence characteristics, SEM and FTIR of mixed sulphate phosphor, such as $K_2CaMg(SO_4)_3$: Ce^{3+}, $K_2CaMg(SO_4)_3$: Ce^{3+}, Tb^{3+} and $K_2CaMg(SO_4)_3$: Gd^{3+}, Tb^{3+} are reported in this paper. Phosphor is prepared by single step wet chemical synthesis. Photoluminescence of $K_2CaMg(SO_4)_2$: Ce^{3+} and $K_2CaMg(SO_4)_3$: Ce^{3+} co-doped with Tb^{3+} and $K_2CaMg(SO_4)_3$: Gd^{3+}, Tb^{3+} shows strong emission. This phosphor is also efficient for $Ce^{3+} \rightarrow Tb^{3+}$, and $Gd^{3+} \rightarrow Tb^{3+}$ energy transfer. $K_2CaMg(SO_4)_3$: Ce^{3+} shows single emission band at 323 nm for ultraviolet excitation at 280 nm. $K_2CaMg(SO_4)_3$: Ce^{3+} Tb^{3+} shows blue and green emission at 439nm, 490 nm, 545 nm , 585 nm and 622nm of Tb^{3+} for the excitation of 280 nm. Emission spectra of $K_2CaMg(SO_4)_3$: Gd^{3+} Tb^{3+} shows luminescence in visible blue and green emission at the UV excitation of 273 nm. It is observed that energy transfer take place from $Ce^{3+} \rightarrow Tb^{3+}$ and $Gd^{3+} \rightarrow Tb^{3+}$ in the given matrix, indicating Ce^{3+} or Gd^{3+} could efficiently sensitizes Tb^{3+} in $K_2CaMg(SO_4)_3$ phosphor . The chromaticity coordinates of $K_2CaMg(SO_4)_3$: Ce^{3+} Tb^{3+} and $K_2CaMg(SO_4)_3$: Gd^{3+} Tb^{3+} have been calculated with Commission International I'Eclairage (CIE) diagram .$K_2CaMg(SO_4)_3$ phosphor has many applications in lamp phosphor industry

Keywords: Energy transfer, photoluminescence , wet chemical, mixed sulphate, lamp industry

1.Introduction:

Energy transfer processes among the optical centers in phosphor is of great important due to its utility in the manufacture of different kinds of the devices [1 – 5] ET processes could take place by electric or magnetic multipole interactions, by exchange interaction or by emission or subsequent absorption of photon [2, 4, 5]. ET depends upon the nature of host lattice and the nature of the optical centre. Both excitation and emission position depend on the dopant ion concentration and host matrix. Ce^{3+} can provide strong absorption and an efficient conversion to longer wavelengths. Hence the work is focused on host lattice activated by Ce^{3+} and Gd^{3+} in combination with other rare earth elements (Tb^{3+}). Ce^{3+} ions can be used as sensitize as well as activator, depending on the splitting of 5d excited level by crystal field symmetry. Much work has been done on the energy transfer from Ce^{3+} to different activator ions in different host [6-8] and Gd^{3+} can also act as sensitizer [9]. Mixed sulphate are also known to be good PL and TL martial. Gedam etal have reported the halosulphate material as phosphor [10-12] Sahare etal [13-14] have studied same mixed sulphate co doped with rare each for this applications in dosing of high energy radiation using TL technique. Energy transfer between pair of rare earth ions at dilution level below the self quenching limit has been known to take place generally through multipolar interaction like dipole-dipole interaction and dipole-quadrapole interaction. [15]

In this paper, we report the synthesis of $K_2CaMg(SO_4)_3$ phosphor by wet chemical method and explain energy transfer in $Ce^{3+} \rightarrow Tb^{3+}$ and $Gd^{3+} \rightarrow Tb^{3+}$ ions in $K_2CaMg(SO_4)_3$. The main objective of the present work is to find more effective luminescence in the host by simple method of preparation. Further work shows the very efficient phosphor can be

obtained by sensitizer Ce^{3+} and Gd^{3+} ions on the basis of the Tb^{3+} ions. All the results are reported first time in present sulphate matrix.

2. Experimental:
All the power sample, $K_2CaMg(SO_4)_3$: Ce^{3+}, $K_2CaMg(SO_4)_3$: Ce^{3+} Tb^{3+} and $K_2CaMg(SO_4)_3$: Gd^{3+} Tb^{3+} were prepared by single step wet chemical synthesis K_2SO_4, $CaSO_4$ and $MgSO_4$ of analar grade were taken in a stoichimetric ratio as per following reaction in double distilled water in separated beaker.

K_2SO_4 + $CaSO_4$ + $MgSO_4$ $\rightarrow$ $K_2CaMg(SO_4)_3$

water soluble sulphate salt of cerium, terbium and godelium were dissolved separately. These sulphates then mixed with $K_2CaMg(SO_4)_3$ solution to obtained required phosphor. The solution was slowly evaporated at 80^0C in oven for 24 h and dry material was crushed in mortal to form fine particles. Then fine particles in crucible was annealed at 800^0C for 4 hrs and slowly cooled to room temperature. The resultant phosphor materials used for further studies.

3. Results & Discussion:
3.1. Phase and SEM analysis of the samples
The phase purity of sample was characterized by X-ray diffraction. XRD of $K_2CaMg(SO_4)_3$ is shown in Fig.[1] . All the diffraction peaks are found to be matched well with those standard of JCPDF20-0866 No other XRD peak from K_2SO_4, $MgSO_4$ and $CaSO_4$ were detected. The crystal as cubic symmetry with lattice a = b = c = 10.1622A^0. In order to study the morphological structure of phosphor scanning electron microscope has been performed. Fig.[2] shows SEM images of $K_2CaMg(SO_4)_3$. It is evident that the surface morphology of crystalline or gain sizes of phosphor varies from 2 μm to 10 μm.

3.2. FTIR study
Fig. [3] shows the FTIR spectra of $K_2CaMg(SO_4)_3$ host sample. The FTIR spectrum shows the presence of several weak bands in the region 600-850 cm^{-1} which are due to S-O bonding. Deep band at 1075 cm^{-1} is due to S=O symmetrical stretch and another deep peak at 1368 cm^{-1} is arising from S-O asymmetrical stretching. Presence of weak deep in the region of 3000-4000 cm^{-1} indicate existence of moisture.

3.3 Ce^{3+} emission
Ce^{3+} can provide strong absorption of UV and efficient conversion to longer wavelength. The photoluminescence excitation spectrum for $K_2CaMg(SO_4)_3$: Ce^{3+} is as shown in Fig. [4]. The excitation spectrum for the emission of 323 nm in $K_2CaMg(SO_4)_3$: Ce^{3+} shows a strong band at 280 nm The emission spectrum for the excitation at 280 nm exhibits broad emission band at 300 nm to 380 nm shown in Fig. [5] .The emission spectra were recorded for the sample of different concentrations (1, 2,3 and 5mol % of Ce). Generally, the Ce^{3+} emission band shows doublet structure due to spin orbit splitting of ground state ($^2F_{7/2}$ and $^2F_{5/2}$). However the presence of a single band emission indicates weak spin orbit coupling of ground state of Ce^{3+}, in $K_2CaMg(SO_4)_3$. The excitation bands can be assigned to the transition from the ground 4f state of Ce^{3+} to the excited 5d state of Ce^{3+}. The 5d-4f transition of Ce^{3+} is highly depending upon crystal field symmetry of host lattice which causes the splitting of excited state involving 5d orbit. The Ce^{3+} concentration dependence on emission intensity and it can be seen that emission intensity increases with increase in Ce^{3+} concentration. No concentration quenching took place up to 5mol% of Ce. The observed increased in emission intensity may be due to cross relaxation between Ce^{3+} ions. This indicate that this $K_2CaMg(SO_4)_3$ lattice more suitable for higher concentration of Ce^{3+} ions.

3.4 Energy transfer in $Ce^{3+} \rightarrow Tb^{3+}$
It is well known that the rare earth Ce^{3+} ions shows 4f-5d transition resulting in a broad band in ultraviolet to visible range. Because one electron within the 5d orbit taking part in the formation of chemical bonding, the position of the excitation and emission bands strongly depends on the host lattice i.e. crystal structure and composition . Since Ce^{3+} has strong absorption in many hosts, and emission matching with 4f level or other RE impurities, it can be used as a sensitize for other rare earth [16]. In comparison with Ce^{3+}, the ground state configuration of the Tb^{3+} ions is $4f^8$ and the excited state configuration is $4f^7$ $5d^1$, in which the 4f shell is half filled. As the 4f shell is well shielded by the outer electrons within the 5S and 5p orbitals , the 4f-4f transition of Tb are hardly influenced by the environments. Thus Tb^{3+} shows 4f-4f sharp line emission. Additionally, the $4f^7$ $5d^1$ excitation band is

normally located at higher energies, so in order to absorb the UV radiation (220 – 300) efficiently, the Ce^{3+} ions is used as a sensitize through the energy transfer $Ce^{3+} \rightarrow Tb^{3+}$.

Fig. [6] and Fig. [7] show excitation and emission spectra of $K_2CaMg(SO_4)_3 : Ce^{3+}, Tb^{3+}$ respectively. The excitation spectra at emission of 545 nm shows broad band which already assigned to 4f-5d of Ce^{3+} and it also contain excitation of Tb^{3+} at 352 nm (5d – 4f) but having very small intensity. The emission spectra were recorded for the sample of different concentration (5 mol %of Ce and 0.5,1 and 1.5mol %of Tb).The emission spectra of $K_2CaMg(SO_4)_3 : Ce, Tb$ shows peak at 494 nm, 545 nm and 590 nm excited at 280 nm. From the result, five emission have been observed (1) $^5D_3 \rightarrow {}^7F_4$ (439nm) ;(2) $^5D_4 \rightarrow {}^7F_6$ (490 nm); (3) $^5D_4 \rightarrow {}^7F_5$ (545) ;(4) $^5D_4 \rightarrow {}^7F_4$ (585 nm) and (5) $^5D_4 \rightarrow {}^7F_3$ (622 nm) at a excitation of 280 nm. Among these a more intense peak at 545 nm corresponds to strong green emission. We have observed on intense green emission at 545 nm ($^5D_4 \rightarrow {}^7F_4$) which is a magnetic dipole transition ($\Delta J = \pm 1$). These result indicate that the energy is transfer from Ce^{3+} to Tb^{3+} in $K_2CaMg(SO_4)_3 : Ce\ Tb$ phosphor, is shown in Fig. [8] and the chromaticity Coordinate(X,Y) are summarized in Table1

3.5   Energy transfer in $Gd^{3+} \rightarrow Tb^{3+}$

The rare earth ions are characterized by a partially filled 4f-shell that is well shielded by $5S^2$ and $5P^6$ orbit. Therefore, emission transition yield sharp lines in the optical spectra [17]. It is consider that the emission of a $Gd^{3+}\ ^6P_J \rightarrow {}^8S_{7/2}$ transition located at 273 nm overlapps well with 4f-4f absorption lines of rare earth ions, so that incorporation of Gd^{3+} could improve luminescence of rare earth ions, therefore Gd^{3+} can be used as sensitize of Tb^{3+}. Fig. [9] shows the excitation spectrum of Gd^{3+} and Tb^{3+} co-activated in $K_2CaMg(SO_4)_3$ monitored at 545 nm ($^5D_4 \rightarrow {}^7F_5$) of Tb^{3+} transition. Excitation spectrum shows broad band peak at about 250 nm, 273 nm which are assigned to the Gd transitions and it also contain excitation of Tb^{3+} at 352 nm, 370 nm and 380 nm. The presence of Gd^{3+} transition in the excitation spectrum monitored with the Tb^{3+} transitions indicates that the Gd^{3+} to Tb^{3+} energy transfer channel is active [17]. The excitation spectrum of Tb^{3+} and emission spectrum of Gd^{3+} do not overlap perfectly. It is considered that phonon may

involved in the process. This observation has been previous reported [18-19] and suggests that the excitation of Tb^{3+} occurs mainly through the excitation of Gd^{3+}. Because of the strong interaction between Gd^{3+} and Tb^{3+}, Tb^{3+} is easily excited by Gd^{3+}. The possible energy transfer process between Gd^{3+} and Tb^{3+} is depicted by Fig. [11]

Fig. [10] shows the emission spectra of $K_2CaMg(SO_4)_3 : Gd^{3+}, Tb^{3+}$ at the excitation of 273 nm. The emission spectra were recorded for the sample of different concentration (1 mol %of Gd and 0.5,1,and 1.5mol % of Tb).The emission spectra exhibit a series of sharp peaks assigned to $^5D_3 \rightarrow 7F_2$ corresponds to 470nm transition of Tb^{3+} and $^5D_4 \rightarrow {}^7F_J$ (J = 3, 4, 5, 6) transition of Tb^{3+}, $^5D_4 \rightarrow {}^7F_6$ corresponds to 490 nm, $^5D_4 \rightarrow {}^7F_5$ assigned to 545 nm, $^5D_4 \rightarrow {}^7F_4$ assigned to 585 nm and $^5D_4 \rightarrow {}^7F_3$ assigned to 622nm.Among these $^5D_4 \rightarrow {}^7F_5$ corresponds to strong green emission. The spectra also display a sharp peak (312) attributed to the $Gd^{3+}\ ^6P_J \rightarrow {}^8S_{7/2}$ transition. and the chromaticity Coordinate(X,Y) are summarized in Table2

4.   Conclusion

The present Phosphor $K_2CaMg(SO_4)_3 : Ce$, $K_2CaMg(SO_4)_3 : Ce, Tb$ and $K_2CaMg(SO_4)_3 : Gd\ Tb$ were prepared by wet chemical method. From the result, it is concluded that, $K_2CaMg(SO_4)_3$ is suitable host for PL emission of Ce^{3+} ions, Ce^{3+} shows emission at around 323 nm due to $5d \rightarrow 4f$ transition at the excitation of 280 nm. An efficient energy transfer can also took place in $K_2CaMg(SO_4)_3 : Ce\ Tb$ under the excitation of 290 nm of Ce^{3+}. In presence of Ce^{3+} intensity of Tb^{3+} ions enhanced, the result indicated that energy efficiently transferred to Tb^{3+} in presence of Ce^{3+}. Thus, Ce^{3+} sensitizes Tb^{3+} ions which may be useful in lamp industry.

Gd^{3+} and Tb^{3+} activated $K_2CaMg(SO_4)_3$ phosphor show excitation spectrum monitored at $Tb^{3+}\ ^5D_4 \rightarrow {}^7F_5$ transition contain the presence of Gd^{3+} transition indicate that energy is transfer from Gd^{3+} to Tb^{3+}. The emission spectra exhibits as series of sharp peak assigned to Tb^{3+} (420 nm, 490 nm, 545 nm and 622 nm) for the 273 nm excitation of Gd^{3+}. This phosphor may use for lamp industry for green phosphor. This preparation technique of these phosphors is very simple and well established which makes it in expensive lamp phosphor.

1.1. Tables
Table 1 - Chromaticity Coordinate for $K_2CaMg(SO_4)_3$: Ce, Tb

$K_2CaMg(SO_4)_3$:Ce 5%Tb x%	(x,y) Coordinates
	(0.2276,0.6451)
$K_2CaMg(SO_4)_3$:Ce 5% Tb 0.5%	
$K_2CaMg(SO_4)_3$:Ce 5% Tb 1%	(0.2307 ,0.6485)
$K_2CaMg(SO_4)_3$:Ce 5% Tb 1.5%	(0.2283,0.6381)

Table 2 – Chromaticity Coordinate for $K_2CaMg(SO_4)_3$: Gd Tb

$K_2CaMg(SO_4)_3$:Gd 1% Tb x%	(x,y)Coordinates
$K_2CaMg(SO_4)_3$: Gd 1% Tb 0.5%	(0.2236,0.6075)
$K_2CaMg(SO_4)_3$: Gd 1% Tb 1%	(0.2132 ,0.5736)
$K_2CaMg(SO_4)_3$: Gd 1% Tb 1.5%	(0.2461,0.6484)

2. Illustrations
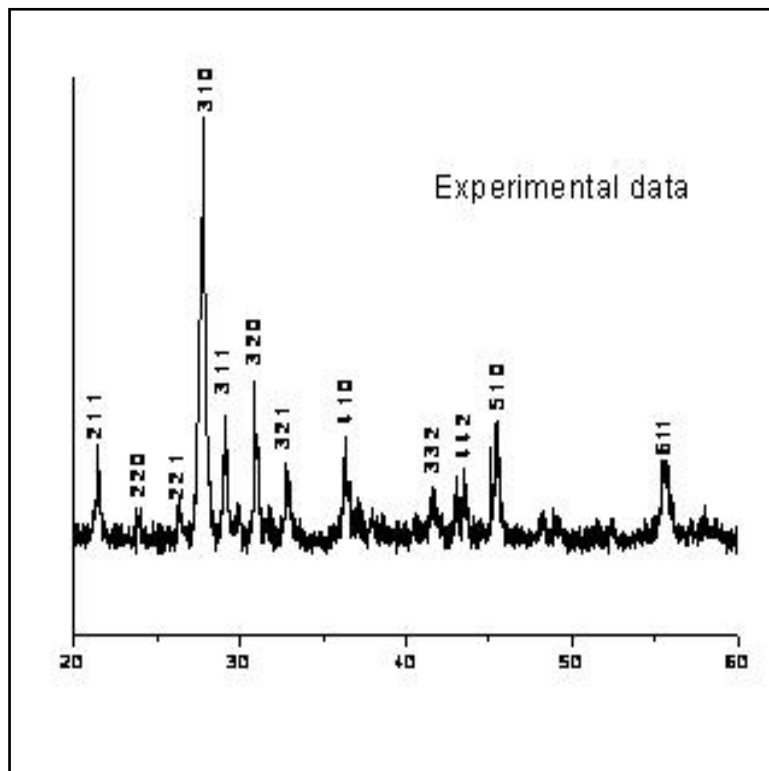
Fig. 1 XRD pattern of $K_2CaMg(SO_4)_3$ powder
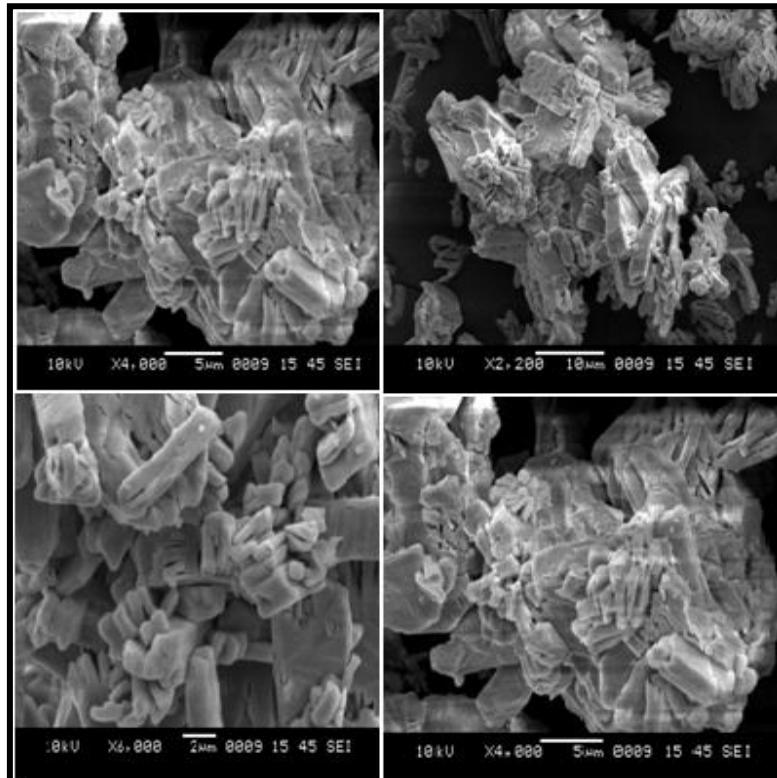
Fig. 2 SEM images of the synthesized $K_2CaMg(SO_4)_3$ phosphor
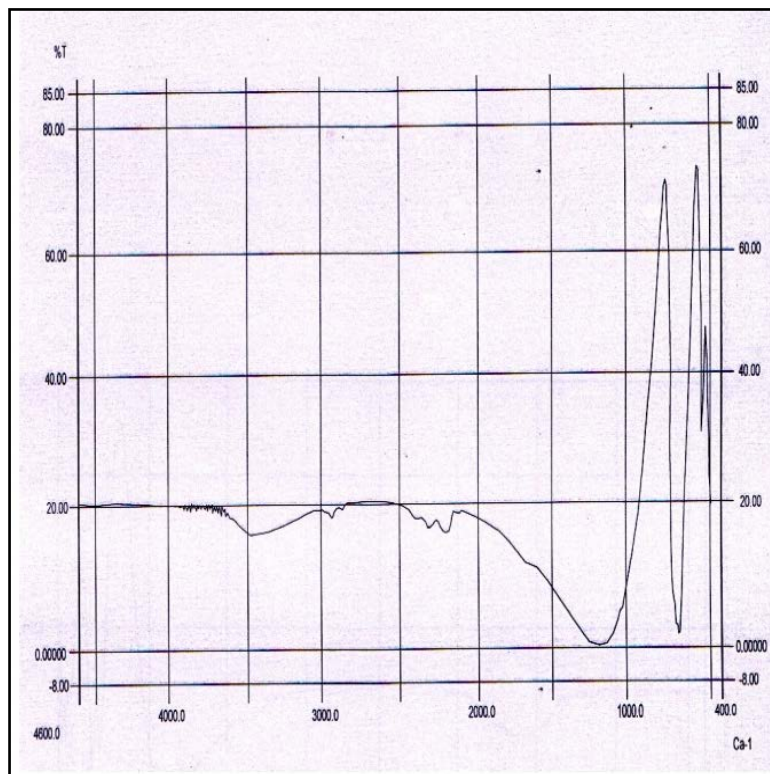
Fig.3 FTIR of $K_2CaMg(SO_4)_3$
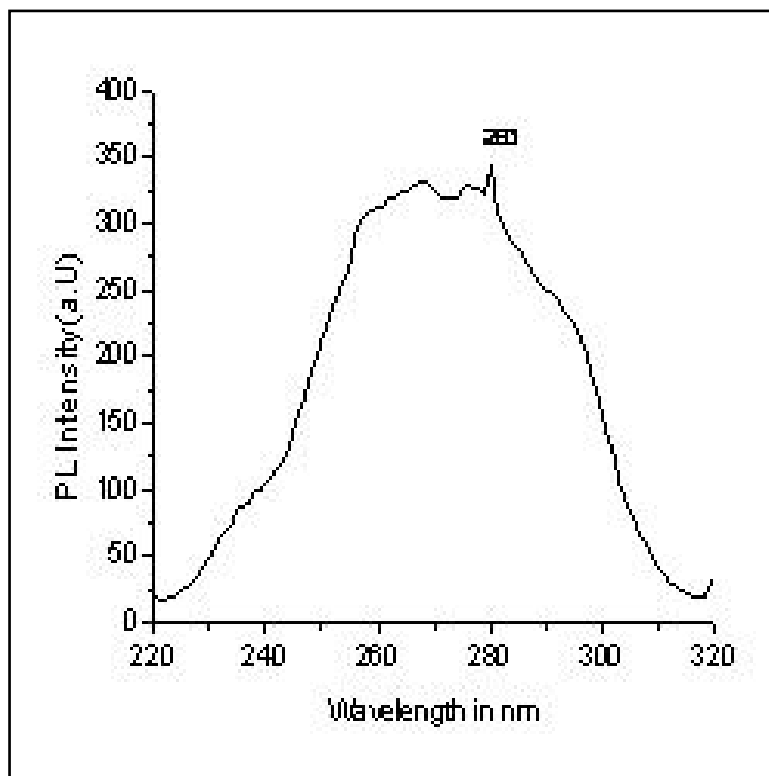
Fig. 4 PL excitation spectra of $K_2CaMg(SO_4)_3$ $_4$: $Ce_{5\,mol\%}$ phosphor Monitored at 323 nm
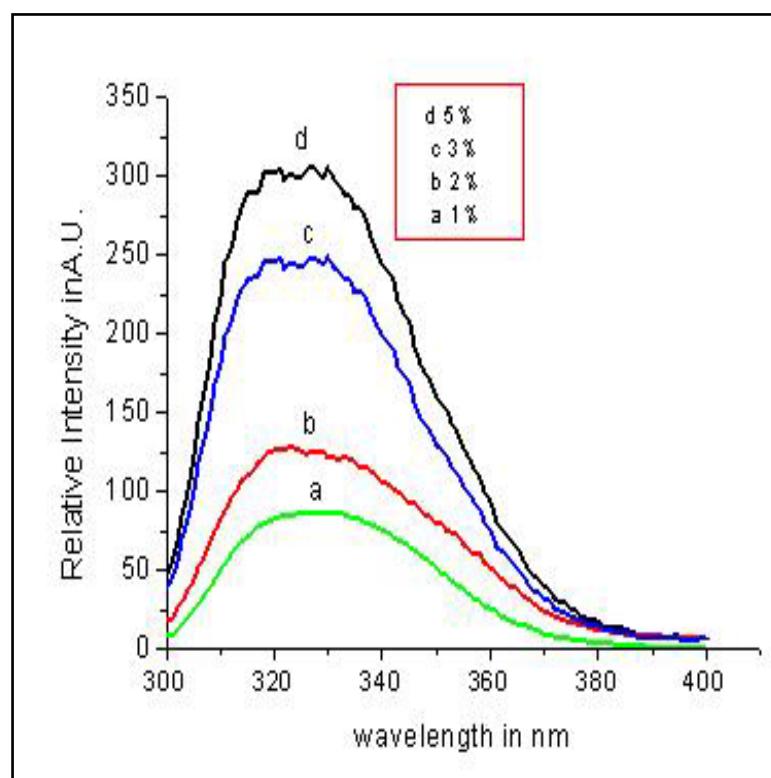

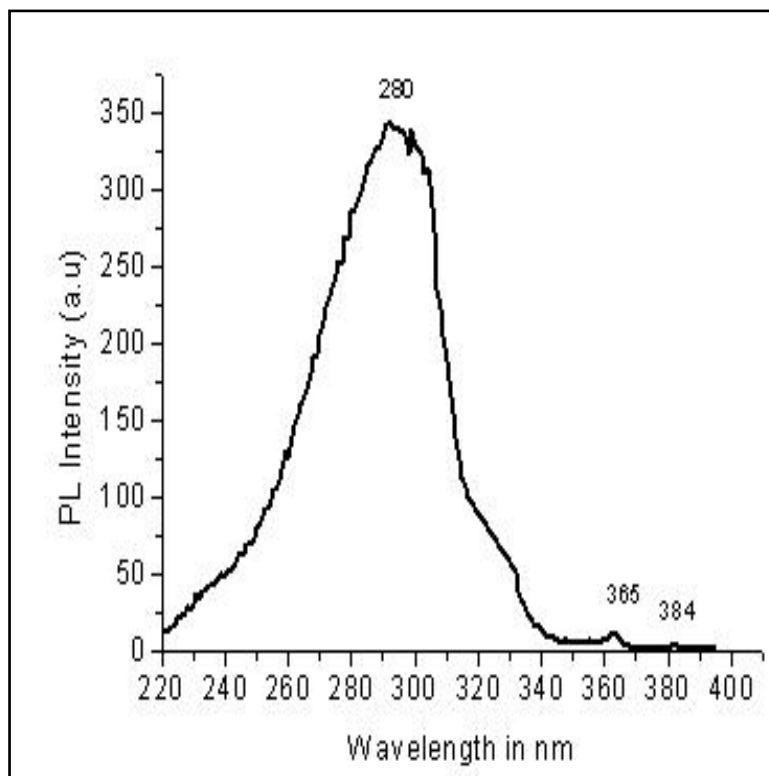Fig. 5 PL emission spectra of $K_2CaMg(SO_4)_3$; Ce^{3+} at an excitation of 280nm.

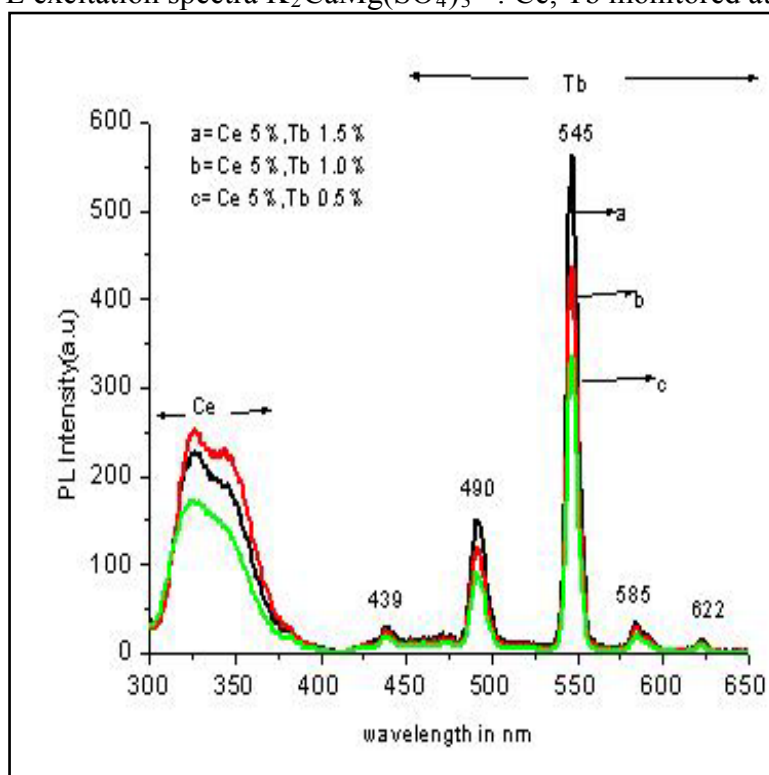Fig. 6 PL excitation spectra $K_2CaMg(SO_4)_3$: Ce, Tb monitored at 545 nm.

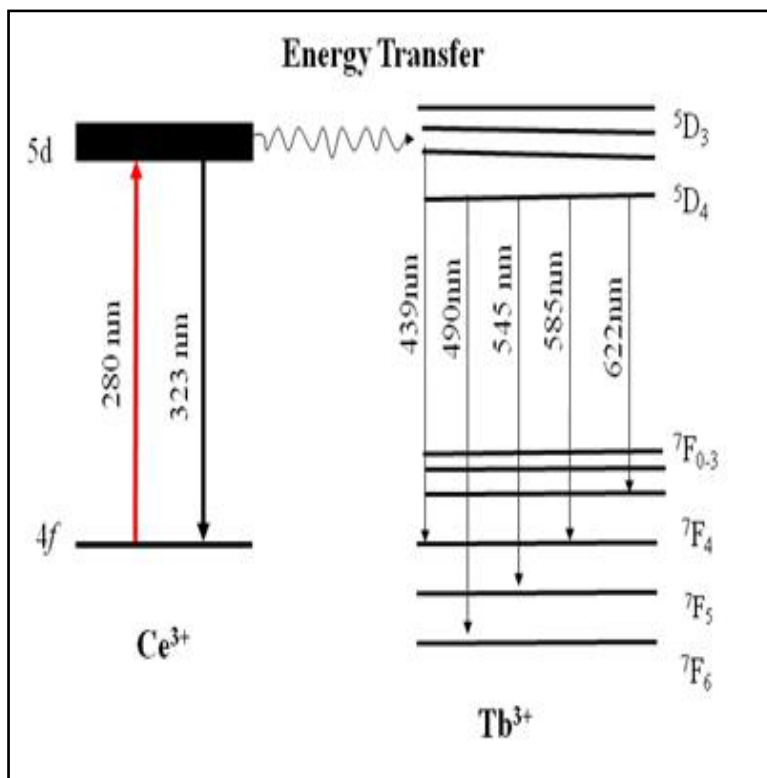Fig. 7 PL emission spectra $K_2CaMg(SO_4)_3$: Ce^{3+} , Tb^{3+} at an excitation 280 nm.

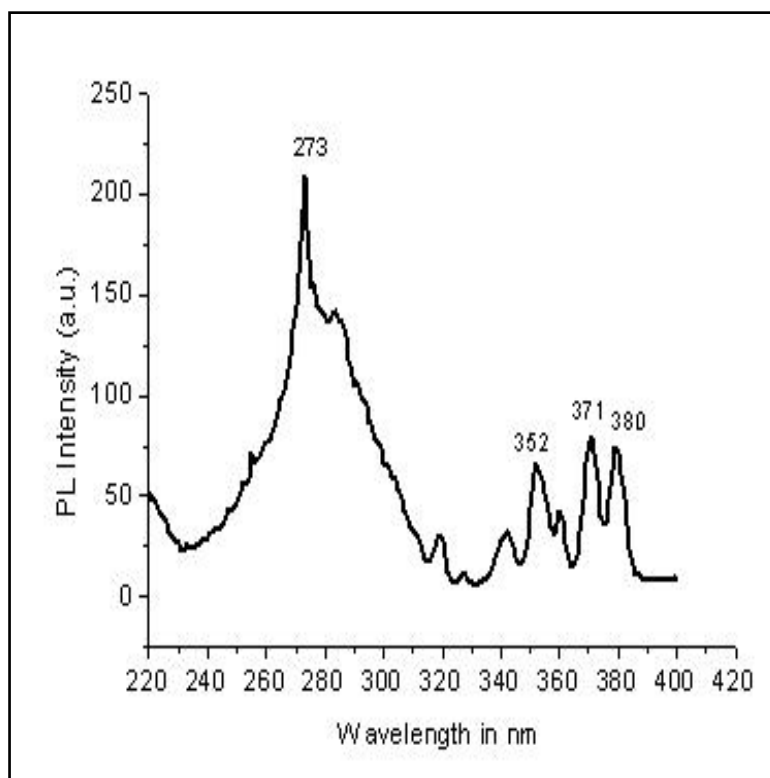Fig. 8 Energy level diagram of $K_2CaMg(SO_4)_3$ ₄ : Ce, Tb.

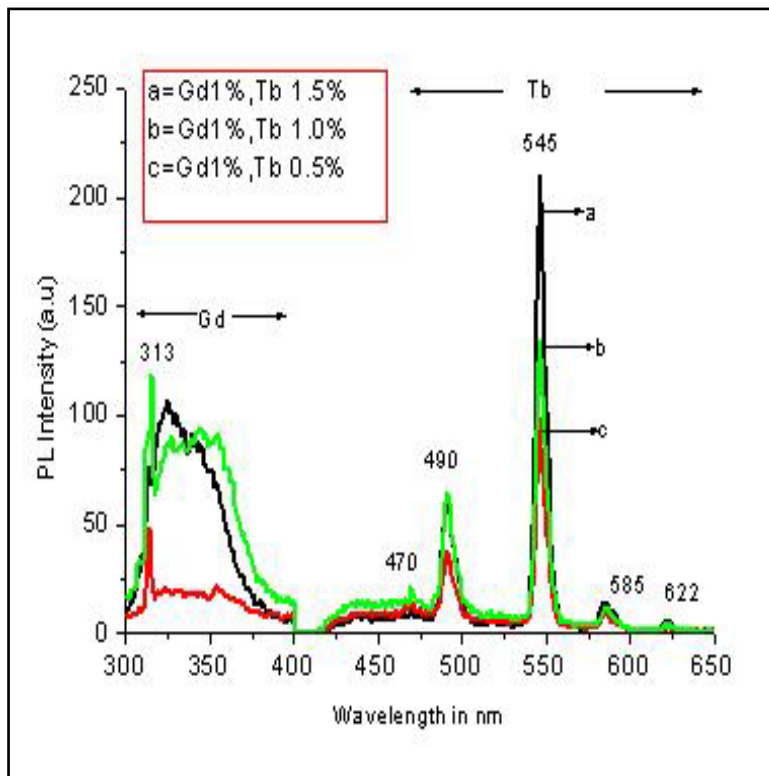Fig. 9 PL excitation spectra of $K_2CaMg(SO_4)_3$: Gd Tb monitored at 545 nm.

Fig. 10 PL emission spectra of $K_2CaMg(SO_4)_3$:Gd^+, Tb^3 at an excitations 273 nm.
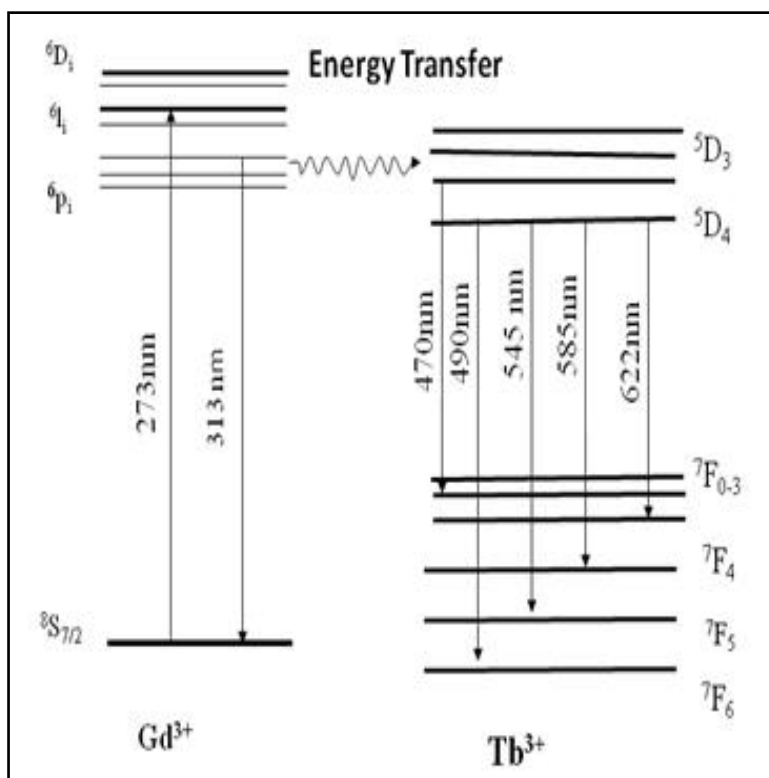

Fig. 11 Energy level diagram $K_2CaMg(SO_4)_3$: Gd, Tb.

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