



ENERGY TRANSFER IN $\text{K}_2\text{Ca}(\text{SO}_4)_3:\text{Ce}^{3+}, \text{Dy}^{3+}$

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ABSTRACT

The Phosphor $\text{K}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}^{3+}$ and $\text{K}_2\text{CaMg}(\text{SO}_4)_2:\text{Ce}^{3+}, \text{Dy}^{3+}$; were prepared by wet chemical method. 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. $\text{K}_2\text{CaMg}(\text{SO}_4)_3: \text{Dy}^{3+}$ shows characteristics emission of Dy^{3+} peaking at 483 nm and 573 nm due to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ and ${}^6\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ under the excitation of 290 nm of Ce^{3+} . In this phosphor Ce^{3+} could effectively sensitizes Dy^{3+} via dipole-dipole interaction. This phosphor may useful for white light LED.

Keywords: Halosulphate, Quenching, sensitizer.

1. Introduction

Energy transfer processes among the optical centers in phosphor is of great importance due to its utility in the manufacture of different kinds of the devices [1–2]. ET processes could take place by electric or magnetic multipole interactions, by exchange interaction or by emission or subsequent absorption of photon [3-5]. Also there are several possible mechanisms by which ET can occur: cross relaxation, energy migration, back-transfer and frequency up conversion [6-7]. A alternative path has been work out which is called luminescence sensitization. Ce^{3+} doped martial could especially shows one or two broader emission bands (320 – 480 nm) that are identified as the $5d \rightarrow 4f^1$ radiative recombination at two different Ce^{3+} centers because of a strong electron-phonon interaction in 5d excited state with excitation bands located in the UV wavelength of 220-300 nm [8]. Hence the work is focused on host lattice

(sulphate) activated by Ce^{3+} in combination with rare earth elements Dy^{3+} . Ce^{3+} ions can be used as sensitizer 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 [9]. Gedam et. al. have reported the halosulphate material as phosphor. They were synthesized and characterized $\text{K}_2\text{Ca}_2(\text{SO}_4)_3:\text{Eu}^{3+}, \text{Dy}^{3+}$; $\text{LiNaSO}_4:\text{Eu}^{3+}, \text{Dy}^{3+}$ and many more. 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-quadrupole interaction [10].

2. Experimental

$\text{K}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}^{3+}$ and $\text{K}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}^{3+}, \text{Dy}^{3+}$ are prepared by single step wet chemical synthesis. K_2SO_4 , CaSO_4 , and MgSO_4 of analar grade were taken in a stoichiometric ratio as per following reaction in double distilled water in separated beaker.



Water soluble sulphate salt of Ce and Dy were dissolved separately. These then mixed with $\text{K}_2\text{CaMg}(\text{SO}_4)_3$ solution to obtained required phosphor. The solution was slowly evaporated at 80°C 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°C for 4 h and slowly cooled to room temperature. Formation of compound was confirmed by taking XRD pattern. The photoluminescence measurement of excitation

and emission at room temperature were recorded on the Shimadzu RF 5301 PC. Excitation and emission spectra were recorded using slit width of 1.5 nm.

3. Result and Discussion

3.1 X-ray diffraction pattern and Phase Analysis

The phase purity of sample is characterized by X-ray diffraction. XRD of $K_2CaMg(SO_4)_3$ phosphor is shown in Fig. 1. All the diffraction peaks are found to be matched well with those standard of JCPDS No. 20-0866. No other XRD peak from K_2SO_4 , $MgSO_4$ and $CaSO_4$ are detected. The crystal as cubic symmetry with lattice $a=b=c=10.1622\text{\AA}$.

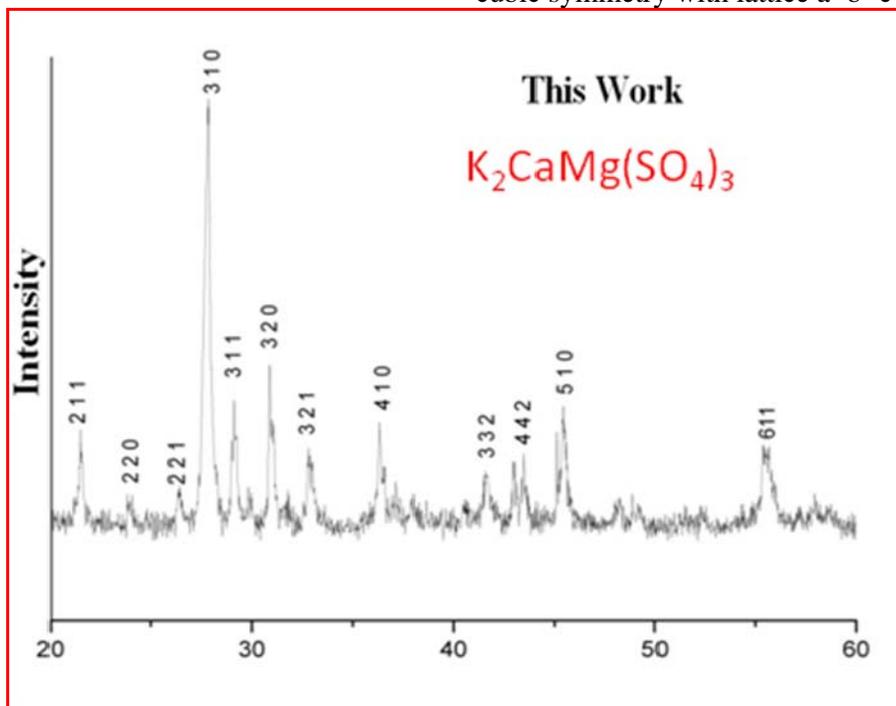


Fig. 1: XRD pattern of $K_2CaMg(SO_4)_3$ powder

3.2 Photoluminescence studies in $K_2CaMg(SO_4)_3$

3.2.1 Photoluminescence of Ce^{3+} in $K_2CaMg(SO_4)_3$ Phosphor

Ce^{3+} can provide strong absorption of UV and efficient conversion to longer wavelength. The photoluminescence excitation spectra for $K_2CaMg(SO_4)_3:Ce^{3+}$ phosphor is as shown in Fig.2A. The excitation spectra (for the emission at 323 nm) of $K_2CaMg(SO_4)_3:Ce^{3+}$ phosphor shows a strong band at 280 nm. The emission spectra for the excitation at 280 nm exhibits broad emission band in between 300 nm to 380 nm shown in Fig.2 B. The emission

spectra were recorded of the sample for different concentrations (1, 2, 3 and 5 mol% of Ce^{3+}).

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 $K_2CaMg(SO_4)_3$ host [22]. From Fig. 2 B, it is observed that emission intensity is found to be gradually increasing with increased of Ce^{3+} concentration. No concentration quenching take place till 5 mol% of Ce^{3+} .

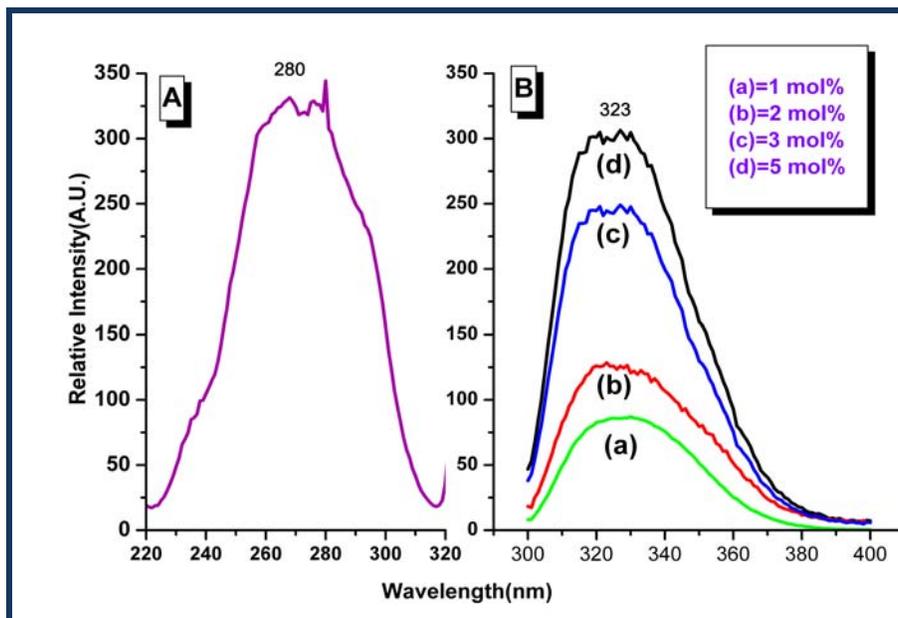


Fig. 2 (A, B): Excitation and Emission spectra of $\text{K}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}^{3+}$ phosphor

3.2.3 $\text{Ce}^{3+} \rightarrow \text{Dy}^{3+}$ energy transfer in $\text{K}_2\text{CaMg}(\text{SO}_4)_3$ phosphor

Energy transfer from Ce^{3+} to Dy^{3+} has been extensively investigated in different host lattices [11-12]. Fig.3A and Fig.3 B represent excitation and emission spectra of $\text{K}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}^{3+},\text{Dy}^{3+}$ respectively. The excitation spectra shows broad band with maximum intensity at 290 nm which is corresponding to 4d-5f band of Ce^{3+} and it also

contain weak excitation of Dy^{3+} at 348 nm, when monitored at 573 nm. For the excitation of 290 nm, emission spectra were recorded of the samples for different concentration (5 mol% of Ce^{3+} and 0.5, 1 and 1.5 mol% of Dy^{3+}). The emission spectra shows broad band at 323 nm (Ce^{3+}) and two very intense and sharp peaks are observed at 482 nm and 573 nm (Dy^{3+}).

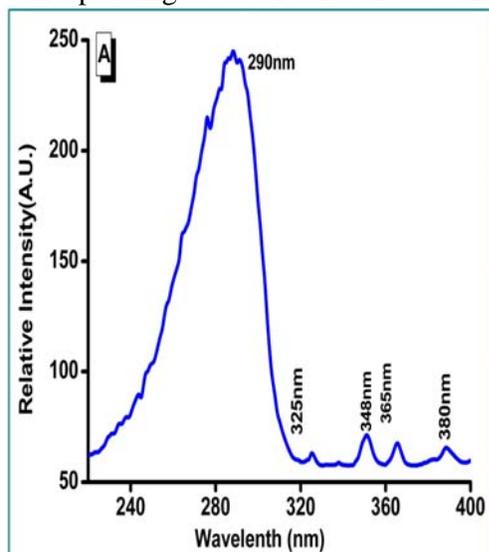


Fig. 3 A: Excitation spectra of $\text{K}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}^{3+},\text{Dy}^{3+}$

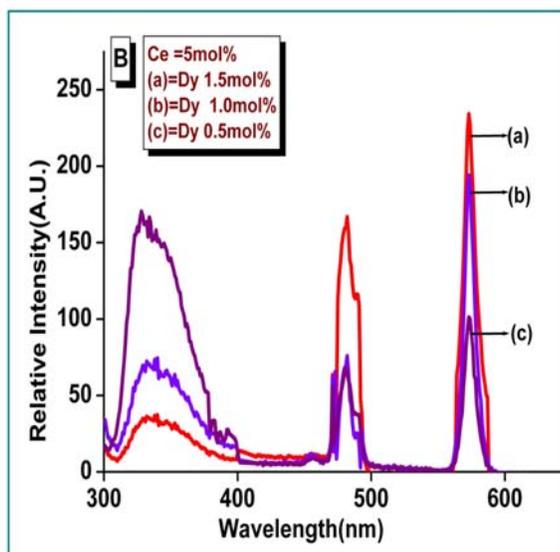


Fig. 3 B: Emission spectra of $\text{K}_2\text{CaMg}(\text{SO}_4)_3:\text{Ce}^{3+},\text{Dy}^{3+}$

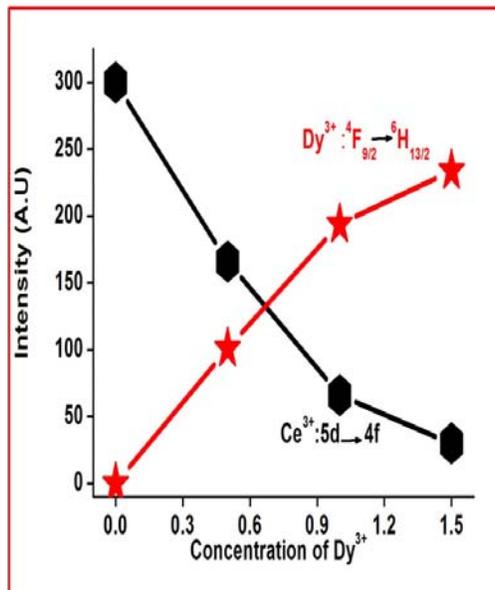


Fig. 4: Variation in intensity of Ce³⁺ and Dy³⁺

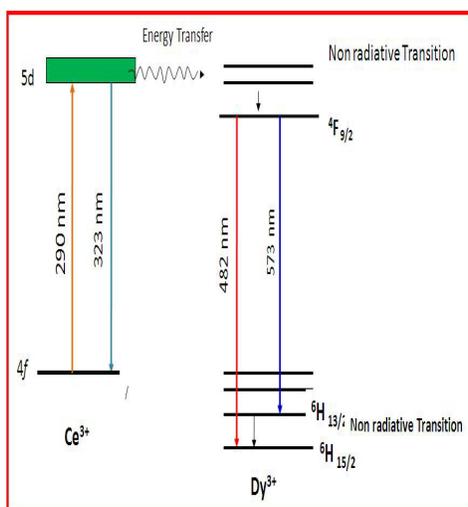


Fig. 5: Energy level diagram K₂CaMg(SO₄)₃:Ce³⁺, Dy³⁺ phosphor

Dy³⁺ emission of 482 nm and 573 nm is due to ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition respectively. The content of co-activators affects the intensity of emission but positions of peak remain same. From Fig 4, it is clear that the emission intensity Dy³⁺ increases relatively with the increasing content of Dy³⁺ while intensity of Ce³⁺ decreases monotonically, which indicates that Ce³⁺ transfer some energy to Dy³⁺ in the present host matrix. According to Fig.3 B, the broad emission band of Ce³⁺ in K₂CaMg(SO₄)₃ is located from 300 to 400 nm. As mention in the literature (Blassé and Grabmaier, 1994), the main excitation peaks monitoring Dy³⁺ emission are also located in this wavelength region. The perfect overlap of emission spectrum of Ce³⁺ and the excitation

spectrum of Dy³⁺ provides advantageous condition for resonant energy transfer from Ce³⁺ to Dy³⁺. Energy transfer from Ce³⁺ to Dy³⁺ ions in K₂CaMg(SO₄)₃ lattice bring Dy³⁺ to the excited state. The emission in Dy³⁺ comes via a non radiative transition to the ${}^4F_{9/2}$ level followed by radiative transition to ${}^6H_{15/2}$ and ${}^6H_{13/2}$ levels. Fig 5 shows Ce³⁺ → Dy³⁺ energy transfer mechanism in K₂CaMg(SO₄)₃ host.

4. Conclusion

The present Phosphor K₂CaMg(SO₄)₃:Ce³⁺ and K₂CaMg(SO₄)₂:Ce³⁺, Dy³⁺; were prepared by wet chemical method. From the result, it is concluded that, K₂CaMg(SO₄)₃ is suitable host for PL emission of Ce³⁺ ions, Ce³⁺ shows emission at around 323 nm due to 5d → 4f

transition at the excitation of 280 nm. $\text{K}_2\text{CaMg}(\text{SO}_4)_3$: Dy^{3+} does not show any emission but when it is co-doped with Ce^{3+} , it shows characteristics emission of Dy^{3+} peaking at 483 nm and 573 nm due to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ and ${}^6\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ under the excitation of 290 nm of Ce^{3+} . This result indicated that Ce^{3+} could effectively sensitizes Dy^{3+} in $\text{K}_2\text{CaMg}(\text{SO}_4)_3$ via dipole-dipole interaction. This phosphor may useful for white light LED.

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