

Photoluminescence Spectral Analysis of Eu^{3+} and $\text{Eu}^{3+}, \text{Dy}^{3+}:\text{KMgSO}_4\text{Cl}$ Phosphors

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Abstract. In the present paper, we report results concerning the synthesis and systematic analysis of $\text{Eu}^{3+}:\text{KMgSO}_4\text{Cl}$ and codoped $\text{Eu}^{3+}, \text{Dy}^{3+}:\text{KMgSO}_4\text{Cl}$ phosphors by employing a wet chemical method. X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) characterizations have been carried out in understanding their structural and functional group analysis. Besides that, their photoluminescence (PL) studies of $\text{Eu}^{3+}:\text{KMgSO}_4\text{Cl}$ and $\text{Eu}^{3+}, \text{Dy}^{3+}:\text{KMgSO}_4\text{Cl}$ phosphors have been undertaken. The presence of three overlapping bands at around 594nm, 616nm and 702nm from the PL spectrum of this phosphor clearly confirms the fact on the existence of Eu^{3+} in the host matrix chosen here. Influence of Dy^{3+} co-doping on the PL characteristics of $\text{Eu}^{3+}:\text{KMgSO}_4\text{Cl}$ phosphors has been investigated with an explanation behind the energy transfer process based red emission enhancement in $\text{Eu}^{3+}, \text{Dy}^{3+}:\text{KMgSO}_4\text{Cl}$ phosphors.

Keywords: Energy Transfer, Photo Luminescence, Phosphors.

1. Introduction

Luminescence properties of co-activator doped compounds in recent times, have received a considerable interest. The main interest has been concerned with the utilization of efficient energy migration from sensitizer (donor) ion to acceptor ion. Energy transfer process has significantly resulted in rapid and encouraging development of a variety of new and more efficient photoluminescent materials commercial importance [1].

White-light-emitting diodes (W-LEDs), the next-generation solid state lighting, have attracted much attention due to their superior features such as higher rendering index, higher luminosity efficiency, and lower energy consumption. At present, there are mainly two approaches to produce white light. One is fluorescent conversion, that is to combine a single LED chip and phosphor to make light, and the other one is to combine red, green, and blue tricolor LED chips, namely multichip white LED. Now, fluorescent conversion type white LED is the main production in large-scale and business around the world [2].

Eu emission results from two types of transitions. The most common is that due to $4f65d \rightarrow 4f6$ ($8S7/2$). As the position of the band corresponding to $4f6 \rightarrow 5d$ configuration is strongly influenced by the host. Eu^{2+} -doped compounds, which shows that the emission colour of Eu^{2+} can vary in a broad range, from ultraviolet to red. Since the $4f \rightarrow 5d$ transition is an allowed electrostatic dipole transition, the absorption and emission of Eu^{2+} is very efficient in many hosts, which makes the Eu^{2+} -doped phosphors of practical importance.

Europium ion (Eu^{3+}) is widely used as a luminescent center in a number of phosphors for the exhibited characteristic red emission mainly corresponding to its $5D_0 \rightarrow 7F_2$ transition [3,4]. Phosphates doped with trivalent europium ions have excellent efficiencies and appropriate absorption bands. A great deal of work has been done on Eu^{3+} activation of these hosts Ye et al. Therefore Eu^{3+} doped in phosphates compounds have excellent luminescence [5-7]. Dysprosium ion with a $4f9$ configuration has complicated f-block energy levels and between these levels various transitions results in sharp line spectra [8]. Dy^{3+} ion exhibits there

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visible emission bands including a blue emission at 484 nm, corresponding to the $4F9/2 \rightarrow 6H15/2$ transition, a yellow emission at 575nm, corresponding to the hypersensitive transition $4F9/2 \rightarrow 6H13/2$ and a weak red emission at 665nm, corresponding to the $4F9/2 \rightarrow 6H11/2$ transition. Luminescence materials doped with Dy^{3+} have drawn much interest for its white emission [7].

The combination of Ce and Mn in the CaF_2 lattice, however, gives brilliant Mn^{2+} emission in addition to that of Ce^{3+} on UV excitation, due to energy transfer from Ce^{3+} to Mn^{2+} ions. Similar enhancement in the fluorescence efficiency of Dy and Mn ions was reported in $CaSO_4: Ce, Dy$ and $CaSO_4: Ce, Mn$ [7]. However, the application of similar energy transfer mechanism leads to enhanced sensitivity in the case of TL and PL. During the course of investigation on TL in sulphate-based phosphors, we have reported several sulphate phosphors possessing properties useful to TL dosimetry of ionizing radiations. Other than sulphate material, some investigations are in progress on halosulphate –based materials [8].

Moreover mixed sulfates are also known to be good photoluminescence thermo luminescence (PL) and (TL) materials. Sahare and co-workers have studied some mixed sulfate systems for their applications in the dosing of high-energy radiations using the TL technique. They have synthesized and characterized $K_2Ca_2(SO_4)_3: Eu, Dy$ and $K_2Ca_2(SO_4)_3: Eu$; $LiNaSO_4: Eu$, $LiNaSO_4: Eu, Dy$ mixed sulfates.

In this paper, we report on the synthesis of $KMgSO_4Cl$ material by a wet chemical technique and we do explain the energy transfer mechanism involved in $Eu^{3+} \rightarrow Dy^{3+}$ ions in $KMgSO_4Cl$ halosulphate phosphors together.

2. Experimental Studies:

Halosulphate phosphors of $KMgSO_4Cl$ (pure), $KMgSO_4Cl: Eu^{3+}$ and $KMgSO_4Cl: Eu^{3+}, Dy^{3+}$ were prepared by the wet chemical method. $MgSO_4$ and KCl of analar grade were taken in stoichiometric ratio and dissolved separately in double-distilled de-ionized water, resulting in a solution of $KMgSO_4Cl$. Water-soluble sulphate salt of europium and dysprosium was then added to the solution to obtain $KMgSO_4Cl: Eu$, $KMgSO_4Cl: Eu, Dy$ the chemical reaction was given in (Eq. (1)). This confirms that no undissolved constituents were left behind, and salts had completely dissolved in water and thus reacted. The compounds $KMgSO_4Cl$, $KMgSO_4Cl: Eu$ and $KMgSO_4Cl: Eu, Dy$ in their powder form were obtained by evaporating under 80° for 8h. The dried samples were then slowly cooled at room temperature. The resultant polycrystalline mass was crushed to fine particle in a crucible. The powder was used in further study.



Formation of the compound was confirmed by taking the XRD pattern that matched with the standard data available (JCPDs file number 74-0383 for $KMgSO_4Cl$). The photoluminescence (PL) emission spectra of the samples were recorded using fluorescence spectrometer (Hitachi F-4000).

3. Results and discussion

3.1. XRD Analysis

Fig. 1 shows the XRD pattern of $KMgSO_4Cl$ phosphors material. The XRD pattern of prepared material matches with the standard data of $KMgSO_4Cl$.

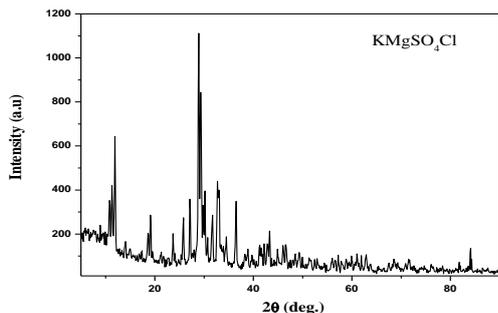


Fig.1. XRD Pattern of the $KMgSO_4Cl$ phosphor.

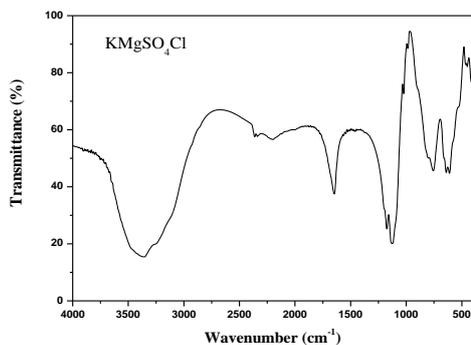


Fig. 2. FTIR spectrum of the $KMgSO_4Cl$ phosphor.

KMgSO₄Cl·2.75H₂O materials show the historical name is kainite. The symmetry class: monoclinic-β, space group: C 2/m, unit cell parameters: a= 19.7200, b= 16.2300, and c= 9.530, β= 94.9200, number of formulae per unit: Z= 16, unit cell volume (Å³): Vc = 3038.89, number of atomic position per full unit cell: P/U= 172, molar volume (cm³/mol): Vm= 114.40, number of reflexes used in structure determination: NR= 1693, X-ray density (g/cm³): p= 2.14, R-factor: R= 0.0470, Mu (1/cm): μ= 126.288, wavelength for calculated powder diffraction patterns: Cu = 1.54056, mass attenuation coefficient (cm²/g): μ/p = 59.109, and θ-interval for CPDP: T/I = 1-35.[11].

3.2. FTIR Analysis

In order to investigate the nature of bonding, the molecular environment FTIR spectroscopy has been quite useful technique in analyzing different inorganic compounds. Fig. 2 shows an FTIR spectrum of KMgSO₄Cl phosphor.

FTIR spectrum shows an absorption in different regions: the bending mode of different water molecules of crystallization is observed at 1647 cm⁻¹. The absorption at 1128cm⁻¹ is due to SO₄²⁻ asymmetric stretching vibrations. Longitudinal optic mode frequency of Mg-O is observed at 754 cm⁻¹. The bending mode of SO₄²⁻ occurs at 642 cm⁻¹. Europium ions can be stabilized in the host lattice in either divalent or trivalent oxidation state. The incorporation and stabilization of Eu³⁺ ions in the sample were confirmed by the luminescence investigations [12].

3.3. PL Analysis

Fig. 3 shows the emission spectrum of KMgSO₄Cl: Eu³⁺ halo-phosphors excited with 350 nm. The emission spectra are recorded with 350 nm excitation, the emission peaks are located at 616 nm, 595 nm and 702 nm, which originate from the electric dipole transition (5D₀→7F₂), and the magnetic dipole transition (5D₀→7F₁) of Eu³⁺, respectively. The strong emission peak at 617 nm indicates site lack of inversion symmetry [11,12]. Eu³⁺, Dy³⁺: KMgSO₄Cl phosphors related excitation and emission spectra are shown in the Figs. 4

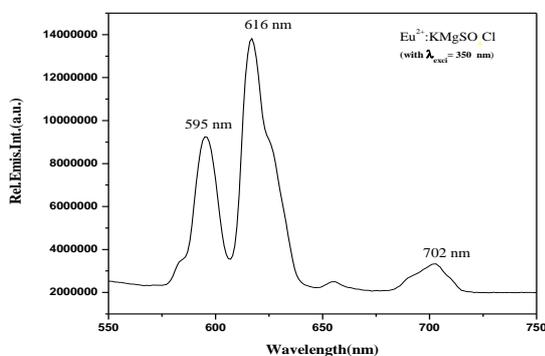


Fig.3.Emission spectra of Eu³⁺: KMgSO₄Cl Phosphors

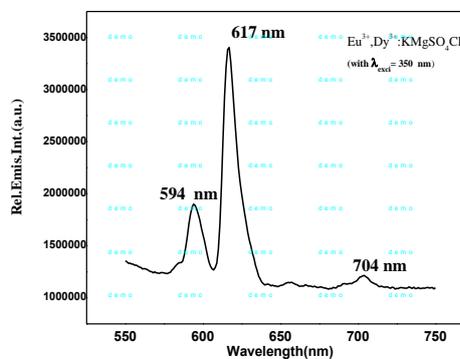


Fig.4.Emission spectra of Eu³⁺,Dy³⁺: KMgSO₄Cl Phosphors

4. Conclusions

It could be summarized that Eu³⁺: KMgSO₄Cl and Eu³⁺,Dy³⁺: KMgSO₄Cl phosphors have successfully been synthesized by using a wet chemical technique. FTIR spectrum of this phosphor confirms the presence of water molecules of crystallization, Mg-O bond and sulphate group in the compound. The Photoluminescence spectra Eu³⁺: KMgSO₄Cl of phosphors show, emission at 595 nm, 616nm, 702 nm and a clear enhancement in the red (617nm) emission performance from Eu³⁺ due to the presence of the another rare earth ion namely Dy³⁺.

5. References

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