

Optical study of Gd³⁺ and Tb³⁺ in KZnSO₄Cl: Ce³⁺ Phosphor

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Abstract

The optical and spectroscopic study of Gd^{3^+} and Tb^{3^+} ions in KZnSO₄Cl matrix have been studied in this paper. The compound KZnSO₄Cl: Ce, X (X= Gd or Tb) is prepared by wet chemical method. Photoluminescence (PL) of KZnSO₄Cl: Ce^{3^+} co-doped with Gd or Tb shows strong emission, and this phosphor is also efficient for $Ce^{3^+} \rightarrow Gd^{3^+}$ and $Ce^{3^+} \rightarrow Tb^{3^+}$ energy transfer. The Gd^{3^+} emission by $Ce^{3^+} \rightarrow Gd^{3^+}$ under UV wavelength peaking at 310 nm and 337 nm for an excitation of 254 nm due to ${}^{6}P_{7/2} \rightarrow {}^{8}S_{7/2}$ transitions, whereas the Tb^{3^+} emission by $Ce^{3^+} \rightarrow Tb^{3^+}$ under UV wavelength peaking at 490, 547, 585 nm, for the excitation of 350 nm due to ${}^{5}D_4 \rightarrow {}^{7}F_J(J = 4, 5, 6)$ transitions. The purpose of the present study is to develop and understanding the photoluminescence and effect of Gd^{3^+} and Tb^{3^+} co-doping in KZnSO₄Cl: Ce^{3^+} new luminescent materials, which can be the green phosphor in many applications such as lamp phosphors.

Keywords: Inorganic material; wet chemical; Photoluminescence; green phosphor; energy transfer; lamp phosphor.

Introduction

The luminescence properties of Gd^{3+} compounds have been of considerable interest in recent years. This interest is based on the occurrence of a number of energy transfer processes which yield high luminescence efficiencies. Also these compounds can be used as efficient phosphors in a new generation of fluorescent lamps. Gd^{3+} ion is isoelectronic with Eu^{2+} ion, but its 4f ⁶ 5d state lies at much higher energy, as a consequence, the luminescence of Gd^{3+} ion consist of sharp lines ${}^{6}\text{P} \rightarrow {}^{8}\text{S}$ transitions, mainly at 313 nm. Due to its high energetic position, this emission can only be observed in lattices with optical absorption at high energy.

 Gd^{3+} emission can be sensitized by a variety of ions. Sm^{3+} Gd³⁺ energy transfer was the first instance of such phenomena in RE doped materials (Tomaschel-1924). Ce³⁺ ion which has strong UV absorption can act as sensitizer if the Ce³⁺ emission in given host matches with Gd^{3+} absorption^{1,2}. Bi^{3+} , Pb^{2+} , tantalate ion³ and Pr^{3+} (an also sensitize Gd^{3+} ion. The sensitization is possible when emission of these ions is in UV, thus having a small Stoke's shift. Otherwise energy transfer takes place from Gd^{3+} to these ions. Quite often energy transfer from ⁶P manifold of Gd^{3+} to other RE ions or host lattice group occurs. Particularly, Gd^{3+} can act as a sensitizer for $Tb^{3+5,6}$ and efficient phosphor based on this transfer has been obtained. e.g. GdMgB₅O₁₀: Ce, Tb is a green component of 3 color lamp phosphor. Gadolinium oxysulphide, silicate and germanate doped with Tb are efficient phosphors for X-ray imaging. In Tb doped phosphors, Tb³⁺ concentration has to be high (around 5at%), however, by using Gd³⁺ as sensitizer intermediate, efficient phosphors can be obtained for Tb concentration of 1at %.

 Gd^{3+} can also act as sensitizer for Dy^{3+} and Mn^{2+7} . By exciting Gd^{3+} containing phosphors by X-rays, it is possible to observe the emission from higher levels like 6I and ⁶G. ⁶G \rightarrow ⁸S emission is at 187 nm ⁸. Gd^{3+} ion is very suitable for studying vibronic transitions. This is due to the fact that the ground state ⁸S is non-degenerate. In host lattices with low frequencies anti-Stokes vibronic lines can also be observed, e.g. in Y₂O₂S: Gd ⁹.

In case of Tb^{3+} ion, the absorption is usually due to allowed f-d transition. From excited state of 4f ⁷ 5d¹ configuration, the electron loses energy to lattice and comes to ${}^{5}\text{D}_{j}$. ${}^{5}\text{D}_{3} \rightarrow {}^{7}\text{F}_{j}$ emission is in UV and blue region while ${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{j}$ emission is predominantly green. At lower concentrations, blue emission is observed, but at higher concentration, there is an energy transfer between Tb³⁺ ions, e.g. the cross relaxation-

$$Tb^{3+}(^{5}D_{3}) + Tb^{3+}(^{7}F_{j}) \rightarrow Tb^{3+}(^{5}D_{4}) + Tb^{3+}(^{7}F_{0})$$

Due to which the blue emission gets quenched increasing the green emission at the same time. The terms 'low' and 'high' are relative. In some hosts, even at the lowest concentrations only green emission is observed, while in others the blue emission may be predominant even for concentrations as high as fraction of a mol.%. The blue emission is also quenched by Dy^{3+} ions.f-d excitation is strong when Tb^{3+} occupies site of inversion symmetry. The quantum efficiency of luminescence is high usually when the f-d absorption is at longer wavelengths¹⁰. In hosts, where relaxed 5d band overlaps 7F_j states, no Tb^{3+} emission is observed, as there is no excitation into 5D_j states (e.g. in YAG:Tb). Tb^{3+} emission may be sensitized by transfer from sensitizer to 4f ⁿ levels. Gd and Ce are good sensitizers de Haair 1979¹¹. An interesting example is the energy transfer from Yb³⁺ to Tb³⁺ which leads to up-conversion.

In this paper, the synthesis of KZnSO₄Cl material by wet chemical technique and energy transfer mechanism in $Ce^{3+}\rightarrow Gd^{3+}$ and $Ce^{3+}\rightarrow Tb^{3+}$ ions have been explained. The work shows that very efficient phosphors can be obtained by sensitizer Ce^{3+} ions on the basis of the Gd^{3+} or Tb^{3+} ions.

Material and Methods

KZnSO₄Cl (pure) and KZnSO₄Cl: Ce, X (Gd or Tb) phosphors were prepared by a wet chemical method. ZnSO₄ and KCl of analar grade were taken in a stoichimetric ratio and dissolved separately in double distilled de-ionized water, resulting in a solution of KZnSO₄Cl. Water soluble sulphate salt of Cerium and Gadolinium or Terbium was then added to the solution to obtain KZnSO₄Cl: Ce, Gd; KZnSO₄Cl: Ce, Tb. Confirming that no undissolved constituents were left behind and all the salts had completely dissolved in water and thus reacted. All the compounds in their powder form were obtained by evaporating on 80 ^oC for 8 hours. The dried samples were then slowly cooled at room temperature. The resultant polycrystalline mass was crushed to fine particle in a crucible. The power was used in further study.

Formation of the compound was confirmed by taking the x-ray diffraction (XRD) pattern. The photoluminescence (PL) emission spectra of the samples were recorded using Fluorescence spectrometer (Hitachi F-4000). The same amount of sample was used in each case. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

Results and Discussions

Energy Transfer from Ce³⁺ to Gd³⁺: During phototherapy investigations using UVB (270-320 nm) it was found¹² that UV in the region 270-300 nm is not much effective, on the contrary

it leads to side effects, while that in the narrow region 300-320 nm showed remarkable therapeutic effects. UV emission in a narrow band centered on 310 nm is thus required. ${}^{6}P_{7/2} \rightarrow {}^{8}S$ transition of Gd³⁺ is ideal for such emission. The most suitable choice for the sensitizer have been the Ce³⁺(4f¹) ions and we used the Gd³⁺ ion as activator. For efficient energy transfer, the theory of Dexter requires high spectral overlap between the Ce³⁺ emission and Gd³⁺ absorption. The ultraviolet emission of Ce³⁺ in the host has a small spectral overlap with the absorption transition of the Gd³⁺ ion. Hence, weak Ce³⁺ \rightarrow Gd³⁺ energy transfer occurs in sulphate host. This can be seen from the emission spectrum of the different samples.

Figure 1 shows the X-ray diffraction pattern of KZnSO₄Cl sulphate host¹³. The XRD pattern did not indicate presence of the constituents ZnSO₄ or KCl and other likely phases like ZnCl₂ or K₂SO₄, which is an indirect evidence for the formation of the desired compound. These results indicate that the final product was formed in homogeneous form. PL spectrum of the $Ce^{3+} \rightarrow Gd^{3+}$ co-doped KZnSO₄Cl sulphate host are shown in figure 2 which shows the emission and excitation spectra of the co-doped Ce \rightarrow Gd ions in sulphate host. The excitation spectrum has the maximum position at 263 nm, and a small shoulder observed at about 254 nm. With this excitation wavelength $\lambda ex = 254$ nm, the emission spectrum for KZnSO₄Cl: Ce, Gd sample have been recorded. In this emission spectrum we observed two peaks, one is sharp and intense at 310 nm and the other is broad at around 337 nm. The intensity of second peak is very low; this shows the emission position of Ce³⁺, whereas the sharp line emission at 310 nm shows the emission of Gd³⁺ due to the transition ${}^{6}P_{7/2} \rightarrow {}^{8}S_{7/2}$. Figure 3 shows the energy transfer mechanism in KZnSO₄Cl: Ce, Gd phosphor.



Figure-1 X-ray diffraction (XRD) pattern of KZnSO₄Cl material



(A).Excitation of KZnSO₄Cl: Ce_{1 mol.%}, Gd (B) Emission of KZnSO₄Cl: Ce_{1 mol.%}, Gd for a) 1, b) 0.5, c) 0.2 and d) 0.1 mol.% of Gd



Figure-3 Energy transfer mechanism in KZnSO₄CI: Ce, Gd phosphor

Energy Transfer from Ce^{3+} to Tb^{3+}: Energy transfer finds applications in lamp phosphors, laser etc. and it is controlled by luminescent kinetics, which is affected by energy level, lifetime, distance between co-dopants, etc. One of the dopant is called as activator from where the emission takes place and other is sensitiser, which will improve the luminescence efficiency of activator emission.

 Ce^{3+} to Tb^{3+} energy transfer process in different host matrices is well known^{14,15}. Broad band emitters are often used to sensitize the luminescence of RE ions. Optical transitions within a 4f ⁿ configuration are so strongly forbidden that they appear in the absorption spectra as very weak. However, excitation resulting in high light output can be achieved by exciting a different ion (i.e., sensitiser) with an optically allowed transition which transfers the excitation energy to the RE activator. Efficient energy transfer from the broad (i.e., Ce³⁺) to the narrow-line emitter (i.e., Tb³⁺) is possible only between nearest neighbors in the crystal lattice and optimal spectral overlap. If the spectral overlap is small, only partial energy transfer is possible. The energy transfer process between Ce^{3+} and Tb^{3+} is depicted in figure 4. The lowest 5d level of Ce^{3+} lies near the excited 4f levels of the Tb^{3+} in sulphate: Ce^{3+} , Tb^{3+} and hence an energy transfer can take place between the excited states of Ce^{3+} and Tb^{3+} ions. Sensitization of Tb^{3+} green emission at 545 nm by the addition of Ce³⁺ finds application in fluorescent lamp industry. Presently in the trichromatic phosphor for the green emission KZnSO₄Cl: Ce, Tb is used and in this phosphor for the complete Ce^{3+} –Tb³⁺ energy transfer, about 35 mol% of Tb is put along with 65 mol% of Ce. It is well known that the 5d ions such as Ce³⁺ can be used as a sensitizer. Optical excitation energy of Ce^{3+} can be easily and efficiently transferred to Tb^{3+} ions¹⁶. Present studies concentrate on energy transfer process in the KZnSO₄Cl sulphate with Ce^{3+} and Tb^{3+} co-doping. Figure 4 (A) shows excitation of KZnSO₄Cl: Ce, Tb and (B) KZnSO₄Cl: Ce, Tb emission in for 1, 0.5, 0.2, and 0.1 mol. %. The excitation spectra were obtained by monitoring emissions peaks for Ce^{3+} (350 nm), The emission spectra were measured upon excitation

at 350 nm corresponding to peak of the Ce^{3+} absorption. The emission of Ce^{3+} in the co-doped sample disappeared upon excitation at 254 nm, and the features of Ce^{3+} excitation appear in the excitation spectrum of Tb^{3+} when monitored at $Tb^{3+} 490$ nm emission. These facts indicate that energy transfer from Ce^{3+} to Tb^{3+} in the co-doped sample takes place. This shows that the

emission peaks at 490, 547 and 585 nm. The emission peaks at 490 nm and at 547 nm are relatively more intense in these compounds. The phosphor is suitable for higher concentrations of Tb ions, as the intensity increases with increase in concentrations. Figure 5 shows the energy transfer mechanism in KZnSO₄Cl: Ce, Tb phosphor.



Figure-4 (A) Excitation of KZnSO₄Cl: Ce, Tb (B) KZnSO₄Cl: Ce, Tb emission in for 1, 0.5, 0.2, and 0.1mol.%



 $Ce^{3+} \rightarrow Tb^{3+}$ energy transfer in KZnSO₄Cl_. Arrows show the excitation and emission transitions

Conclusion

The presented compound KZnSO₄Cl: Ce, X (X= Gd or Tb) is prepared by wet chemical method. Phosphor is efficient for Ce³⁺ \rightarrow Gd³⁺ and Ce³⁺ \rightarrow Tb³⁺ energy transfer. With an excitation wavelength of 254 nm, the emission spectrum for KZnSO₄Cl: Ce, Gd sample two peaks have been observed, one is sharp and intense at 310 nm and the other is broad at around 337 nm due to the transition ${}^{6}P_{7/2} \rightarrow {}^{8}S_{7/2}$. In KZnSO₄Cl: Ce, Tb phosphor, three peaks are observed at 490, 547, 585 nm due to ${}^{5}D_{4} \rightarrow {}^{7}F_{1}$ (J = 4, 5, 6) transitions. In KZnSO₄Cl: Ce, Tb; Ce acts as a sensitizer and Tb as an activator. It can be used as the green phosphor. The emission of Gd³⁺ and Tb³⁺ in KZnSO₄Cl phosphor may be useful for lamp Industry. No previous investigation was reported utilizing this host to reveal Ce³⁺ and Tb³⁺ sites and this technique would give a new clue to probe activator sites in phosphor.

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