



Comparative study of Ce³⁺ activated chlorosulphate phosphors

Nita Shinde¹, N. S. Dhoble², S.C. Gedam³ and S. J. Dhoble¹

¹Department of Physics, RTM Nagpur University, Nagpur-440033, India

²Department of Chemistry, Sevadal Mahila Mahavidyalaya, Nagpur-440018, India

³Department of Physics, KZS Science College, Kalmeshwar, Nagpur-441501, India

Abstract

The synthesis, X-ray diffraction (XRD) and photoluminescence characteristics in chloride based halosulphate phosphors, such as KZnSO₄Cl: Ce; KMgSO₄Cl: Ce; have been reported in this paper. The Ce³⁺ emission in KMgSO₄Cl: Ce phosphor is more intense than KZnSO₄Cl: Ce and it may be useful for scintillation applications.

Keywords: XRD, halosulphate phosphors, photoluminescence.

INTRODUCTION

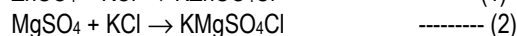
Luminescent materials are used for various purposes such as making lamps [1-3], CR tubes and TV screens [4], electroluminescent lamp and display panels, LEDs, detectors for x-ray imaging [5-8], scintillation detectors [9], laser crystals [10], paints [11], solar concentrators [12]. In many of these applications inorganic solids doped with rare earth impurities are used. Rare earth (RE) ions possess unique optical behavior when doped in to materials and have paved the way for the development of optical amplifiers and phosphors. The optical value of these ions results from the electronic transitions occurring with in the partially filled 4f energy shell of the lanthanide series. Traditionally, inorganic scintillators have played an important role in the detection and visualization of high-energy radiation. Applications in medical diagnostics and dentistry are only a few examples in which inorganic scintillators are used. At present, the most popular scintillators are sodium iodide doped with thallium, NaI:TI⁺ and cesium iodide doped with thallium, CsI:TI⁺. However, their light yield is rather low. In recent years, lutetium based compounds have emerged in the field of dense, high Z materials. Lu₂SiO₅:Ce³⁺, utilized in positron emission tomography (PET), LuAlO₃:Ce³⁺ and LuPO₄:Ce³⁺. Nevertheless, there is still a demand for scintillators with improved characteristics for specialized applications and the scintillator that has both a high light yield and a fast response has yet to be found. Rare earths Ce, Pr or Nd give UV or VUV emission corresponding to d → f transitions. Decay times of the order of several nanoseconds are expected [13]. In case of Pr and Nd, 5d → 4f transition will be observed if the 4fⁿ⁻¹ 5d → 4fⁿ transition is suppressed. This can be realized in rigid lattices [14]. Such emission have been reported in YAlO₃: Ce [15], CeF₃ [16] and Gd₂SiO₅: Ce [17]. All these are the good inorganic scintillators. Inorganic scintillators reviewed up till now have rather long decay time (100ns). Two schemes have been worked out to obtain scintillators with short decay time. The first one utilizes the cross over transitions in the insulators, while the second makes use of the fact that d → f transitions in the rare earth elements are allowed and have short decay times. Scintillations resulting from these fall in UV and VUV range, but with use of photosensitive gas counters as the detectors, efficient counting can be done.

In this paper, we report the synthesis of KZnSO₄Cl: Ce;

KMgSO₄Cl: Ce materials by wet chemical technique and explain the comparison of Ce³⁺ emission in present halosulphate phosphors, which may be applicable in the field of scintillators.

EXPERIMENTAL

All here reported halosulphate phosphors were prepared by the wet chemical method. For the synthesis of KZnSO₄Cl (pure) and KZnSO₄Cl: Ce phosphors, ZnSO₄ and KCl of anar grade were taken in stoichiometric ratio and dissolved separately in double distilled de-ionized water, resulting in a solution of KZnSO₄Cl. Water-soluble sulphate salt of cerium was then added to the solution to obtain KZnSO₄Cl: Ce (equation -1). Confirming that no undissolved constituents were left behind, and salts had completely dissolved in water and thus reacted. The compounds KZnSO₄Cl and KZnSO₄Cl :Ce in its powder form was obtained by evaporating on 80°C 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 powder was used in further study. The same process was adopted for the sample KMgSO₄Cl:Ce as shown in equation (2), respectively.



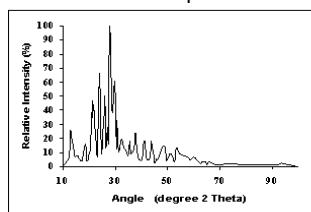
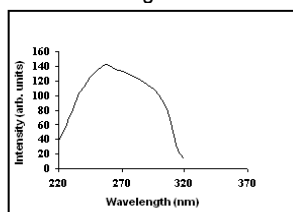
Formation of the compound was confirmed by taking the x-ray diffraction (XRD) pattern that matched with the standard data available (JCPDs file number 74-0383 for KMgSO₄Cl materials). The photoluminescence (PL) emission spectra of the samples were recorded using fluorescence spectrometer (Hitachi F-4000). 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 DISCUSSION

Ce³⁺ emission in KZnSO₄Cl

After the XRD characterization of the phosphors following results are obtained in KZnSO₄Cl:Ce; KMgSO₄Cl:Ce; NaMgSO₄F:Ce and Na₃SO₄F:Ce halosulphate phosphors. Fig. 1 shows the X-ray diffraction (XRD) pattern of KZnSO₄Cl material. The XRD pattern did not indicate presence of the constituents ZnSO₄ or

KCl and other likely phases like $ZnCl_2$ or K_2SO_4 , which is an indirect evidence for the formation of the desired compound. These results indicate that the final product was formed in homogeneous form.

Fig1. XRD pattern of KZnSO₄ClFig 2. Excitation Spectra of KZnSO₄Cl : Ce 10

Photoluminescence excitation spectra of $KZnSO_4Cl: Ce^{3+}$ phosphor shown in figure 2. The broad band is observed at around 254 nm with a prominent shoulder at around 274 nm ($\lambda_{em} = 327$ nm).

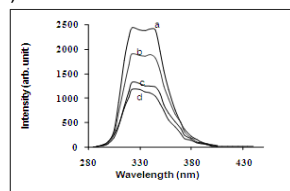
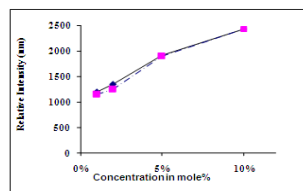
Fig 3 a) Emission Spectra of KZnSO₄Cl: Ce 10%
b) Emission Spectra of KZnSO₄Cl: Ce 5%
c) Emission Spectra of KZnSO₄Cl: Ce 2%
d) Emission Spectra of KZnSO₄Cl: Ce 1%Fig 4. Increased intensity with concentration in KZnSO₄Cl: Ce
— 327 nm and - - - 340 nm

Fig. 3 shows the PL emission spectra of Ce^{3+} ions in $KZnSO_4Cl$ phosphors with different concentrations under the excitation 254 nm wavelengths of light. Two unresolved peaks are observed at 327 nm and 340 nm, which are assigned to the $5d \rightarrow 4f$ transition of Ce^{3+} ions. With increasing concentration of Ce^{3+} ions intensity of both peaks increases and relative intensity of 340 nm peak also increases slightly. The 340 nm peak more intense than 327 nm peak with increasing concentration of Ce^{3+} ions in $KZnSO_4Cl$ at higher concentration of Ce^{3+} ion intensity of both peaks almost being equal and is shown in Fig 4. This indicates a change of the surrounding of the Ce^{3+} ions at higher concentration in the $KZnSO_4Cl$ lattice.

The intensity of Ce^{3+} emission at 327 nm is less as the compared to 340 nm peak intensity, where as the intensity of emission peak at 340 nm increases as compared 327 nm peak with increasing Ce^{3+} concentration in $KZnSO_4Cl$. The observed variations of PL emission intensities, it may be cross relaxation between Ce^{3+} ions in the case of heavy concentration of Ce^{3+} .

Ce^{3+} emission in $KMgSO_4Cl$

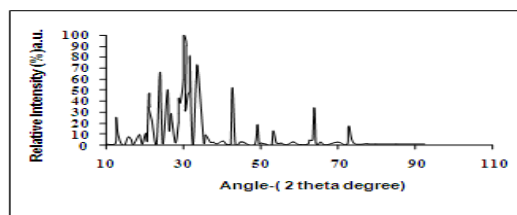
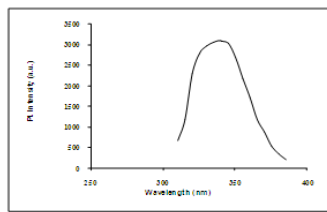
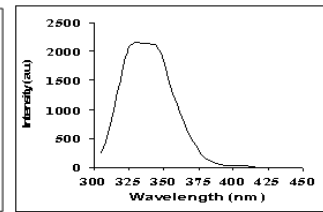
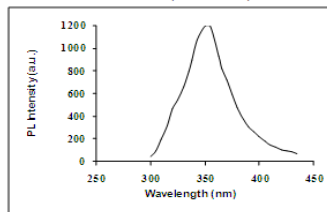
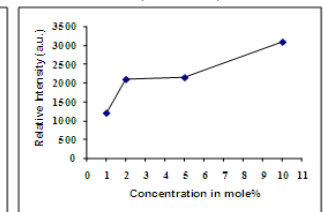
Fig 5. XRD pattern of $KMgSO_4Cl$

Figure 5 shows the X-ray diffraction (XRD) pattern of $KMgSO_4Cl$ material. The XRD pattern of prepared material match with standard data of $KMgSO_4Cl$ (JCPDs file number 74-0383). Photoluminescence excitation spectra of $KMgSO_4Cl:Ce^{3+}$ phosphor shows broadband is observed at 254 nm with a prominent shoulder

around 274 nm ($\lambda_{em} = 340$ nm).

Fig.6 PL emission spectra of $KMgSO_4Cl:Ce 10\%$
($\lambda_{ex} = 254$ nm)Fig.7 PL emission spectra of $KMgSO_4Cl:Ce 20\%$
($\lambda_{ex} = 254$ nm)Fig.8 PL emission spectra of $KMgSO_4Cl:Ce 1\%$
($\lambda_{ex} = 254$ nm)Fig.9 Variation of intensity with concentration in $KMgSO_4Cl:Ce$

Figures 6-8 show the PL emission spectra of Ce^{3+} ions in $KMgSO_4Cl$ phosphors with different concentration under excitation 254 nm wavelength of light. Two unresolved peaks are observed at 327 nm and 340 nm, which are assigned to the $5d \rightarrow 4f$ transition of Ce^{3+} ions. With increasing concentration of Ce^{3+} ions the peaks intensity of 340 nm peak increases and maximum intensity observed for 10 mole % of Ce^{3+} ion (table-1). This indicates that the $KMgSO_4Cl$ lattice more suitable for higher concentrations of Ce^{3+} ions. The PL emission spectra of $KMgSO_4Cl:Ce$ (10 mol%) phosphors show the Ce^{3+} emission at 327 and 340 nm due to $5d \rightarrow 4f$ transition of Ce^{3+} ion. The intensity of Ce^{3+} emission at 327 nm is less, as compared to that of 340 nm peak. The variation of PL emission intensity observed may be due to cross-relaxation between Ce^{3+} ions in case of heavy concentration of Ce^{3+} .

Table 1. Comparison between Ce doped $KZnSO_4Cl$ and $KMgSO_4Cl$ phosphors

Phosphors	Emission peak wavelength (nm) $\lambda_{ex} = 254$ nm	Relative Intensity (a.u.)
$KZnSO_4Cl: Ce 10\%$	327, 340	2441, 2441
$KZnSO_4Cl: Ce 5\%$	327, 340	1925, 1900
$KZnSO_4Cl: Ce 2\%$	327, 340	1350, 1250
$KZnSO_4Cl: Ce 1\%$	327, 340	1200, 1150
$KMgSO_4Cl: Ce 10\%$	340	3100
$KMgSO_4Cl: Ce 5\%$	327, 340	2150, 2100
$KMgSO_4Cl: Ce 2\%$	327, 340	2150, 2100
$KMgSO_4Cl: Ce 1\%$	347.6	1198

CONCLUSIONS

The synthesis of Ce^{3+} activated halosulphate phosphors prepared by wet chemical method. Table-2 shows the comparison between $KZnSO_4Cl: Ce$; $KMgSO_4Cl: Ce$; for 10 mole% higher concentration. From table it is clear that for the same concentration of various phosphors, $KMgSO_4Cl: Ce$ phosphor has highest intensity. However the PL emission spectra of above phosphors show Ce^{3+} emission at 327, 340 nm in $KZnSO_4Cl$; 340 nm in $KMgSO_4Cl$ due to $5d \rightarrow 4f$ transition of Ce^{3+} ion. Hence Ce^{3+} emission in above chlorosulphate-based phosphors may be useful for scintillation applications.

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