



PHOTOLUMINESCENCE STUDIES OF $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{RE}$ (RE=Ce, Tb and Cu)

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Abstract- Luminescent materials based on lanthanide phosphors have made outstanding progress in revolutionizing the display and lighting industry. The optical properties of rare-earth ion (RE^{2+} and RE^{3+}) ions are valuable when these ions are doped into host lattices. The electronic transitions taking place within the partially filled 4f shell, or involving the 4f and 5d shells, gives rise to the luminescence. In present study the preparation of $\text{Na}_6(\text{SO}_4)_2\text{ClF}$ doped with rare earth ions Tb, Ce and transition metal ion Cu by wet chemical method was described. All the compounds were prepared by wet chemical method as it requires very less instrumentation and less electrical power too. Under UV excitation (250nm) of $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Ce}^{3+}$ showed emission (359nm) in UV range. When $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Tb}^{3+}$ phosphor was excited at 379 nm, the emission spectrum showed intense bands at 490 nm (blue) and 546 nm (green). The peaks at 490, 546, can be attributed to $^5\text{D}_4\text{-}^7\text{F}_6$ and $^5\text{D}_4\text{-}^7\text{F}_5$ transitions, respectively. In Cu activated $\text{Na}_6(\text{SO}_4)_2\text{ClF}$ phosphor, the emission spectrum showed a dominant peak at 357 nm when excited at 252 nm.

Keywords- Phosphor, halosulphate, photoluminescence

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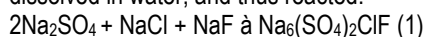
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Introduction

In the past centuries, once a new kind of light source with higher energy efficiency and lower power consumption was invented, like incandescent filament and fluorescent lamp, it would make a great difference in the human's life. In recent years, the studies on solid-state light sources, especially white light emitting diodes (w-LEDs), attracted increasing attention and became a hot issue in the energy saving, environment-friendly materials research [1]. The sulphates are an important mineral class and include some very interesting and attractive specimens. Although many minerals belong to this class only barite, gypsum, and anhydrite can be considered common. The basic chemical unit is the (AO_4) complex anion with a charge of negative two (2^-) [2]. Thakre et al reported $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{RE}$ (RE=Dy, Ce or Eu) by solid state method [3]. Moharil and co-workers reported some sulphate based materials such as $\text{KMgSO}_4\text{Cl}:\text{Eu}$; $\text{KMgSO}_4\text{Cl}:\text{Ce}$, $\text{Na}_5(\text{PO}_4)\text{SO}_4:\text{Ce}$, $\text{KZnSO}_4\text{Cl}:\text{Ce}$; $\text{NaMgSO}_4\text{F}:\text{Ce}$ and $\text{Na}_3\text{SO}_4\text{F}:\text{Ce}$ phosphors prepared by a wet chemical method have been studied for its photoluminescence (PL) and thermoluminescence (TL) characteristics [3,4].

Experimental

$\text{Na}_6(\text{SO}_4)_2\text{ClF}$ (pure), $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Ce}$, $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Cu}$, and $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Tb}$ phosphors were prepared by a wet chemical method. NaCl, Na_2SO_4 and NaF of analar grade were taken in a stoichiometric ratio and dissolved separately in single distilled de-ionized water, resulting in a solution of $\text{Na}_6(\text{SO}_4)_2\text{ClF}$ (Eq. (1)). Water soluble sulphate salts of cerium, copper and terbium were then added to the solution to obtain $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Ce}$, $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Cu}$, and $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Tb}$. confirming that no undissolved constituents were left behind and all the salts had completely dissolved in water, and thus reacted:



The compounds $\text{Na}_6(\text{SO}_4)_2\text{ClF}$ (pure), $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Ce}$, $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Cu}$, and $\text{Na}_6(\text{SO}_4)_2\text{ClF}:\text{Tb}$ in their powder form were obtained by evaporating at 80°C for 8 h. The dried samples were then slowly cooled to room temperature. The resultant polycrystalline mass was crushed to fine particles in a crucible. The powder was used in further study. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

Results

I] $\text{Na}_6(\text{SO}_4)_2\text{ClF:Ce}$ Figure 1.1 shows the excitation and 1.2 shows emission spectra of Ce doped $\text{Na}_6(\text{SO}_4)_2\text{ClF}$.

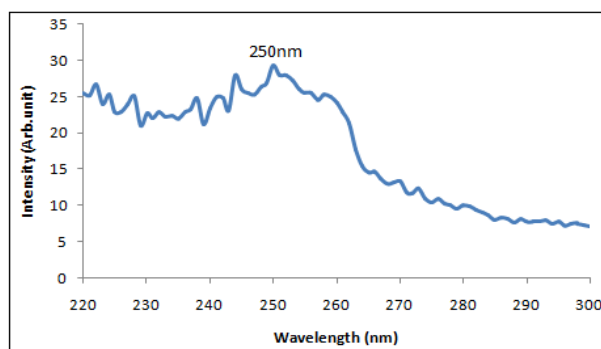


Fig. 1.1- Excitation spectra of $\text{Na}_6(\text{SO}_4)_2\text{ClF:Ce}$ monitored at 357nm emission wavelength.

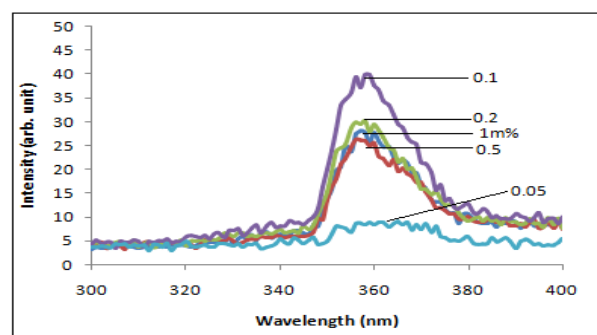


Fig. 1.2- Emission spectra of $\text{Na}_6(\text{SO}_4)_2\text{ClF:Ce}$ at 250nm excitation wavelength.

PL excitation spectra of $\text{Na}_6(\text{SO}_4)_2\text{ClF:Ce}^{3+}$ phosphor shows broadband is observed at 250 nm with $\lambda_{em} = 359$ nm. Fig. 1.2 show the PL emission spectra of Ce^{3+} ions in $\text{Na}_6(\text{SO}_4)_2\text{ClF}$ phosphors with different concentrations under excitation at 250 nm wavelength of light. Single peak is observed at 359nm, which are assigned to the 5d-4f transition of Ce^{3+} ions. With increasing concentration of Ce^{3+} ions, the peak intensity of 359 nm peak decreases and maximum intensity is observed for 0.1 mol% of Ce^{3+} ions. This indicates that the $\text{Na}_6(\text{SO}_4)_2\text{ClF}$ lattice is more suitable for lower concentrations of Ce^{3+} ions.

II] $\text{Na}_6(\text{SO}_4)_2\text{ClF:Cu}$

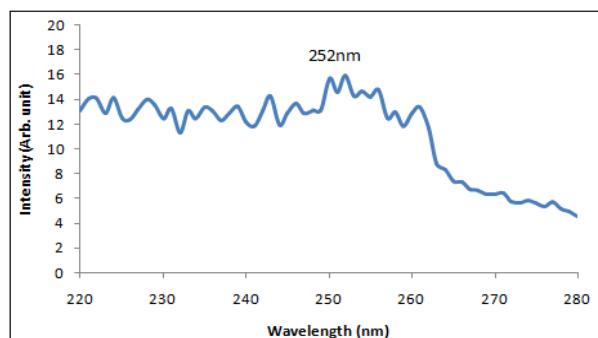


Fig. 2.1- Excitation spectra of $\text{Na}_6(\text{SO}_4)_2\text{ClF:Cu}$ monitored at 357nm emission wavelength.

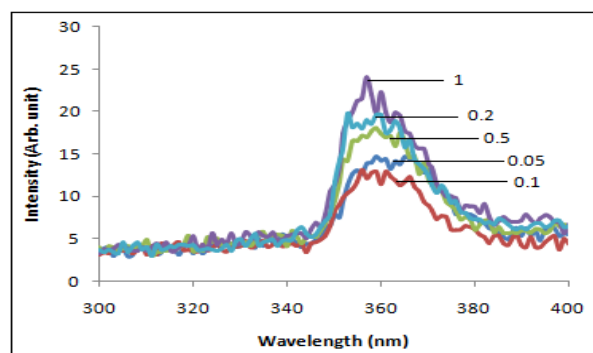


Fig. 2.2- Emission spectra of $\text{Na}_6(\text{SO}_4)_2\text{ClF:Cu}$ at 252nm excitation wavelength.

Emission and excitation spectra of Cu doped $\text{Na}_6(\text{SO}_4)_2\text{ClF}$ are shown in Fig.2.1& Fig.2.2. The excitation wavelength 252nm was used for recording spectra of the samples. The presence of intense emission at 357nm, which is a characteristic of Cu^+ ions, suggests the presence of Cu^+ emission centers in the phosphor [5].

III] $\text{Na}_6(\text{SO}_4)_2\text{ClF:Tb}$

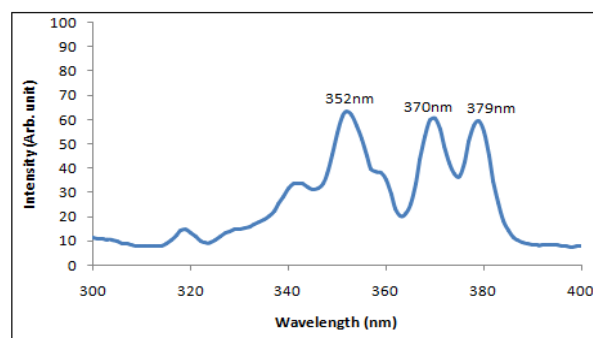


Fig. 3.1- Excitation spectra of $\text{Na}_6(\text{SO}_4)_2\text{ClF:Tb}$ monitored at 546nm emission wavelength.

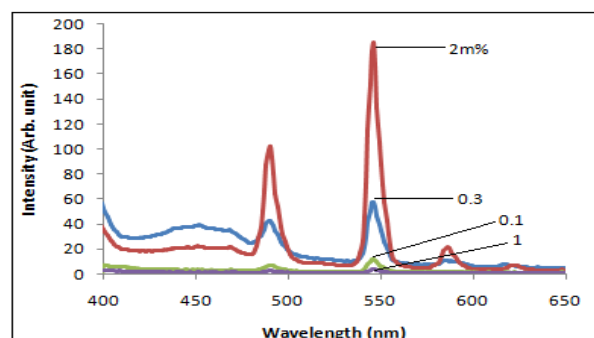


Fig. 3.2- Emission spectra of $\text{Na}_6(\text{SO}_4)_2\text{ClF:Tb}$ at 379nm excitation wavelength.

On exciting the phosphor with 379nm light, emission bands at 490nm, 546nm & 587nm were observed, Fig. 3.1 on exciting the Tb^{3+} doped $\text{Na}_6(\text{SO}_4)_2\text{ClF}$ phosphor at 379nm emission bands at 490nm and 546nm & 587nm have been observed. The emission is stronger under 379nm excitation than 254 nm excitation. Among these the intensity of 546nm emission band dominates over 490nm and 587nm. When $\text{Na}_6(\text{SO}_4)_2\text{ClF:Tb}^{3+}$ phosphor was excit-

ed at 379 nm, the emission spectrum showed intense bands at 490 nm (blue) and 546 nm (green). The peaks at 490, 546, can be attributed to $^5D_4-^7F_6$ and $^5D_4-^7F_5$ transitions, respectively [6].

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