CHAPTER SIX

Sensitised luminescence of SrS: Dy, Cu, Cl phosphor

6.1 Abstract

SrS:Dy,Cu,Cl phosphors for fixed Dy concentration and different Cu concentrations were prepared by solid state reaction method. Studies of the structural and optical properties of the samples were carried out. From the analysis of the photoluminescence measurements it was observed that, the excitation in the absorption bands of Cu$^+$ ion leads to transfer of energy to Dy$^{3+}$ ion thereby enhancing the intensity of its luminescence.

6.2 Introduction

More recently intensive research is going on in developing phosphors for use in light emitting devices such as electroluminescent (EL) devices, plasma display panels (PDP), and vacuum fluorescent displays (VFD). The increasing demand of phosphors for wide applications has created interest in the study of spectroscopic properties, defects and energy transfer processes in phosphors due to doping with different materials. Alkaline earth sulphide phosphors especially strontium sulphide is considered as a potential host for phosphor applications. SrS:Cu was first reported as a potential blue electroluminescent emitter by Kane et al. [1]. The two component SrS:Cu,Ag phosphor has been shown to exhibit an efficient blue colour, due
to the efficient energy transfer from Cu to Ag [2]. SrS:Dy based electroluminescent devices were found to give a yellow emission [3,4]. In SrS:Ce,Dy the emission intensity of Dy$^{3+}$ ion increases due to energy transfer from one activator to another [5]. Although considerable attention has been paid to the study of SrS phosphors activated with dysprosium or copper, very few or little quantitative data are available relating to the properties of two component SrS phosphors activated with copper and dysprosium. In this chapter the structural and luminescence properties of SrS:Cu,Dy,Cl phosphor are presented.

6.3 Experimental

The phosphor samples for the present study were prepared from starting materials, strontium sulphide, copper chloride (CuCl$_2$) and dysprosium chloride (DyCl$_3$) by solid state reaction. Required proportions of copper chloride and dysprosium chloride were mixed with strontium sulphide and 5wt. % of ammonium chloride in ethanol medium. The mixture, after drying in an oven, was fired in H$_2$S atmosphere at 850$^\circ$C for two hours. Different samples were prepared with different copper concentrations (0.01 at. % to 0.2 at. %) for the same dysprosium (0.25 at.%) concentration. The structural and optical characterizations of these samples were then performed. The crystal structures of the synthesized phosphors were studied using a Rigaku X-ray diffractometer with Cu K$\alpha$ x-ray. The PL and PLE spectra were recorded with Jobin Yvon Fluoromax-3 Flourimeter. The absorption spectra of the samples were recorded with Jasco-V-570 uv-vis-nir spectrophotometer.
6.4 Results and discussion

The crystallinity, lattice strain and crystallite size of the samples were analyzed from the X-ray diffraction patterns. Spectra of all the samples closely matched the JCPDS file no.8-489 for cubic SrS without any traces of impurities (Figure 6.1). Copper and dysprosium enters and replaces Sr$^{2+}$ ion in the SrS lattice as Cu$^{+}$ and Dy$^{3+}$ ions. The ionic radii of Sr$^{2+}$, Cu$^{+}$, and Dy$^{3+}$ are 1.12Å, 0.77Å and 1.05Å respectively.

Discrepancies between the activator ion and the host cation lead to lattice strain induced defects, poor crystallinity, and device stability problems. The grain size and lattice strain of the different samples were evaluated from the graph between $B_r \cos \theta$ and $\sin \theta$ where $B_r$ is the full width at half maximum values in radians of X-ray diffraction peaks and $\theta$ is the diffraction angle[6]. The lattice parameter of the samples were calculated using the formula $a = \lambda (h^2 + k^2 + l^2)^{1/2}/2 \sin \theta$, where $\lambda$ is the x-ray wavelength; $h$, $k$ and $l$ are the Miller indices and $\theta$ is the Bragg angle. These values are tabulated in table 6.1. The strain in the SrS host lattice increase with doping concentration of Cu whereas the lattice parameter and grain size show a random variation.

The absorption spectra of SrS:Cu,Dy (0.25at.%) for three different Cu concentrations are shown in figure 6.2. The absorption spectra of two different ions concurrently present in a crystal are simply a superposition of each of their absorption spectra.
Figure 6.1. X-ray diffraction pattern of SrS: Dy, Cu, Cl phosphor.

Table 6.1. Table illustrating the lattice parameter, grain size and lattice strain of different SrS: Cu, Dy, Cl samples.

<table>
<thead>
<tr>
<th>Copper doping concentration (at.%)</th>
<th>Lattice parameter (nm)</th>
<th>Grain size (nm)</th>
<th>Lattice strain ($\times 10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy = 0.25 at.%</td>
<td>0.6066</td>
<td>28.5</td>
<td>1.25</td>
</tr>
<tr>
<td>0.01</td>
<td>0.6054</td>
<td>29.34</td>
<td>1.28</td>
</tr>
<tr>
<td>0.05</td>
<td>0.604</td>
<td>26</td>
<td>1.95</td>
</tr>
<tr>
<td>0.1</td>
<td>0.6067</td>
<td>37.2</td>
<td>2.37</td>
</tr>
<tr>
<td>0.15</td>
<td>0.605</td>
<td>33.12</td>
<td>2.85</td>
</tr>
</tbody>
</table>
Three absorption peaks around 260nm, 280nm and 320nm are observed. 260nm peak corresponds to absorption in the host lattice, whereas 280nm and 320nm peaks correspond to intracenter absorption in Cu\(^{+}\) levels in octahedral crystal field. In the sample with least doping concentration of Cu (0.01at.%), absorption at 280nm is absent and host lattice absorption has maximum intensity. The high energy absorption in Cu\(^{+}\) at 280nm appears for a doping concentration of 0.05at.% and it has maximum intensity of the three absorption peaks. On increasing Cu doping further, the absorption at 320nm dominates.

![Absorption spectra of SrS: Dy,Cu, Cl phosphor samples](image)

Figure 6.2. Absorption spectra of SrS: Dy,Cu, Cl phosphor samples for Dy concentration=0.25at.% and various Cu concentrations (a). 0.01at.% (b). 0.05at.% and (c). 0.2at.%

In the emission spectra of phosphor with two activators, either the position of emission lines of each of them does not change in the presence of the other, i.e., superposition of emission spectra from two ions occur, or the
luminescence spectrum intensity of one ion gain in strength at the expense of the diminishing intensity of the other.

\[ S^* \rightarrow A^* \]

Here \( S \) is the sensitizor (energy donor); \( A \) is the activator (energy acceptor); asterisks denote their excited states.

These changes in luminescence from one ion in the presence of the other are due to transfer of excitation energy from one to the other. Luminescence of ions excited as a result of the energy transfer from other ions excited in the absorption band is termed sensitized luminescence.

The transfer of energy from sensitizer to activator is accomplished through the following three main types of transfer - (1) emission - reabsorption, (2) resonance radiationless and (3) the nonresonance radiationless. The resonance radiationless mechanism of energy transfer is effected between interacting ions behaving like a single system. A condition necessary for this mechanism of transfer to show itself is coincidence or a close distance between energy level pairs of the ion sensitizer and the ion activator. Sensitization can be accomplished with the help of admixture ions (impurity sensitization), or with the aid of ions entering the composition of the crystal itself (lattice sensitization). Since trivalent rare earth (\( \text{RE}^{3+} \)) activators are...
devoid of intense absorption bands, impurity sensitization is of greatest importance [7].

Cu\(^+\) ion have strong absorption bands in the UV region and display emission bands in the near-neighboring UV and visible region. In SrS:Dy,Cu,Cl phosphor energy transfer is by resonance radiationless mechanism where Dy\(^{3+}\) plays the role of activator and Cu\(^+\) that of sensitizer. Excitation in the absorption bands of Cu\(^+\) ions leads to transfer of energy to Dy\(^{3+}\) ion. Figure 6.3 demonstrates the sensitizing behaviour of Cu\(^+\) in SrS:Cu,Dy,Cl phosphor.

Figure 6.3. PL spectra of (a) SrS:Dy (0.25at.%) Cl phosphor. \(\lambda_{ex}=274\) nm, (b) SrS:Cu (0.2at.%) Cl phosphor. \(\lambda_{ex}=280\) nm and (c) SrS:Dy (0.25at.%) Cu (0.2at.%), Cl phosphor. \(\lambda_{ex}=280\) nm.
In figure 6.3, (a) represents the PL spectrum of SrS activated with Dy at an excitation wavelength of 274 nm. Dy$^{3+}$ luminescent centre is excited via the energy transfer from the host matrix and the two main luminescence peaks are at 486nm and 581nm ($^{4}F_{9/2} \rightarrow ^{6}H_{15/2}$ and $^{6}H_{13/2}$) [8]. The resultant of PL emission from the sample was yellow with chromaticity coordinates $x=0.40$, $y=0.42$. Figure 6.3.(b) is the PL spectrum of copper activated strontium sulphide phosphor. The excitation was given at 280nm which is one of the intracenter excitation ($^{1}A_{1g} \rightarrow ^{1}T_{2g}$) in Cu$^{+}$ ion in octahedral crystal field [9]. The broad emission obtained was blue in colour peaking at 471 nm. Blue luminescence in SrS:Cu is produced by [Cu$^{+}_{Sr}$] centers with coordination number 6 whereas [Cu$^{+}_{Sr}$] centers with coordination number 5 give rise to green luminescence [10]. In SrS:Dy,Cu,Cl phosphor also excitation is through the Cu$^{+}$ center at 280nm and 320nm. But the luminescence from this two component phosphor is not just a superposition of emissions from Cu$^{+}$ and Dy$^{3+}$ centers.

In the SrS:Dy,Cu,Cl two component phosphor the intensity of blue emission in Cu$^{+}$ center at 471nm was $(1/30)^{th}$ of it's value for the sample doped with same concentration of copper alone. But the intensity of emission lines at 486 nm and 581nm from Dy$^{3+}$ became 8 times and twice respectively on codoping with copper. The resultant emission is bluish white with chromaticity coordinates $x=0.19$ and $y=0.27$. Figure 6.4 demonstrates the resonance radiationless mechanism of energy transfer from Cu$^{+}$ to Dy$^{3+}$. The energy transfer from Cu$^{+}$ to Dy$^{3+}$ does not proceed directly from the absorption band ($^{1}T_{2g}$ and $^{1}E_{g}$) of Cu$^{+}$, but there first occurs a rapid radiationless transition to $^{3}E_{g}$ and only from this the energy is transferred to $^{4}F_{9/2}$ of Dy$^{3+}$. 
Figure 6.4. Resonance radiationless transfer of energy from Cu\(^{2+}\) to Dy\(^{3+}\). 1 denotes excitation in Cu\(^{2+}\) absorption bands; 2- radiationless transitions in Cu\(^{2+}\) ion; 3-normal Cu\(^{2+}\) ion luminescence; 4-energy transfer from Cu\(^{2+}\) to Dy\(^{3+}\); 5-radiationless transition in Dy\(^{3+}\) ion; and 6-sensitized luminescence of Dy\(^{3+}\).

Photoluminescence excitation spectra of three samples are shown in figure 6.5 for comparison. Spectrum (a) peaking at 274nm is the PLE spectrum of Dy doped sample. It corresponds to near band edge absorption in host lattice. Spectrum (b) demonstrates the excitation in SrS:Dy,Cu,Cl sensitised phosphor and (c) that in copper doped SrS. The two bands located at 284nm and 320nm in (c) are due to the transitions \(^1A_{1g} \rightarrow ^1T_{2g}\) and \(^1A_{1g} \rightarrow ^1E_g\) in Cu\(^{2+}\)[11]. In (c) these bands undergo a slight shift towards lower energy.
This may be due to the presence of additional impurity (Dy$^{3+}$) which change the crystal field and hence the separation between $^1A_{1g}$, $^1T_{2g}$ and $^1E_g$ levels of Cu$^+$.

The photoluminescence from SrS:Dy,Cu,Cl phosphor for various concentrations of Cu (0.01at.%, 0.05at.%, 0.1at.%, 0.15at.% and 0.2at.%) keeping the concentration of Dy at 0.25at.% were also studied. One broad blue emission at 471nm due to Cu$^-$ and another blue emission at 486nm due to Dy$^{3+}$ were observed. The yellow emission line was at 581nm with a shoulder peak at 574 nm. The resultant emission was found to vary from bluish white to white which is demonstrated by CIE chromaticity.
diagram (Fig. 6.6). For 0.01at.% doping of Cu the luminescence of the sensitised phosphor was white with chromaticity coordinates $x = 0.37$ and $y = 0.37$.

![CIE chromaticity diagram](image)

Figure 6.6. CIE chromaticity diagram for SrS:Dy,Cu,Cl sensitised phosphor samples with Dy concentration 0.25at.% and various Cu concentrations.

1. 0.05at.%,
2. 0.1at. %,
3. 0.15at. % and 0.2at. % and
4. 0.01at. %.

6.5 Conclusion

A model is proposed demonstrating the sensitizing behaviour of Cu$^+$ ion in SrS:Dy,Cu,Cl phosphor. Energy is transferred from $^3E_g$ of Cu$^+$ to $^4F_{9/2}$ of Dy$^{3+}$. Resultant emission colour from the samples vary with the variation in doping concentration of Cu.
6.6 References

1. J.Kane, W.Harty, M.Ling, P.N. Yocom, SID’85 Digest, SID, Santa Ana 1985, 163