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Original Research Article

Effects of doping on photoluminescence excitation and emission spectra of SrS: Cu, Cl phosphor

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ABSTRACT

Cu,Cl phosphors are produced using a solid state process to produce stoichiometric SrS. The samples' copper doping concentrations range from 0.1 mol% to 2.5 mol%. Researchers are looking at how doping affects the PLE and PL spectra of photoluminescence. With the emission wavelength of 0.473 μm , the copper doped SrS phosphor displays excitation maxima at 0.315 μm and 0.284 μm . A sample doped with 0.2 mol% of Cu exhibits the highest PL emission intensity. With an enhancement in copper content to 2.5 mol% at the excited wavelength 0.3 μm , it is discovered that the emission wavelength shifts from 0.470 μm to 0.520 μm . This is due to the development of isolated off-centered sites and copper couples.

1. Introduction

There are several methods reported for producing brilliant and effective primary colour phosphors, but sulphide phosphors receive special attention because of their significance for thin-film electroluminescence. Strontium sulphide (SrS:Cu) with copper as a dopant has been firstly described as the possible bluish electroluminescence emitter [1]. Alkali metal ions cause an emission of SrS:Cu to change the bluish to the greenish regime [2] of visible light of the electromagnetic spectrum. The luminescent process is not well understood, and the observed SrS:Cu emission possess a single or multiple wide bands with emission colours ranging from the bluish to the greenish [3-7] of visible light of electromagnetic spectrum. In this study, we investigated the photoluminescence of SrS:Cu, Cl phosphors with a range of copper concentrations, and we saw a red shift in the PL when a doping level is enhanced from 0.1% to 2.5 mol%.

2. Experiment

CuCl_2 and powdered SrS were mixed to create SrS:Cu. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99.889%, Alderich) and SrS (99.98%, α -Asear) are high purity compounds that were employed for this. These extremely pure precursors were precisely weighed in the required ratios and properly blended in an ethanol medium. The powder is then dried for two hours in an oven at 55°C. Following thorough grinding in an agate, the powder is burned for 1h at 890°C in the hydrogen sulfide environment. The samples' photoluminescence (PL) emission spectra were captured using a 200 watt xenon flashed light and a Spex-Fluoromax-2 fluorimeter.

3. Results and discussion

The produced samples with various Cu concentrations had their photoluminescent emission (PL) and photoluminescent excitation (PLE) spectra recorded at room temperature. Figures 1 and 2 show the PL emission and excited spectrum of SrS:Cu,Cl phosphor at various Cu levels. When the emitted wavelength is 0.473 μm , the excited spectrum of our sample, viz. SrS:Cu,Cl powder phosphor show two maxima at 0.284 μm and 0.315 μm . The excitation peaks did not significantly vary in relation to the Cu content. With an enhancement in copper concentration with the excited wavelength of 0.310 μm , this is discovered that an emission wavelength shifts from 0.470 μm to 0.520 μm . The peak emission wavelength's relationship to Cu concentration is depicted in Figure 3. With increasing doping concentration, PL emission intensity rises to a maximum at 0.2 mol% (Figures 1 and 4).

The following explanation explains how the emission colour changes as a function of Cu concentration. An effective blue-emitting sulphide phosphor is SrS:Cu. Nevertheless, SrS:Cu powders and films have been found to emit blue and green light. At room temperature, the green as well as the blue emissions occur, whereas green emission has always been present at lower temperatures [8]. The precise nature of the emission centres in SrS:Cu phosphors, however, is unclear.

The copper (+2) ions have been decreased in number in the presence of H_2S atmosphere into the copper (+1) ions and their diffusion occurs in SrS sites during fire at moderately high temperatures and in an H_2S environment. In the SrS



lattice, the copper (+1) ions have been intended to substitute the Sr^{2+} ions at the octahedral locations [9].

Figure 5 depicts the energy levels of free copper (+1) ions and the copper (+1) ions into the octahedral sites. The bands (with maxima at 0.283 μm and 0.310 μm) are visible in the excitation spectra of SrS:Cu, Cl (Cu - 0.1 to 2.5 mol%) phosphors and are attributed to transition between the following energy levels: $3d^{10} [^1A_{1g}] \rightarrow 4s^1, 3d^9 [^1T_{2g}, ^1E_g]$ inside the isolated copper (+1) ions. In copper (+1) ions, the transition: $3d^{10} [^1S_0] \rightarrow 4s, 3d^9 [^1D_2, ^3D_{3,2,1}]$ is parity and J. prohibited but relaxed in a disturbed crystal field. The transitions $4s^1, 3d^9 [^3E_g] \rightarrow 3d^{10} [^1A_{1g}]$ has been implicated in the emission process [10].

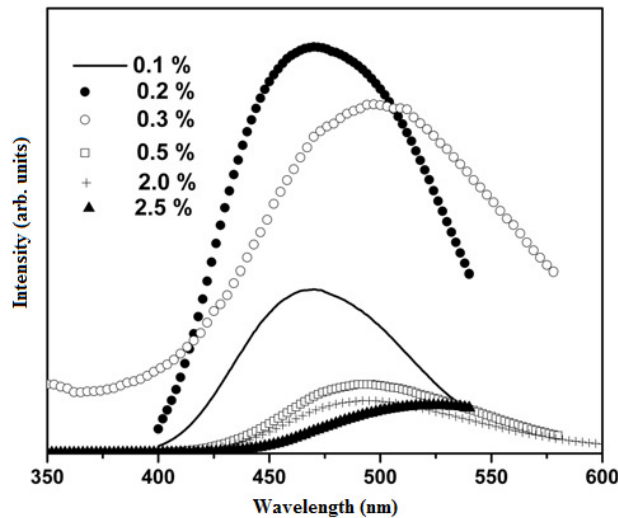


Figure 1: PL emission spectra of SrS:Cu, Cl phosphors at various copper dopings, $\lambda_{\text{ex}} = 0.310 \mu\text{m}$.

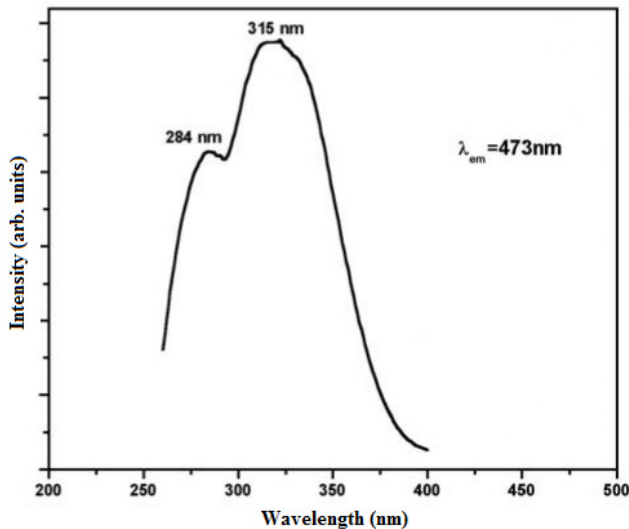


Figure 2: PL excitation spectrum of SrS:Cu, Cl phosphors for 0.2 mol.% Cu, $\lambda_{\text{em}} = 0.473 \mu\text{m}$.

The temperature, co-dopants, and Cu concentration all affect the Cu^+ luminescence's emission wavelength in SrS:Cu [4]. The $[\text{Cu}^+\text{Sr}]^-$ centres with coordination number six in SrS:Cu are responsible for producing the colour blue. The concentration of sulphur (-2) ions nearest to the copper (+1) ion is referred to as the coordination number. The fifth

coordination indicates the presence of sulphur vacancies close to $[\text{Cu}^+\text{Sr}]^-$ centre, thereby reducing the regularity of the copper (+1) ion centre and results in the production of green luminescence. The concentration of $[\text{Cu}^+\text{Sr}]^-$ centres having a coordination number six would be raised in comparison to concentration of $[\text{Cu}^+\text{Sr}]^-$ centres having a coordination number five, so as to enhance a blue colour contrast of the SrS:Cu phosphors. If the copper (+1) ion is in a tetrahedral configuration that is off-center and is coordinated by four sulphur atoms, blue emission is also seen [11]. We anticipate green emission at room temperature since sulphur vacancy is unavoidable to make up for charge imbalance.

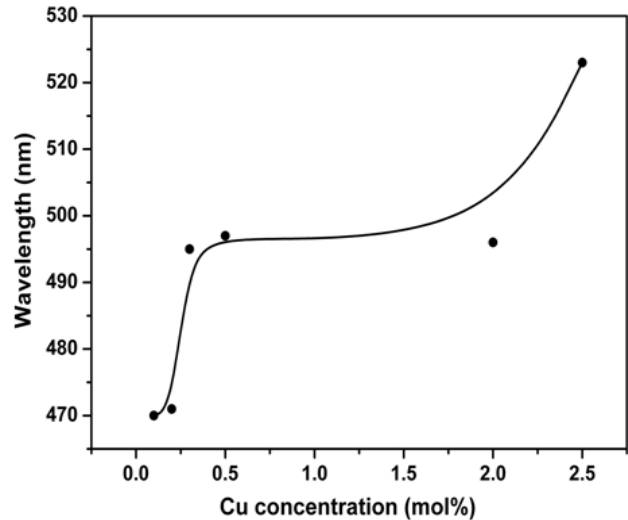


Figure 3: Variation of PL emission peak wavelength with concentration of Cu in SrS:Cu, Cl .

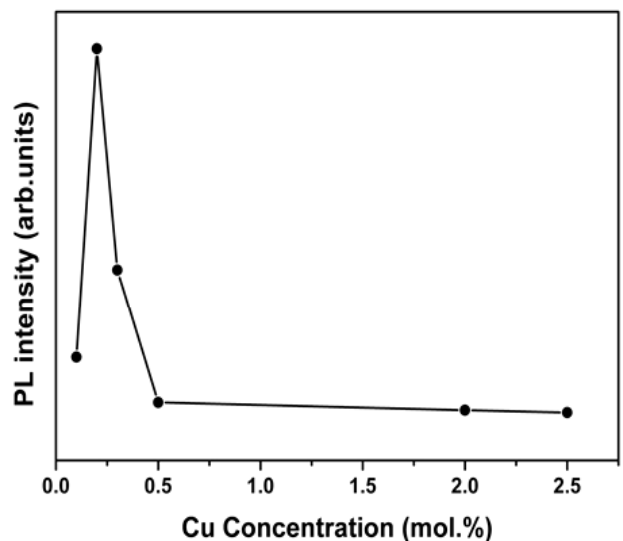


Figure 4: Variation of PL emission intensity with concentration of Cu in SrS:Cu, Cl .

Copper (+1) ions are not as much of to be expected to put back Sr^{2+} because their ionic radius (0.77 \AA vs. 1.18 \AA) is significantly lower. Hence, there are more off-centered Cu^+ ions present (often in larger quantities), which will result in green emission.

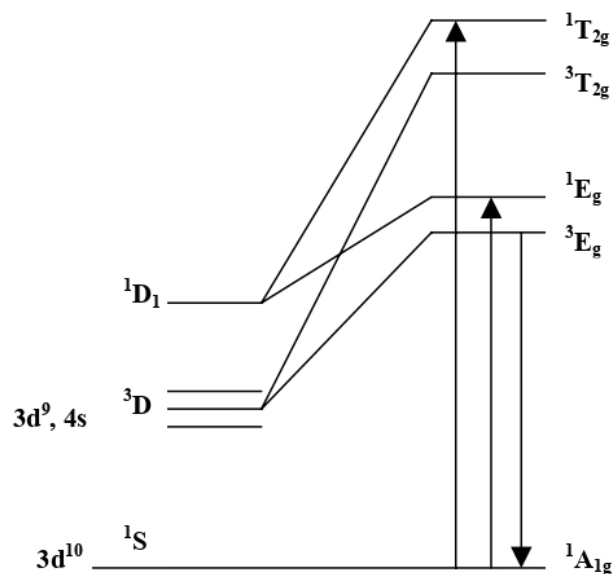


Figure 5: Schematic representation of the energy levels of free copper (+1) ions and the copper (+1) ions into the octahedral sites.

In the current investigation, a PL emission peak at 0.470 μm is seen at lower concentrations. This suggests that the chlorine ion is absorbed into the SrS:Cu phosphor as the substitute donor on sulphur lattice positions, hence lowering sulphur vacancies. SrS:Cu,Cl phosphors are externally reimburse as a result of the inclusion of chlorine ions, either completely removing or at the minimum significantly limiting self-compensating phenomenon. There are more six coordinated kind $\text{Cu}^+\text{-Cl}^-$ complexes that emit blue light than green light due to the extrinsic compensation's dramatic reduction of sulphur vacancies.

As the concentration rises, the colour of the PL emission turns green. This is explained by the development of isolated off-centered sites and copper couples [4]. We can anticipate Cu^+ entering SrS both interstitially and substitutionally at higher concentrations, which will neutralise the impact of Cl^- on the lattice. We anticipate a steady shifting of emission maxima towards the higher wavelengths on enhancing the doping levels as a result of higher disturbance if the Cu^+ ion is in the interstitial location.

According to the finding that PL intensity is maximum at 0.2 mol% (Figure 4), there is a critical concentration of copper for which copper (+1) ions begin to scatter evenly into the SrS crystal upon burning in an H_2S atmosphere. The creation of coupled Cu^+ ions is assumed to be the reason for the decrease in aggregate PL intensity that has been noted [2, 6]. This decrease in PL strength was caused by an additional rise in the amount of copper in SrS:Cu,Cl.

4. Conclusions

SrS and CuCl_2 powders were used in a solid state process to create green and blue emitted SrS:Cu,Cl phosphor. Copper concentrations ranging from 0.1% to 2.5% were used to create the samples. The photoluminescent emission spectra of doped samples display red shift (0.520 μm for 2.5 mol%) when the concentration of the substance is raised from 0.1 mol% to 2.5 mol% at the surrounding temperature, and blue fluorescence at modest concentrations (0.468 μm for 0.1 mol%). It was discovered that the Cu content affected the PL emission intensity. The sample with 0.2 mol% copper had the highest intensity. Peaks at 0.283 μm and 0.310 μm may be observed in the photo-luminescent excitation spectrum of all samples, respectively.

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