# Various Cu<sup>+</sup>, Mg<sup>2+</sup> and S<sup>2-</sup> ionic concentration effects on a novel Cu<sub>2</sub>ZnMgS<sub>4</sub> quaternary compound synthesis for various scientific applications

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Copper zinc magnesium sulfide semiconducting material (Cu<sub>2</sub>ZnMgS<sub>4</sub>) compound is slightly new in electronics, opto-electronics and photo emissive field research. So that, we examined the Cu<sub>2</sub>ZnMgS<sub>4</sub> compound formation characteristics step by step using the Copper sulfate (CuSO<sub>4</sub>.XH<sub>2</sub>O), Zinc sulfate (ZnSO<sub>4</sub>.XH<sub>2</sub>O), Magnesium sulfate (MgSO<sub>4</sub>.XH<sub>2</sub>O) and Sodium sulfide Na<sub>2</sub>S salt solutions. Characterizations such as pH, Electrical conductivity (EC), TDS were carried out for several concentrations. Further its optics properties of Cu<sub>2</sub>ZnMgS<sub>4</sub> compound in liquid form were investigated through photo-colorimeter measurements (at various color  $\lambda$  including mixed band wavelengths), photo-fluorometer (using various primary and secondary filters) and UV-Vis spectrophotometer (at wavelength range of 300 to 900 nm) measurements. The investigated long term results are presented and discussed in this research article.

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### **1. Introduction**

Copper sulfide nanostructures synthesis and its biological applications more recently reported by Noor ul Ain et al. [1]. Nanotechnology applied in many fields including cancer treatment. Nano technology applications cover many medical applications such as drug delivery, bio-imaging and the therapeutic nature of nanomaterials. Nano-medicines reached better approach for diagnosing and treating cancer owing to its enhanced efficiency [2-4].  $Cu_xS_y$  material nanostructures are promising materials for both sensors and bio medical imaging applications. The major use of  $Cu_xS_y$  nano particles is not just limited to cancer curing applications but they can also be used for the treatment of many other in vitro antibacterial diseases owing to their versatility and multifunctional properties including more holes concentration photo conducting activity [5]. With the rapid development of various energy technologies, electric energy production and its storage has become the protagonist of the energy era [6]. More and more high-efficient and environment friendly new energy production sources and energy-storage devices are needed to meet the present day field requirements.

Super capacitors with dominant properties such as high-power density, a long cycle life, and a fast-charging capacity have attracted much attention of electrochemical researchers and materials science researchers in recent years. In this regard the effect of copper sulfide stoichiometric coefficient and morphology on electrochemical performance was reported most recently. In this reported research article, CuS, Cu<sub>7</sub>S<sub>4</sub>, Cu<sub>9</sub>S<sub>5</sub>, Cu<sub>7.2</sub>S<sub>4</sub>, and Cu<sub>2</sub>S with the same morphology were successfully synthesized by the hydrothermal method. This report showed that the energy storage capacity of copper sulfide with the same morphology increased with respect to the increase of the copper sulfide stoichiometric coefficient [7-9]. Further the preparation of nano-

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copper sulfide and its adsorption properties for  $17\alpha$ -ethynyl estradiol was reported in year 2020. In this research work, the tubular like nano-copper sulfide structures was synthesized by hydrothermal method. The synthesized copper sulfide materials were used as an adsorbent for  $17\alpha$ -ethynyl estradiol (EE2) and exhibited very excellent adsorption properties [10].

Peter A. Ajibade and Nandipha L. Botha reported the synthesis, optical and structural properties of copper sulfide nanocrystals from single molecule precursors and the obtained optical studies showed that the absorption spectra of the as-prepared nanoparticles are blue-shifted and the emission maxima showed a narrower size distribution, which indicates a size quantum effect. The X-ray diffraction patterns showed the hexagonal morphology CuS nanocrystals with estimated particle sizes of 17.3–18.6 nm. Further the TEM images showed the CuS nanoparticles has spherical in shape and fairly mono dispersed which exhibited the average crystallite sizes of 3–9.8 nm. Both X-ray diffraction studies and TEM results showed relatively similar nano particle size [11].

The synthesis and studies on metal chalcogenide materials have received considerable attention in the last decades due to quantum confinement effects associated with their confined crystallites sizes. This quantum confinement showed many novel physical, chemical and physic-chemical properties that make them useful in light-emitting p-n junction diodes, p-n junction solar cells, fuel cells, drug delivery, and used for catalysts in industrial transformations [12–27]. Further the group 12 chalcogenide materials such as  $Z_nS$  and  $C_dS$  nanoparticles have been widely studied but  $C_dS$  toxicity limits some further possible applications. As of result of the inherent toxicity of group 12 metal chalcogenides, copper sulfide nanocrystals are being explored for different applications. CuS nanoparticles are also attractive because they exist in different stoichiometric compositions and its corresponding applications with varying its crystalline phases.

Copper sulfide nanoparticles were successfully synthesized on the base of functionalized nitrile butadiene rubber (FNBR) at room temperature by the successive ionic layer adsorption and reaction (SILAR) method using  $CuSO_4 \times 5H_2O$ ,  $CuCl_2 \times 2H_2O$  aqueous solutions as a copper precursors;  $Na_2S \times 9H_2O$  and thiourea  $[CS(NH_2)_2]$  aqueous solutions as sulfur precursors. Synthesis and characterization of  $Cu_{2-x}S$  structures by different chemical routes for electronic applications explained by João Lima et al. [28-29]. Synthesis and characterization of copper zinc iron sulphide (CZFS) thin films were reported by Joseph Onyeka Emegha et al. [30]. Synthesis and characterization of copper zinc sulfide ( $cu_xzn_{1-x}S$ ) ternary thin film by using acidic chemical bath deposition method was reported in recent research article [31].

Quarternary selenide and sulfide based compounds played a very important role in optoelctronics and electronics filed. Among this copper indium gallium diselenide (CIGS) is one of the important direct band gap I-III-VI<sub>2</sub> thin film absorber material composed of copper, indium, gallium, and selenium. Band gap of the CIGS thin film can modified from 1.1 to 1.6 eV by tuning the gallium and Indium composition. Very high energy conversion efficiency of CuInGaSe<sub>2</sub> (CIGS) solar cell devices has been largely issued for the last decades. The CIGS devices have proved superior laboratory scale photo power conversion efficiency (PCE) over 18% and a successful installation of plant scale level with megawatt power conversion for the past decades. In our previous research article we reported the surface and optical properties of Cu<sub>2</sub>InGaSe<sub>2</sub> thin film absorber layer for high efficiency solar cells [32-41]. In the present research article we did a long term and real time research on various Cu<sup>+</sup>, Mg<sup>2+</sup> and S<sup>2-</sup> ionic concentration effects on a novel Cu<sub>2</sub>ZnMgS<sub>4</sub> quaternary compound synthesis for various scientific applications. Few hundred real time reactions conducted over many years and the real time measured results are presented and discussed.

### 2. Experiment

For this experiment CuSO<sub>4</sub>.XH<sub>2</sub>O (0.1 M), ZnSO<sub>4</sub>.XH<sub>2</sub>O (0.1 M), MgSO<sub>4</sub>.XH<sub>2</sub>O (0.1 M) positive (+ ionic) elements concentrations and Na<sub>2</sub>S (0.1 M) negative (- ionic) elements concentrations were kept constant for all of our present research work. For each experiment this 0.1 M each salt solution taken in a small size micro filler and gentle drop wise added in reaction bath with constant pressure to maintain each drop almost constant. Characterizations such as pH,

electrical conductivity (EC), TDS were carried out for several concentrations. Digital pH meters measurements were taken from two various instrumentations for getting perfect result and precise calibration. Further three standard pH buffers (i) pH buffer 4.00, (ii) pH buffer 6.86 and (iii) pH buffer 9.18 were used sequentially during each sample measurement.

After each measurement the both pH meter and EC meters cleaned by distilled water, alcohol and then gentle cleaned by wet filter sheet. To avoid contamination related instrumental measurement error, both meters kept in distilled water for 1 minute after each measurement completed. Even TDS measurement is a base basic measurement here we also used TDS meter measurements to compare the EC value difference and on the other hand TDS value simultaneous variation. UV-Vis transmittance measurements were taken for all the material compound concentrations at real time in the wavelength range of 300nm – 950 nm. Further its optics properties of Cu<sub>2</sub>ZnMgS<sub>4</sub>during compound formation in liquid form and liquid state to solid form conversion were investigated through photo-colorimeter measurements (at various color  $\lambda$  including mixed band wavelengths).Photo luminescence properties of each Cu<sub>2</sub>ZnMgS<sub>4</sub> compound formation concentrations real time investigated by digital photo-fluorometer (2 primary filters 5840 A<sup>0</sup> and 5113 A<sup>0</sup> and three secondary filters used) instrumentation.

### 3. Results and discussion

Actually real time measurement mostly not done much in worldwide materials science and engineering filed. Because it is directly contaminate and spoil the measurement instrument system. Due to this reason most of research work measurements conducted after material compound fabrication. In this research article we reported our several years long term and real time systematic investigated interesting results on Cu<sub>2</sub>ZnMgS<sub>4</sub> compound. Real time measurement most advantages are (1) we can get liquid state property, (2) (liqid + solid) or colloidal state property and finally (3) solid state compound property at one instant within few minutes time interval.

### 3.1. Various sodium sulfide (Na<sub>2</sub>S) concentrations (pH, TDS and EC value)

Figure 1 (a, b, c) showed the pH value, TDS value and Electrical conductivity (EC) real time measured values of Cu<sub>2</sub>ZnMgS<sub>4</sub> compound. Here CuSO<sub>4</sub>.XH<sub>2</sub>O (1-drop), ZnSO<sub>4</sub>.XH<sub>2</sub>O (1-drop), MgSO<sub>4</sub>.XH<sub>2</sub>O (1-drop) positive (+ ionic) elements concentrations were kept constant and only Na<sub>2</sub>S negative (- ionic) elements concentrations varied from 1-drop to 4-drops. This real time measurement showed both pH, EC and TDS values showed similar increasing trend.

The pH values suddenly vary from pH-3.6 to pH-5.1 with respect to Na<sub>2</sub>S negative (ionic) elements concentrations increment. In case of TDS and EC measurement value Na<sub>2</sub>S 1-drop to 2-drops not much change observed. But Na<sub>2</sub>S 3-drop to 4-drops during Cu<sub>2</sub>ZnMgS<sub>4</sub> compound formation showed drastically increased TDS value because TDS value changed from 430 ppm to 450 ppm and 450 ppm to 480 ppm. Further Na<sub>2</sub>S 3-drop to 4-drops during Cu<sub>2</sub>ZnMgS<sub>4</sub> compound formation showed drastically increased EC value because electrical conductivity value changed from 860  $\mu$ s/cm - 900  $\mu$ s/cm and 900  $\mu$ s/cm - 960  $\mu$ s/cm.



Fig. 1 (a, b, c) The pH value, TDS value and Electrical Conductivity (EC) real time measured values during Cu<sub>2</sub>ZnMgS<sub>4</sub> compound formation (Various Na<sub>2</sub>S concentrations).

## **3.2.** Various magnesium sulphate (MgSO<sub>4</sub>.XH<sub>2</sub>O) concentrations (pH, TDS and EC value)

Figure 2 ( $a_1$ ,  $a_2$ ,  $a_3$ ) showed the pH value, TDS value and electrical conductivity (EC) real time measured values of Cu<sub>2</sub>ZnMgS<sub>4</sub>compound formation. Here CuSO<sub>4</sub>.XH<sub>2</sub>O (1-drop), ZnSO<sub>4</sub>.XH<sub>2</sub>O (1- drop) positive (+ ionic) elements, Na<sub>2</sub>S (3-drop) negative ionic element concentrations were kept constant and only MgSO<sub>4</sub>.XH<sub>2</sub>Opositive (+ ionic) elements concentrations varied from 1-drop to 10-drops. This real time measurement showed both EC and TDS values showed similar increasing trend. But pH value showed opposite decreasing trend.

The pH values suddenly decreased from pH-4.1 to pH-3.93 with respect to MgSO<sub>4</sub>.XH<sub>2</sub>O positive (+ ionic) elements concentrations increment from 1-drop to 9-drops and at 10-drops again pH value started to increase. In case of TDS measurement value MgSO<sub>4</sub>.XH<sub>2</sub>O 1-drop to 10-drops drastic change observed. The TDS value reached from 400 ppm – 1400 ppm. During Cu<sub>2</sub>ZnMgS<sub>4</sub> compound formation EC value also showed drasticchange because electrical conductivity value changed from 750  $\mu$ s/cm - 2700  $\mu$ s/cm. Even within few drops MgSO<sub>4</sub>.XH<sub>2</sub>O change showed this much variation in EC and TDS value and we hope this is one of a most important result observation for future researchers.

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Fig. 2. (a1, a2, a3) The pH value, TDS value and Electrical Conductivity (EC) real time measured values during Cu<sub>2</sub>ZnMgS<sub>4</sub> compound formation (Various MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations).

#### 3.3. Various copper sulphate (CuSO<sub>4</sub>.XH<sub>2</sub>O) concentrations (pH, TDS and EC value)

Figure 3 ( $a_4$ ,  $a_5$ ,  $a_6$ ) showed the pH value, TDS value and Electrical Conductivity (EC) real time measured values during Cu<sub>2</sub>ZnMgS<sub>4</sub> compound formation. Here MgSO<sub>4</sub>.XH<sub>2</sub>O (10-drop), ZnSO<sub>4</sub>.XH<sub>2</sub>O (1- drop) positive (+ ionic) elements, Na<sub>2</sub>S (3-drop) negative ionic element concentrations were kept constant and only CuSO<sub>4</sub>.XH<sub>2</sub>O positive (+ ionic) elements concentrations varied from 1-drop to 5-drops. This real time measurement showed both EC and TDS values showed similar increasing trend. But pH value showed completely different trend.

The pH values suddenly decreased from pH-3.82 to pH-3.79 with respect to CuSO<sub>4</sub>.XH<sub>2</sub>O positive (+ ionic) elements concentrations increment from 1-drop to 2-drops and then pH value again reached pH-3.83 at 3-drops again pH value started to decrease for 4-drops pH-3.81 and for 5-drops pH-3.8. Three times this measurement repeated and the obtained results are same. In case of TDS measurement value CuSO<sub>4</sub>.XH<sub>2</sub>O 1-drop to 5-drops drastic change observed. The TDS value reached from 900 ppm – 1250 ppm. During Cu<sub>2</sub>ZnMgS<sub>4</sub> compound formation EC value also showed drastic change because electrical conductivity value changed from 1800  $\mu$ s/cm - 2500  $\mu$ s/cm. Even within few drops CuSO<sub>4</sub>.XH<sub>2</sub>O change showed this much variation effect in EC and TDS value.



Fig. 3. (a<sub>4</sub>, a<sub>5</sub>, a<sub>6</sub>) The pH value, TDS value and Electrical conductivity (EC) real time measured values during Cu<sub>2</sub>ZnMgS<sub>4</sub> compound formation (Various CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations).

### 3.4. Colorimeter studies on various sodium sulfide (Na<sub>2</sub>S) concentrations

There are both visible monochromatic wavelengths and mixed band such as violet, violet blue, green, blue green, green blue, green, yellow and red wavelengths were used in present colorimeter study. Mixed band wavelength study on materials science and engineering is very rare due to instrumentations unavailability even in this advanced modern trend. So that we concentrate more on this mixed band wavelength investigation on our Cu<sub>2</sub>ZnMgS<sub>4</sub> compound real time formation. This total study results outputs taken in real time. In this experiment CuSO<sub>4</sub>.XH<sub>2</sub>O (1-drop), ZnSO<sub>4</sub>.XH<sub>2</sub>O (1- drop), MgSO<sub>4</sub>.XH<sub>2</sub>O (1-drop) positive (+ ionic) elements concentrations were kept constant and only Na<sub>2</sub>S negative (- ionic) elements concentrations varied from 1-drop to 5-drops.

Figure 4 shows the photo colorimeter results of our Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation. From violet wavelength to green blue wavelengths we obtained increase in absorption and then for green blue to blue green we received decreased in absorption. Further blue green to green again absorption increased further green to red wavelengths real time Cu<sub>2</sub>ZnMgS<sub>4</sub> compound absorption decreased. This rhythmic photo colorimeter absorption response showed very interesting symmetric trend for all of Na<sub>2</sub>S concentrations.





*Fig. 4. Photo colorimeter results of our Cu*<sub>2</sub>*ZnMgS*<sub>4</sub>*real time compound formation. Here violet, violet blue (V Blue), green blue (G Blue), blue green (B Green), green, yellow and red wavelengths were used in present colorimeter result.* 

## 3.5. Colorimeter studies on various magnesium sulphate (MgSO<sub>4</sub>.XH<sub>2</sub>O) concentrations

There are both visible monochromatic wavelengths and mixed band such as violet, violet blue, green, blue green, green blue, green, yellow and red wavelengths were used in present colorimeter study. Mixed band wavelength study on materials science and engineering is very rare due to instrumentations unavailability even in this advanced modern trend. So that we concentrate more on this mixed band wavelength investigation on our Cu<sub>2</sub>ZnMgS<sub>4</sub> compound real time formation. This total study results outputs taken in real time. In this experiment CuSO<sub>4</sub>.XH<sub>2</sub>O (1- drop), ZnSO<sub>4</sub>.XH<sub>2</sub>O (1- drop), Na<sub>2</sub>S negative (- ionic) elements concentrations 3-drops were kept constant and MgSO<sub>4</sub>.XH<sub>2</sub>O positive (+ ionic) elements concentrations only varied from 1-drop to 10-drops.

Figure 5 shows the photo colorimeter results of our  $Cu_2ZnMgS_4$  real time compound formation. From violet wavelength to green blue wavelengths we obtained increase in absorption and then for green blue to blue green we received decreased in absorption. Further blue green to green again absorption increased further green to red wavelengths real time  $Cu_2ZnMgS_4$  compound absorption decreased.

This rhythmic photo colorimeter absorption response showed very interesting symmetric trend for all of MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations. But only one concentration completely showed different absorption trend (ie) MgSO<sub>4</sub>.XH<sub>2</sub>O 5-drops concentration showed drastically reduced absorption at violet blue mixed band region and then followed the similar absorption trend of all other wavelengths. Many times we repeated this experiment but similar results we observed.





Fig. 5.Shows the photo colorimeter results of our  $Cu_2ZnMgS_4$  real time compound formation with various  $MgSO_4.XH_2O$  concentrations.

#### 3.6. Colorimeter studies on various copper sulphate (CuSO<sub>4</sub>.XH<sub>2</sub>O) concentrations

There are both visible monochromatic wavelengths and mixed band such as violet, violet blue, green, blue green, green blue, green, yellow and red wavelengths were used in present colorimeter study. Mixed band wavelength study on materials science and engineering is very rare due to instrumentations unavailability even in this advanced modern trend. So that we concentrate more on this mixed band wavelength investigation on our Cu<sub>2</sub>ZnMgS<sub>4</sub> compound real time formation.

This total study results outputs taken in real time. In this experiment ZnSO<sub>4</sub>.XH<sub>2</sub>O(1drop), MgSO<sub>4</sub>.XH<sub>2</sub>O (10-drops) positive (+ ionic) elements concentrations, Na<sub>2</sub>S negative (- ionic) elements concentrations 3-drops were kept constant and only CuSO<sub>4</sub>.XH<sub>2</sub>O varied from 1-drop to 5-drops. Figure 6 shows the photo colorimeter results of our Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation. Maximum absorption we received at CuSO<sub>4</sub>.XH<sub>2</sub>O 1-drop and 2-drops than other concentrations. From violet wavelength to green blue wavelengths we obtained increase in absorption and then for green blue to blue green we received decreased in absorption. Further blue green to green again absorption increased further green to red wavelengths real time Cu<sub>2</sub>ZnMgS<sub>4</sub> compound absorption decreased. This similar photo colorimeter absorption response showed very interesting trend for all of CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations.



Fig. 6.Shows the photo colorimeter results of our  $Cu_2ZnMgS_4$  real time compound formation with various  $CuSO_4.XH_2O$  concentrations.

## **3.7.** UV-Vis spectrophotometer studies on various sodium sulfide (Na<sub>2</sub>S) concentrations

UV-Vis spectrophotometer studies on  $Cu_2ZnMgS_4$  real time compound formation were investigated in the wavelength range of 300 nm – 950 nm. In this experiment CuSO<sub>4</sub>.XH<sub>2</sub>O 1drop, ZnSO<sub>4</sub>.XH<sub>2</sub>O (1-drop), MgSO<sub>4</sub>.XH<sub>2</sub>O (1-drops) positive (+ ionic) elements concentrations were kept constant and Na<sub>2</sub>S negative (- ionic) elements concentrations only varied from 1-drop to 5-drops. Figure 7 shows the UV-Vis spectrophotometer results of our Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation. Maximum transmittance % we received at Na<sub>2</sub>S 1-drop and transmittance % started to decrease gradually for all other Na<sub>2</sub>S high concentrations. Transmittance variation within few drops variation of Na<sub>2</sub>S is a very important characteristic result that we have obtained. Similarly for opto-electronic materials and its related products fabrication this transmittance % tuning is a very important criterion to receive high efficient tunable performance.





Fig. 7.The UV-Vis spectrophotometer results of our  $Cu_2ZnMgS_4$  real time compound formation in the wavelength range of 300 nm – 950 nm.

## **3.8.** The UV-Vis spectrophotometer studies on various magnesium sulphate (MgSO<sub>4</sub>.XH<sub>2</sub>O) concentrations

UV-Vis spectrophotometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation were investigated in the wavelength range of 300 nm – 950 nm. In this experiment CuSO<sub>4</sub>.XH<sub>2</sub>O 1drop, ZnSO<sub>4</sub>.XH<sub>2</sub>O (1-drop), Na<sub>2</sub>S negative (- ionic) elements concentrations 3-drops were kept constant and MgSO<sub>4</sub>.XH<sub>2</sub>O positive (+ ionic) elements concentrations only varied from 1-drops to 10-drops. Figure 8 shows the UV-Vis spectrophotometer results of our Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations. Maximum transmittance % we received at MgSO<sub>4</sub>.XH<sub>2</sub>O 4-drops and transmittance % started to decrease gradually. From MgSO<sub>4</sub>.XH<sub>2</sub>O 1-drop to 4-drops transmittance % increased and from 5-drops onwards transmittance % started to decrease and finally reached lower transmittance % value of around 50% for MgSO<sub>4</sub>.XH<sub>2</sub>O 10-drops concentrations. This property is slightly different from usual elemental concentration variation and its corresponding UV-Vis transmittance property.





Fig. 8. The UV-Vis spectrophotometer results of Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations varied from 1-drops to 10-drops.

## **3.9.** UV-Vis spectrophotometer studies on various copper sulphate (CuSO<sub>4</sub>.XH<sub>2</sub>O) concentrations

UV-Vis spectrophotometer studies on  $Cu_2ZnMgS_4$  real time compound formation were investigated in the wavelength range of 300 nm – 950 nm. In this experiment ZnSO<sub>4</sub>.XH<sub>2</sub>O (1drop), MgSO<sub>4</sub>.XH<sub>2</sub>O 10-drops positive (+ ionic) elements concentrations, Na<sub>2</sub>S negative (- ionic) elements concentrations 3-drops were kept constant and CuSO<sub>4</sub>.XH<sub>2</sub>O 1-drop, only varied from 1drops to 5-drops. Figure 9 shows the UV-Vis spectrophotometer results of our Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations. Maximum transmittance % we received at CuSO<sub>4</sub>.XH<sub>2</sub>O 3-drops and all other concentrations showed similar transmittance % within ±5% variation.



Fig. 9. The UV-Vis spectrophotometer results of Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations varied from 1-drops to 5-drops.

## 3.10. Digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various Na<sub>2</sub>S concentrations

Figure 10 (a) shows the digital photo-flourometer studies on  $Cu_2ZnMgS_4$  real time compound formation with various Na<sub>2</sub>S concentrations. Here we used the primary excitation filter 5113 and three secondary filters 3385, 3486 and 4308. The observed fluorescence emission results with respect to Na<sub>2</sub>S negative (- ionic) elements concentrations from 1-drops to 4-drops were recorded and presented. Na<sub>2</sub>S 1-drop showed lower emission intensity and Na<sub>2</sub>S 4-drops showed high fluorescence.



Fig. 10. (a) Digital photo-flourometer studies on  $Cu_2ZnMgS_4$  real time compound formation with various  $Na_2S$  concentrations varied from 1-drop to 4-drops. Primary excitations filter 5113.



Fig. 10. (b) Digital photo-flourometer studies on  $Cu_2ZnMgS_4$  real time compound formation with various  $Na_2S$  concentrations varied from 1-drop to 4-drops. Primary excitations filter 5840.

Figure 10 (b) showed the digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various Na<sub>2</sub>S concentrations varied from 1-drop to 4-drops. Primary excitations filter 5840. The observed fluorescence emission results with respect to Na<sub>2</sub>S negative (-ionic) elements concentrations from 1-drops to 4-drops were recorded. Na<sub>2</sub>S 2-drop and 3-drops showed relatively high emission intensity and Na<sub>2</sub>S 1-drops and 4-drops showed lower fluorescence for this specific 5840 filter.

## 4. Digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations.

Figure 11 (a) shows the digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations. Here we used the primary

excitation filter 5113 and three secondary filters such as 3385, 3486 and 4308 respectively. The observed fluorescence emission results with respect to MgSO<sub>4</sub>.XH<sub>2</sub>O positive (+ ionic) elements concentrations from 1-drops to 10-drops were recorded and showed in the following graph. MgSO<sub>4</sub>.XH<sub>2</sub>O 1-drop, 5-drops and 9-drops showed relatively lower emission intensity and all other concentrations showed high fluorescence emission intensity.



Fig. 11. (a) Digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations varied from 1-drop to 10-drops.

Figure 11 (b) showed the digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various Na<sub>2</sub>S concentrations varied from 1-drop to 4-drops. Primary excitations filter 5840 and the secondary filters are 3385, 3486 and 4308. The observed fluorescence emission results showed the 3385 and 3486 filters showed high emission intensity for all of concentrations. Lower emission intensity 130 a.u. and 183 a.u. highest emission intensity recorded from filter 3486. Filter 4308 showed lowest emission intensity values for all MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations. So one can easily understand from this detailed emission result the excitation primary and secondary filter sources also played the very important role in materials fluorescence emission property investigation.



Fig. 11. (b) Digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations varied from 1-drop to 10-drops.

## 4.1. Digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations

Figure 12 (a) shows the digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations. Here the primary excitation filter 5840 and three secondary filters such as 3385, 3486 and 4308 were used respectively. The observed emission results with respect to CuSO<sub>4</sub>.XH<sub>2</sub>O positive (+ ionic) elements concentrations from 1-drops to 5-drops were recorded and exhibited in the following graph. CuSO<sub>4</sub>.XH<sub>2</sub>O 5-drop showed relatively lower emission intensity and all other concentrations showed high fluorescence emission intensity. Among these CuSO<sub>4</sub>.XH<sub>2</sub>O 2-drops using filter 3486 showed maximum emission intensity than all others. Especially secondary filter 4308 showed almost no emission for all of MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations.



Fig. 12. (a) Digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations using secondary filters 3385, 3486 and 4308 and primary excitation filter 5840.

Figure 12 (b) shows the digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations. Here the primary excitation filter 5113 and three secondary filters such as 3385, 3486 and 4308 were used. The observed emission results with respect to CuSO<sub>4</sub>.XH<sub>2</sub>O positive (+ ionic) elements concentrations from 1-drops to 5-drops were recorded and presented in the following graph. CuSO<sub>4</sub>.XH<sub>2</sub>O 2-drops and 4-drop showed relatively lower emission intensity. All other concentrations showed relatively lower fluorescence emission intensity. Among these CuSO<sub>4</sub>.XH<sub>2</sub>O 4-drops using filter 4308 showed maximum emission intensity than all other emission intensity.



Fig. 12. (b) Digital photo-flourometer studies on Cu<sub>2</sub>ZnMgS<sub>4</sub> real time compound formation with various CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations using secondary filters 3385, 3486 and 4308 and primary excitation filter 5113.

### 5. Conclusions

In the first step the Cu<sub>2</sub>ZnMgS<sub>4</sub> quaternary compound synthesized with various Na<sub>2</sub>S concentrations and its real time measurement investigated successfully.

The real time investigated pH and TDS measurement showed both the pH and TDS value gradually increased with respect to Na<sub>2</sub>S concentrations increment. Electrical measurement drastically varied and for Na<sub>2</sub>S concentration 1 drop showed 860 µs/cm and for Na<sub>2</sub>S concentration 4 drops showed nearly 960 µs/cm. Even few drops Na<sub>2</sub>S concentration variation showed the tremendous change in its chemical and electrical properties. In the second stage Cu<sub>2</sub>ZnMgS<sub>4</sub> quaternary compound synthesized with various MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations. The real time measured pH value gradually decreased when MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations drop wise increased systematically. But TDS value and electrical conductivity value increased much with respect to MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations increment. In the third stage the Cu<sub>2</sub>ZnMgS<sub>4</sub> quaternary compound synthesized with various.

The real time pH measurement showed different characteristics than other said compositions. When CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations increased drop wide then the pH value first decreased and then increased considerably. Further TDS value and electrical conductivity value increased much with respect to CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations increment. In these photo colorimeter measurements especially we measured the mixed band wavelength responses for all samples. The photocolorimeter results showed the increase in absorbance noticed at all of lower elemental (Na<sub>2</sub>S, MgSO<sub>4</sub>.XH<sub>2</sub>O, CuSO<sub>4</sub>.XH<sub>2</sub>O) concentrations. For higher concentrations the corresponding photocolorimeter absorbance reduced much. UV-Vis transmittance real time results in the wavelength range of 300 nm to 950 nm showed the systematic decrease in %Transmittance for increase in Na<sub>2</sub>S and CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations.

In case of MgSO<sub>4</sub>.XH<sub>2</sub>O concentration increment (from 1 drop to 4 drops) we observed the increase in %Transmittance and further increase in concentrations showed reasonably degreased %Transmittance. Photofluorometer real time results (using primary filter 5113) showed the increase in fluorescence when increase the Na<sub>2</sub>S, CuSO<sub>4</sub>.XH<sub>2</sub>O and MgSO<sub>4</sub>.XH<sub>2</sub>O concentrations. Fluorometer real time results (using primary filter 5840) showed the decrease in fluorescence when increase the Na<sub>2</sub>S, CuSO<sub>4</sub>.XH<sub>2</sub>O concentrations. So the primary filter played a very important role in fluorescence property measurement of materials.

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