Influence of Cu$^{2+}$ and Sn$^{2+}$ ions on optical properties of MgS Nanoparticles: A comparative Analysis

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Abstract. Cu$^{2+}$ and Sn$^{2+}$ ions doped MgS nanoparticles were synthesized by chemical route without the aid of any capping agent. The role of Cu$^{2+}$ and Sn$^{2+}$ ions on the structural, optical, photoluminescence properties of MgS nanoparticles have been investigated through various analyses like XRD, TEM, EDX UV-vis absorption, transmittance studies, PL spectra and FT-IR. The average particle size was calculated as ~ 10 nm and it was varied based on the ionic radius of the dopant. From this comparative study, it was observed that Cu$^{2+}$ (2%) doped MgS showed a blue shift in Absorbance spectra, wide optical band gap and also exhibited better photoluminescence property. A strong PL emission was received in UV region and in the Red region. This combination of materials can be utilized in solar panel manufacturing as buffer material, optoelectronic devices and in red-emitting luminescent displays.

1. Introduction
In the past two decades, there has been a keen attraction on MgS is used for optical and imaging applications. Optically stimulated luminescence was exhibited by MgS and finds application in radiation dosimetry [1]. MgS with Ce showed excellent optical transitions [2]. MgS is used in a power-gated hole burning and photon-gated hole burning, a single laser is employed for reading, burning, and erasing the spectral holes [3]. Mg finds Promising applications in electro-optical devices in nanoscale [4]. Mg played an effective role in transition metal ions for band gap engineering and a wide spectrum of Photoluminescence and possessing suitable properties for materials choice in the optoelectronic device [5]. MgS with CdS quantum dots for microcavities resonance applications. When Cu doped with MgO, it produced a remarkable enhancement in PL intensity and exhibited good performance in optical features [6]. Excellent optical responses in the UV region were recorded for Sn-doped MgO nanoparticles [7]. The transition element like Cu, Ni, Sn, Mn, Zn are generally playing an effective role in tuning the optical and structural properties of optical materials. In this paper, we have tried to compare the performance of dopant Cu$^{2+}$ and Sn$^{2+}$ on the MgS host lattice. The structural, Morphological, optical properties were explored. The co-precipitation method is used for the present study since it is identified as simple and its suitability for mass production.
2. Experimental section

2.1 Materials
The magnesium acetate \((\text{Mg(CH}_3\text{COO)}_2\cdot6\text{H}_2\text{O})\) with 99.5% purchased from M/S, Sigma-Aldrich, Sodium sulfide \((\text{Na}_2\text{S})\), Tin II chloride \((\text{SnCl}_2\cdot2\text{H}_2\text{O})\), Copper acetate \((\text{Cu(CH}_3\text{COO)}_2\cdot\text{H}_2\text{O})\) were purchased from M/S Merck. All the chemicals are AR grade and hence avoided from further purification processes. The chemical solution was prepared by using double distilled de-ionized water (DI) water.

2.2 Synthesis
Magnesium acetate, copper acetate, sodium sulfide solutions were prepared using 50 ml DI water in the individual flask. The quantity of chemicals was taken based on the calculated stoichiometry ratio. The chemical solution was prepared under constant stirring until the homogeneous solution was obtained. All the solution was poured dropwise in a common beaker under continuous magnetic stirring with a stirring rate of 600 rpm. Ammonia solution was added to fix the pH value at 9 thereby the chemical reaction will be induced quickly. 2 ml TEA was added as a binding agent. After 5h the precipitate was taken through filtering and washed several times by using DI water and methanol to remove the unnecessary impurities if any. The wet samples are kept in a muffle furnace for drying. Finally, the product was powdered well to get Sn-doped MgS nanoparticles. The composition of Sn was varied from 0 to 4 at. wt%. This procedure was repeated by using Tin II chloride as a dopant instead of copper acetate.

2.3 Characterization
The structural properties of the synthesized nanoparticles were characterized by an X-ray diffractometer (Model X-ray RigaKuC/max-2500, Specifications; CuKa radiation used at 40 kV and 30 mA from \(2\theta = 0^\circ\) to \(80^\circ\) with a scan rate of 0.2°/ S). Structural and morphological information of samples were investigated using a transmission electron microscope (Model: Philips-CM200, Operating voltage = 2-200 kV). Elemental analysis was carryout by using Energy-dispersive X-ray detector (Model: JEOL-JSM-IT 200 with EDS). Absorbance, Transmittance spectra were received by using a UV-vis spectrophotometer (Model: lambda 35, Make: Perkin Elmer). The photoluminescence (PL) spectra were recorded by using a spectrofluorescence photometer (Model: Hitachi, Make: F-2500). The room temperature FTIR spectra were taken using a Fourier transform infra-red (FT-IR) spectrometer (Model: Perkin Elmer, Make: Hitachi).

3. Results and Discussion
3.1. Structural, Morphological and elemental analysis
The phase composition and structure of Cu and Sn-doped MgS nanoparticles were analyzed by XRD study between the \(2\theta\) range of \(20^\circ\) and \(70^\circ\). Fig.1 lucidly explored the diffraction peaks of samples with various doping concentrations. All the peaks are indexed using miller indices and the samples possessed the cubic crystal structure. The observed peak values were confirmed with JCPDS card no. JCPDF n° 88-2131 [8]. No secondary peaks were noticed in these results and it confirmed the phase purity of samples and also ensured that the dopant was well placed in the host lattice site. Few weaker peaks were identified due to the composition of MgS with Cu and Sn.
The diameter of the spherical particles \((D)\) was determined by the debye scherrer’s method given below \([9]\).

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

Where \(k\) is identified as the Scherrer constant and its value is equal to 0.89, \(\lambda\) denotes wavelength of Cu K\(\alpha\) radiation, \(\beta\) refers to the FWHM of the primary peaks and \(\theta\) is the Bragg’s angle measured.

Cu\(^{2+}\) ion and Sn\(^{2+}\) ion doping increased the overall crystallite size due to the variation of the ionic radius. The ionic radius of host and dopant ions are as follows Sn\(^{2+}\) (0.99 Å) > Cu\(^{2+}\) (0.73 Å) > Mg\(^{2+}\) (0.65 Å) \([10]\). A similar increase of particle size is due to Cu doping into MgO lattice was observed \([11]\). Sn\(^{2+}\) doped MgS nanoparticles size increase more due the Mg vacancies are reimbursed by Sn\(^{2+}\) ions and similar increase was noticed in earlier research \([12]\). The primary peak position, FWHM, lattice parameter and crystallite size of all the samples were shown in table 1.

Table 1

| Samples          | Peak position (2\(\theta\) (°)) | FWHM (\(\beta\)) | \(d_{(111)}\) (Å) | Lattice parameter (Å) | Crystallite size \((D)\) (nm) |
|------------------|---------------------------------|-------------------|-------------------|-----------------------|-----------------------------|
| MgS              | 35.9                            | 0.713             | 2.346             | 4.69                  | 11.51                       |
| Mg\(_{0.98}\)Cu\(_{0.02}\)S | 36.8                            | 0.655             | 2.364             | 4.72                  | 11.13                       |
| Mg\(_{0.96}\)Cu\(_{0.04}\)S | 38.0                            | 0.561             | 2.392             | 4.78                  | 11.62                       |
| Mg\(_{0.98}\)Sn\(_{0.02}\)S | 36.8                            | 0.655             | 2.364             | 4.72                  | 12.52                       |
| Mg\(_{0.96}\)Sn\(_{0.04}\)S | 38.0                            | 0.561             | 2.392             | 4.78                  | 14.70                       |
TEM and SAED pictures of Cu$^{2+}$ 2% at. wt doped MgS and Sn$^{2+}$ 2% at. wt doped MgS were presented in fig 2a,b respectively. Small sized spherical shaped particles are able to view in these pictures. The size of the particles was increased for Sn$^{2+}$ incorporation. The diffraction patterns hold good agreement with miller indices indexed in XRD results. The intensity of diffraction peaks are also matched well with XRD peaks. The small sized granule like particles is viewed in this picture. Hence the Cu doping smoothens the surface since the ionic radius of Cu$^{2+}$ than Sn$^{2+}$ ions.

![TEM and SAED pictures of Cu$^{2+}$ 2% at. wt doped MgS and Sn$^{2+}$ 2% at. wt doped MgS](image)

Figure 2. TEM and SAED pictures of (a) Cu$^{2+}$ 2% at. wt doped MgS (b) Sn$^{2+}$ 2% at. wt doped MgS

The elemental analysis of Cu$^{2+}$ and Sn$^{2+}$ ions doped MgS nanoparticles was shown in fig. 3a-c. All the results shown that the doped elements were present with their existing percentages are matched with stoichiometry ratio.

![EDX spectra](image)

Figure 3. EDX spectra of (a) pure MgS (b) 2% at. wt Sn$^{2+}$-doped MgS (c) 2% at. wt Cu$^{2+}$-doped MgS nanoparticles

3.2 UV-vis absorbance, transmittance and band gap calculation

UV-vis absorbance spectra of Cu and Sn- doped MgS nanoparticles were shown in fig. 4a. The absorption peak get blue shifted and high absorption intensity were observed for Cu 2% concentration. This indicates the proper substitution of dopant in host lattice and this shift endorsed to quantum confinement effect. Other samples exhibited red shifts and Cu 4% doped MgS maximum shifting in higher wavelength side. The d-d transitions of Cu$^{2+}$ is ascertained to this shifting of absorption peaks [13] A small absorption peak obtained in 495nm.
Figure 4. a. Absorbance of Sn\textsuperscript{2+} and Cu\textsuperscript{2+}-doped MgS nanoparticles b. Transmittance spectra of Sn\textsuperscript{2+} and Cu\textsuperscript{2+}-doped MgS nanoparticles

UV-vis transmittance spectra of Cu and Sn-doped MgS nanoparticles were shown in fig. 4b. The higher transmittance was obtained for Sn (2%) doped MgS nanoparticles. The transmittance curves suddenly increase on the higher wavelength side. Hence the samples are transparent in high wavelength light irradiation. The optical band gap values of Cu and Sn-doped MgS nanoparticles were calculated using Tauc’s plot as shown in figure 5.

The given Tauc’s used for calculation of band gap [14]

\[ a h \nu = A (h \nu - E_g)^n = A (h \nu - E_a)^{\frac{1}{2}} \]  

Where, \( E_g \) represents the band gap of the material, the exponent \( n \) depends on the type of transition. \( n \) may take values ½ (for allowed direct transition), 2 (for allowed indirect transition), 3/2 (for forbidden direct transition) and 3 (for forbidden indirect transition). Where, \( A \) is a constant. The linear portion of the plots of \((a h \nu)^2\) vs \( h \nu \) to \( \alpha = 0 \) extrapolated to obtain the optical band gap \( E_g \). The largest band gap value was obtained for Cu 2% concentration. The Excessive carriers donated by the impurity atoms are directed to fill up the conduction band edge. This transition produces a blue shift in optical band through blocking the low energy transitions [15]. The increase of Cu concentration decreases the energy gap from 3.98 eV (Cu = 2%) to 3.21 eV (Cu = 4%). The improved photo-absorption at higher Cu concentrations is because of the Cu 3d level that formed donor level over the valence band [16]. Electrons can be moved to attain a high energy state from this Cu 3d level to the conduction band, which brings down the band gap energy making it simpler for electrons to be excited to the conduction band. This would expand the measure of electrons and thus the band gap is decreased. The shrinkage of energy gap is due to the p–d spin-exchange interactions between the band electrons and the localized d electrons of Cu\textsuperscript{2+} ion [17]. The initial doping of Cu, Sn expanded band gap from bulk value but further increase of doping concentration diminished the band gap step by step.
Figure 5. Tauc’s plot for the band gap values of Sn\(^{2+}\) and Cu\(^{2+}\)-doped MgS nanoparticles

3.3 Photoluminescence Characteristics

The photoluminescence characteristics of Cu and Sn-doped MgS nanoparticles were shown in fig.6 (a,b) and CIE chromaticity diagram was shown in fig.5c. The PL peaks were received at 360 nm and 645 nm in UV region and red (visible) region respectively. The red color emission intensity of Cu-doped MgS nanoparticles was higher than the Sn-doped MgS nanoparticles. The increase of doping concentration suppresses the peaks intensity further. The emission peaks obtained in red band region were ascribed to the efficient recombination between hole and free electrons. The near band edge (NBE) emission near 360 nm proves a high crystallinity. The Cu doped MgS showed the enhanced peak in UV region. The NBE Emission decreased with Increase of Cu composition [18]. The high intensity emission peaks at 360 nm may also be ascribed to the scattering from the voids among the MgS nanoparticles. The high intense NBE peaks were attributed to the enhanced defects free concentration and surface passivation [19]. When we compare Sn with Cu, the Sn-doped MgS nanoparticles showed a suppressed UV emission. We didn’t receive any emission wavelength corresponding to blue colour that confirms the non-availability of sulfur vacancies due to the successful incorporation of Cu and Sn into MgS host [20].

Figure 6a,b. PL spectra of Sn\(^{2+}\) and Cu\(^{2+}\)-doped MgS nanoparticles, c. CIE chromaticity diagram of Sn\(^{2+}\) and Cu\(^{2+}\)-doped MgS nanoparticles
The green emission is also not received, and it is confirmed that the MgS crystal structure is formed without defects formation. The emission intensity was attributed to the intrinsic defects, especially sulphur vacancies which would assist the transition MgS host lattice to Cu/ Sn dopant ions.

3.4 FTIR Analysis

FT-IR spectra of Cu and Sn-doped MgS nanoparticles from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) were given in Fig. 7. The peaks intensity received at 3696 cm\(^{-1}\) and 3349 cm\(^{-1}\) were ascertained to the O-H stretching vibrations due to the form of water obtained on the surface of nanocrystals [21]. The C-H asymmetric stretching vibrations produced peaks intensity at 2924 cm\(^{-1}\) 2855 cm\(^{-1}\). H–O–H bending vibration is ascribed to peaks received at 1564 cm\(^{-1}\). Emission peaks received near 1415 cm\(^{-1}\) and 1394 cm\(^{-1}\) are endorsed to C=O stretching modes. The transmittance peaks around 1083 cm\(^{-1}\) were due to the asymmetric stretching mode. Peaks observed near 1117 cm\(^{-1}\) were due to C–C vibrations [22]. As Sn, Cu incorporated into MgS some distortions produced at the lead some minor vibrations between 500 to 550 cm\(^{-1}\). The peaks at 429 cm\(^{-1}\) due to Mg-S stretching vibrations. Peaks received from 664 cm\(^{-1}\) to 443 cm\(^{-1}\) were ascertained to stretching vibrations of Mg-S-Cu and Mg-S-Sn molecules [23].

![Figure 7. FT-IR spectra of Sn\(^{2+}\), Cu\(^{2+}\)-doped MgS nanoparticles](image)

4. Conclusions

Cu\(^{2+}\) and Sn\(^{2+}\) ions doped MgS nanoparticles were synthesized by chemical route. The XRD results and TEM results confirmed the cubic structure of MgS nanoparticles without forming additional peaks. The FT-IR and EDX analysis confirmed the presence of elements in the prepare samples as per the anticipated ratio. The UV- vis absorption and transmittance spectra showed that higher absorbance was exhibited by Cu\(^{2+}\) doping and better transmittance was received through Sn\(^{2+}\) incorporation. Large band gap was received for Cu\(^{2+}\) (2%) doping with MgS nanoparticles. The photoluminescence emission was received in UV region and red color region. As Cu\(^{2+}\)- doped MgS exhibited better optical and photoluminescence properties, this composition is identified as an optimum combination for optoelectronic applications based on the comparative analysis.
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